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MEDIUM EFFECTS IN ETHANOL--WATER SOLVENTS, METHANOL, AND ACETONITRILE

by

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A dissertation submitted to the Graduate Faculty in Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York.

1972

This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

7/12/1972
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To Anna.

Acknowledgements

The author wishes to express his sincere appreciation to Professor Orest Popovych for suggesting the problem and for his continuous guidance and inspiration throughout this research. Thanks are also due to Professor Joseph Glickstein for many hours of stimulating discussions on the subjects included in this dissertation.

Acknowledgement is also due to Brooklyn College of the City University of New York for support in the form of teaching assistantships and to the National Science Foundation for support in the form of salary, equipment, and supplies under grants GP-6553, GP-9417, and GP-25906.

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Presentation of problem.

Introduction.

Electrode potentials and ion-activity scales are conventionally established referring to an ideal solution of unit activity and unit molality in the solvent of interest as the standard state. For convenience, these hypothetical standard state solutions will be referred to as "infinitely dilute solutions". As a result of this choice of standard states, there are as many conventional electrode potential and ion-activity scales as there are solvents. The limitless number of electrochemical scales presents a problem since comparisons between conventional electrochemical measurements are restricted to measurements performed in identical solvents. Many of the early chemical investigators were aware of this restriction (1, 2, 3, 9) but they did not concern themselves with it since most electrochemical measurements were performed in aqueous media. More recently, with the availability of many nonaqueous solvents in bulk quantities, many investigators have been studying nonaqueous electrochemical systems and it has become necessary to seek methods of correlating data obtained in different solvents. In order to accomplish this, the old convention of choosing a different standard state for each solvent must be changed

and a new one substituted that allows only one standard state to be used for all electrochemical measurements. Classical thermodynamicists would be quick to point out that the use of a universal, solvent-independent standard state requires knowledge of energic properties of single ions. Traditionally, studies of the energetics of single ions have been avoided (4, 5, 6) since classical thermodynamics yields information about electroneutral combinations of ions or neutral molecules only. More recently, however, many extrathermodynamic methods have been proposed for estimating single ion properties. The aqueous pH scale has been extremely successful and many investigators (4, 7, 8) feel that properties of single ions are indeed significant and may provide information which would be unobtainable using the classical approach.

In this thesis, the various extrathermodynamic methods for establishing solvent-independent e.m.f. scales and ion-activity scales will be critically reviewed and a new method for establishing these scales will be presented and evaluated. Solvent-independent e.m.f. and ion-activity scales were established in ethanol--water solvents, methanol, and acetonitrile.

The medium effect.

The chemical potential of solute i in solvent s referred to its aqueous standard state, ${}_wG(i,s)$, is defined as

$$ {}_wG(i,s) = {}_wG_i^o + RT \ln a_i \qquad (1) $$

subscripts w refer to the aqueous standard state, ${}_wG_i^o$ is the standard free energy of solute i in water, and a_i is the aqueous activity of solute i given by

$$ a_i = m_i \, {}_w\gamma_i \qquad (2) $$

where m_i is the molality and ${}_w\gamma_i$ is the activity coefficient which approaches unity as the molality approaches zero in water. Similarly, the chemical potential of solute i referred to its nonaqueous standard state, ${}_sG(i,s)$, is defined as

$$ {}_sG(i,s) = {}_sG_i^o + RT \ln a_i^* \qquad (3) $$

where subscripts s refer to the nonaqueous standard state, ${}_sG_i^o$ is the standard free energy of solute i in a nonaqueous solvent and a_i^* is the conventional nonaqueous activity given by

$$a_i^* = m_i \, {}_s\gamma_i \qquad (4)$$

where m_i is the molality of solute i and ${}_s\gamma_i$ is its nonaqueous salt effect activity coefficient which approaches unity as the molality approaches zero in the given nonaqueous solvent. In actuality, the chemical potential of any nonaqueous solution can be defined using either the aqueous or the nonaqueous standard states. Since the chemical potential of a given solution is independent of the choice of standard states, ${}_sG(i,s) = {}_wG(i,s)$, and

$$ {}_sG_i^o - {}_wG_i^o = RT \ln \frac{a_i}{a_i^*} \qquad (5)$$

The ratio a_i/a_i^* represents the activity of a solution referred to its aqueous standard state divided by the activity of this same solution referred to its nonaqueous standard state and represents the most fundamental definition of the medium effect, ${}_m\gamma_i$:

$$ {}_m\gamma_i \equiv \frac{a_i}{a_i^*} \qquad (6)$$

Thus, the medium effect of solute i, ${}_m\gamma_i$, is a measure of the difference between the standard free energy of solute i in water and in the nonaqueous solvent :

$$ {}_{s}G_i^{o} - {}_{w}G_i^{o} = RT \ln {}_{m}\gamma_i \qquad (7) $$

The medium effect is therefore independent of concentration of solute i but dependent on the nature of the interactions between solute i and the nonaqueous solvent, the aqueous solvent (or another reference solvent), and on the temperature and pressure.

With the aid of the medium effect, a conventional nonaqueous activity, a_i^*, can be converted to its value on the aqueous scale, a_i:

$$ a_i = a_i^* \, {}_{m}\gamma_i \qquad (8) $$

Similarly, a conventional nonaqueous activity coefficient, ${}_{s}\gamma_i$, is related to its equivalent value on the aqueous scale, ${}_{w}\gamma_i$, through the medium effect:

$$ {}_{w}\gamma_i = {}_{s}\gamma_i \, {}_{m}\gamma_i \qquad (9) $$

For aqueous solutions, ${}_{s}\gamma_i$ is identical with ${}_{w}\gamma_i$ and the medium effect is unity.

The medium effect of species i can also be expressed in terms of changes in the standard electrode potentials, using the relationship

$$ \Delta G_i^{o} = -nF\Delta E_i^{o} = RT \ln {}_{m}\gamma_i \qquad (10) $$

where ΔE_i^o is the difference between the standard potential of an electrode reversible to species i in water and in the given nonaqueous solvent. For example, in the case of electrodes reversible to a single reducible species in solution, the medium effect for that species is given by:

$$E^o(i,s) - E^o(i,H_2O) = \frac{RT}{nF} \ln {}_m\gamma_i \qquad (11)$$

where $E^o(i,s)$ and $E^o(i,H_2O)$ are the absolute standard potentials of i in the solvent and water, respectively. Similarly, for oxidizable species in solution, the medium effect is given by

$$E^o(i,H_2O) - E^o(i,s) = \frac{RT}{nF} \ln {}_m\gamma_i \qquad (12)$$

where the E^o's are those of an electrode reversible to the oxidizable species.

The difference in standard free energy of solvation between an aqueous and a nonaqueous solution of solute i is due to the difference between the water-solute and nonaqueous solvent-solute interactions. In other words, changing the medium surrounding a solute has the effect of changing its standard free energy of solvation. Because of this, the difference between the aqueous and the nonaqueous standard free energies is termed the

"medium effect" by many investigators (4, 10--19). Various other terms have been used for $_{m}\gamma_{i}$. The term "primary medium effect" has been used by Owen (23), Robinson and Stokes (20), Alfenaar and DeLigny (21), and Bates, Paabo and Robinson (22). Owen was perhaps the first author to recognize the scope of the medium effect. His formulation of the "primary medium effect" was equivalent to the "medium effect" in use today. Owen also used the term "secondary medium effect" to represent the difference in salt effect activity coefficients of solutions of a given substance in two solvents. The term "distribution coefficient" or "partition coefficient" was used by Bjerrum and Larsson (9), Kolthoff and Bruckenstein (24), and Laitinen (25). This term is misleading since it implies that operationally a solute must be distributed between two media for a medium effect to be established. However, it is impossible to distribute a single ion between pairs of solvents and, many solvent pairs are miscible. "Solvent activity coefficient" has been used by Parker and Alexander (26--30). In the case of Parker and Alexander's "solvent activity coefficient", infinitely dilute solutions in methanol were used as the standard state. Most recently, Kolthoff and Chantooni (31) have proposed the term "medium ion activity coefficient" for $_{m}\gamma_{i}$. Popovych (4) feels that the term "medium effect" is the most logical choice for $_{m}\gamma_{i}$ since it is analogous

to the terms "salt effect" or "concentration effect" which are used for $_{s}\gamma_{i}$. The terms "medium effect" and "salt effect" or "concentration effect" identify the causes for a solutes departure from ideal behavior as defined by the standard state. In this thesis, the term "medium effect" will be used exclusively for $_{m}\gamma_{i}$.

The three interrelated problems.

Establishment of a solvent-independent electrode potential scale.

Conventionally, all electrode potentials are measured with respect to the standard hydrogen electrode (SHE) having an assigned standard potential of zero volts in all solvents. This implies that the SHE experiences no change in potential upon change of solvent. Since the potential of an electrode is in part determined by the solvation energy of the electrode-active ion, the convention that $E_H^o = 0$ in all solvents is the same as saying that the solvation energy of the hydrogen ion is constant in all solvents. In actuality, this is an absurd assumption. In basic solvents such as liquid ammonia and hydrazine, the hydrogen ion is much more tightly solvated than it is in water. In acidic solvents, such as glacial acetic acid and formic acid, the hydrogen ion is less tightly solvated than it is in water. Our chemical intuition alone tells us that the solvation energy of hydrogen ions and hence, the potential of the hydrogen electrode must vary from solvent to solvent. Just as a matter of discussion, if we were to assume $E_H^o = 0$ in all solvents, it would be a logical extension to assume that the standard potential of all electrodes remains constant regardless

of solvent. This too is of course, absurd.

Because of the conventional method of establishing electrode potential scales, there are as many different independent scales as there are solvents. One cannot deduce any comparitive information from conventional potential measurements made in different solvents. For example, if a conventional potential of -0.34volts is reported for a Tl/Tl^+ electrode in both water and ethanol, this does not necessarily mean that the Tl^+ is equally strong in terms of redox ability in both solvents.

The ordinary conventional standard potentials of an electrode-active ion, i, is defined by the relationship

$$ {}_sE^o(i,s) \equiv E^o(i,s) - E^o(H,s) \qquad (13) $$

where ${}_sE^o(i,s)$ is the potential of i in solvent s with the subscript s referring to the standard state, $E^o(i,s)$ is the absolute standard potential of i in solvent s and $E^o(H,s)$ is the absolute standard potential of the hydrogen electrode in solvent s. The standard potential of the electrode-active ion, i, on the water scale, ${}_wE^o(i,s)$, is defined by

$$ {}_wE^o(i,s) \equiv E^o(i,s) - E^o(H,H_2O) \qquad (14) $$

where ${}_wE^o(i,s)$ is the standard potential of ion i in

solvent s referred to infinite dilution in water, $E^{o}(i,s)$ is the absolute standard potential of an electrode reversible to species i in solvent s and $E^{o}(H,H_2O)$ is the absolute standard potential of the hydrogen electrode in water; the latter is assumed to be zero volts. ${}_{w}E^{o}(i,s)$ is termed the standard potential on the water scale. Combining Equations 13 and 14, we get an expression which can be used to convert conventional standard potentials into their corresponding value on the water scale

$$ {}_{w}E^{o}(i,s) = {}_{s}E^{o}(i,s) + E^{o}(H,s) - E^{o}(H,H_2O) \qquad (15) $$

The last two terms in the above equation represent the difference in the absolute standard potential of the hydrogen electrode between water and solvent s and are related to the medium effect of the proton as follows:

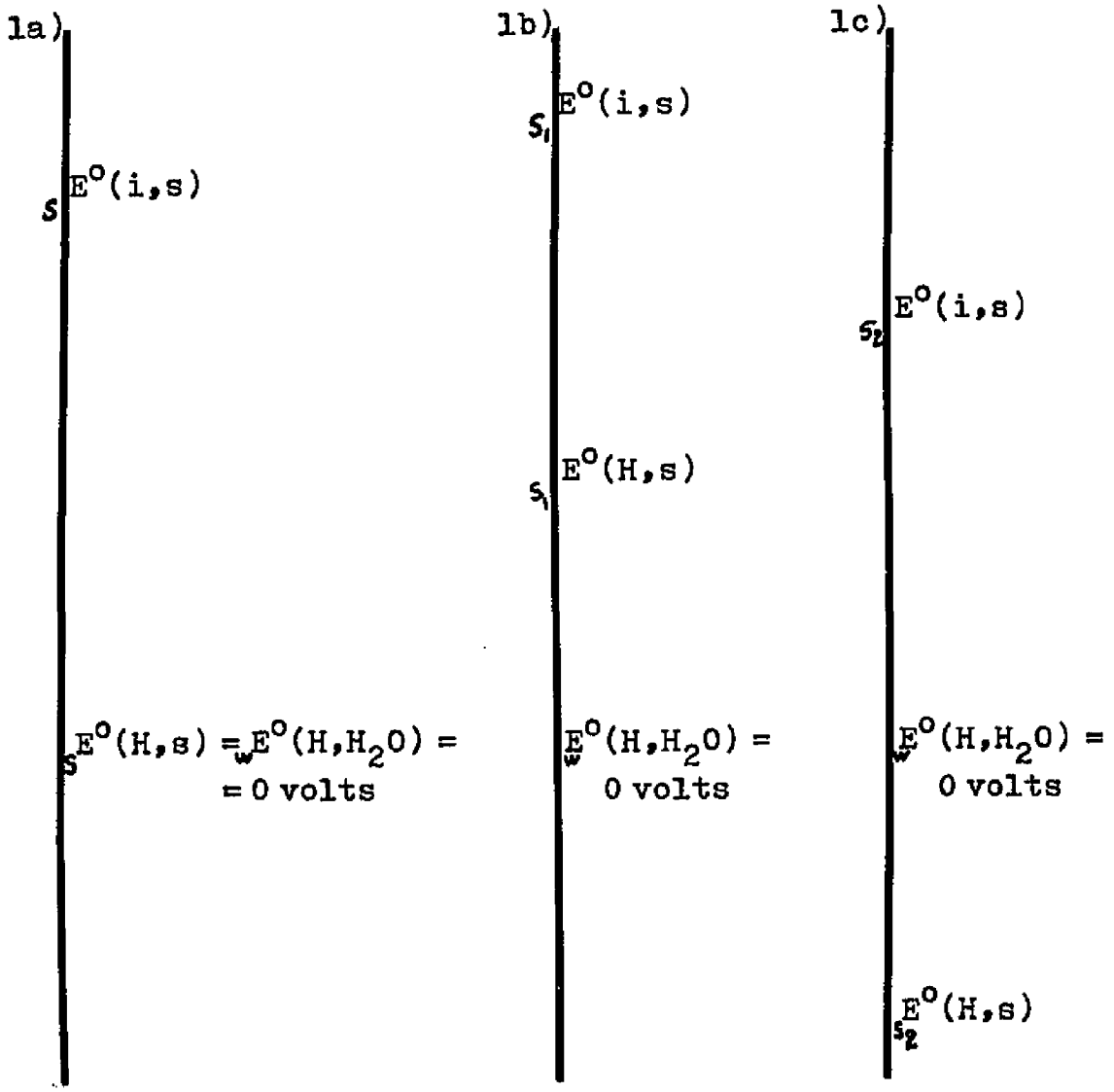
$$ E^{o}(H,s) - E^{o}(H,H_2O) = \frac{RT}{nF} \ln {}_{m}\gamma_{H} \qquad (16) $$

$\ln {}_{m}\gamma_{H}$ is the medium effect for a single ion, the proton. Knowledge of this value is necessary for converting nonaqueous e.m.f. and activity measurements to their values on the aqueous scale. If the medium effect for the proton is known in a given solvent, all conventional potentials measured in that solvent can be converted to their values on the water scale with this equation:

$$ {}_{w}E^{o}(i,s) = {}_{s}E^{o}(i,s) + \frac{RT}{nF} \ln {}_{m}\gamma_{H} \qquad (17) $$

A very nice way of illustrating how the medium effect for the proton aids in establishing a universal electrode potential scale in which all potentials are referred to the aqueous standard state is by means of a bar graph. In Figure 1, we see the three possible relationships between conventional and "aqueous" electrode potential scales. In Figure 1, $E^{o}(i,s)$ and $E^{o}(H,s)$ are the absolute standard potentials of electrodes reversible to i and H in solvent s, and ${}_{w}E^{o}(H,H_2O)$ is the absolute standard potential of H in water. The conventional standard potential of i, the one in which ${}_{s}E^{o}(H,s) = 0$, is equal to the "distance" between ${}_{s}E^{o}(i,s)$ and ${}_{s}E^{o}(H,s)$. The universal or aqueous standard potential of i is equal to the "distance" between ${}_{s}E^{o}(i,s)$ and ${}_{w}E^{o}(H,H_2O)$. As can be seen, to convert from one e.m.f. scale to another, all one has to know is the difference between ${}_{s}E^{o}(H,s)$ and $E^{o}(H,H_2O)$. In the case of water, Figure 1-a, ${}_{s_1}E^{o}(H,s) = {}_{w}E^{o}(H,H_2O)$ and all conventional aqueous standard potentials are equal to standard potentials on the water scale. In some cases, Figure 1-b, ${}_{s_1}E^{o}(H,s)$ is more positive than ${}_{w}E^{o}(H,H_2O)$ and in others, Figure 1-c, it is more negative. In any case, Equation 17 can always be used to convert standard potentials to their corresponding values on the water scale.

Figure 1. Relationships Between Conventional and "Aqueous" Electrode Potential Scales.



In establishing a solvent-independent electrode potential scale in which the standard potential of hydrogen is zero in water only, knowledge of medium effects for single ions is necessary. This presents a problem because medium effects for single ions are not rigorous thermodynamic properties. Nernst (9-a, 9-b) was probably the first investigator to realize that there is a need for single ion medium effects but he was also probably the first to realize that they are not thermodynamically accessible. Since it is impossible to measure directly the solvation energies of a single ion without measuring the properties of its counterion, classical thermodynamicists had given up hope of ever establishing a universal electrode potential scale (5, 6). There has always been a tendency to ignore the problem of universal e.m.f. scales because the solution to the problem is extrathermodynamic. This is probably one of the most important, least investigated problems in the realm of electrochemistry.

Establishment of universal ion-activity scales.

The tremendous success of the aqueous pH scale has made it clear that single-ion activity scales can be extremely useful. Conventionally, the activity of any species, i, is referred to infinite dilution in the solvent of interest just as conventional electrode potentials are referred to ${}_sE^o(H,s) = 0$, the standard potential of the hydrogen electrode in the solvent of interest. There would be no objection to this convention if it would never become necessary to compare aqueous with nonaqueous activities. However, with hydrogen-ion activities alone, intercomparisons between solvents are very important. Does an aqueous solution of $pa_H = 3$ have a greater acidity than a methanolic solution of $pa_H^* = 4$? Does a solution of $pAg^* = 2$ in acetonitrile have the same silver-ion activity as an aqueous solution of $pAg = 2$? These and other questions like them can only be answered with the aid of medium effects for single ions.

From a fundamental expression for the medium effect, Equation 6

$$ {}_m\gamma_i = \frac{a_i}{a_i^*} \qquad (6) $$

it can be seen that aqueous and nonaqueous activities differ from each other. To convert nonaqueous activity

a_i^* of any species i, -be it an uncharged molecule, an electrolyte, or a single ion- to its value on the aqueous scale, a_i, knowledge of the medium effect for that species, ${}_m\gamma_i$, is required. For single-ion scales such as the pH or the pAg scale, knowledge of the medium effect for a single ion is required to convert nonaqueous to aqueous activity. For example, to convert nonaqueous pa_H^* to aqueous pa_H, the medium effect for the proton is used:

$$pa_H = pa_H^* - \log {}_m\gamma_H \qquad (18)$$

Similarly, to convert nonaqueous pa_{Ag}^* values to aqueous pa_{Ag} values, knowledge of the medium effect of silver ion is required:

$$pa_{Ag} = pa_{Ag}^* - \log {}_m\gamma_{Ag} \qquad (19)$$

Without values for the medium effects of single ions, it is impossible to compare quantitatively nonaqueous and aqueous activities. All the arguments that apply to the determination of medium effects for single ions for the purpose of establishing a universal e.m.f. scale apply here. Medium effects for single ions are not rigorous thermodynamic quantities, yet, they are required to establish universal ion-activity scales. The establishment of these scales is another important

fundamental problem that has not received its proper share of attention from chemical investigators.

Evaluation of liquid-junction potentials between aqueous and nonaqueous solutions.

The liquid-junction potential is intimately connected with the measurable cell potential of any galvanic cell with transference. This potential is interfering in its nature since it is not a direct measure of the activities of the electrode-active species. In the simplest case, where both half-cells are aqueous, the best investigators have been able to do is to minimize the potential by including a concentrated salt bridge at the junction between the two half cells. In the case of a liquid-junction between two dissimilar media, the junction potential cannot be suppressed to a negligible value by including a salt bridge.

Cell I is a galvanic cell with liquid junction at an aqueous-nonaqueous interface which is of fundamental importance in this discussion:

$$\underset{H_2O}{Pt;H_2(g)/H^+(a_H=1)}\,/\,\underset{E_j}{}\,/\,\underset{s}{H^+(a_H^*=1)/H_2(g);Pt} \qquad \text{(Cell I)}$$

The left-hand electrode is an aqueous SHE electrode. The right-hand electrode is a nonaqueous SHE electrode. The half-cells are connected by a liquid junction. Experimentally, Cell I will generate a potential which is given by the expression

$$E_{\text{cell I}} = E_{\text{right}} - E_{\text{left}} + E_j \qquad (20)$$

where E_j is the liquid-junction potential between the aqueous and nonaqueous half-cells. In the conventional method of assigning potentials, E_{right} would be equal to E°_{right} which would in turn be equal to zero. Since, conventionally, the standard potential of the hydrogen electrode is defined as zero in all solvents, E_{left} of Cell I would also be zero. Thus, in the conventional manner of defining e.m.f. of galvanic cells, the measured potential of Cell I can be entirely attributed to the liquid-junction potential :

$$E_{\text{cell I}} = E^{\circ}_{\text{right}} - E^{\circ}_{\text{left}} + E_j = E_j \qquad (21)$$

As has been pointed out, however, the conventional manner of assigning potentials goes against our chemical sense. Since the potential of an electrode is directly affected by the solvation energy of the electrode-active ion, the standard potential of the aqueous and nonaqueous hydrogen electrode should differ by an amount corresponding to the difference in the standard free energy of solvation of the proton in the two solvents. If a uniform standard state is adopted for the potentials of both electrodes, part of the measured potential of Cell I would be attributable to the difference between the standard

potentials of the electrodes. Adopting the aqueous standard state, the potential of Cell I can be written

$$E_{\text{cell I}} = {}_wE^{\circ}(H,s) - {}_wE^{\circ}(H,H_2O) + E_j \qquad (22)$$

where the first two terms on the right of Equation 22 are equal to the medium effect for the proton

$${}_wE^{\circ}(H,s) - {}_wE^{\circ}(H,H_2O) = \frac{RT}{nF} \ln {}_m\gamma_H \qquad (23)$$

Thus, the measured potential of Cell I is equal to the sum of the log of the medium effect for a single ion and the aqueous-nonaqueous liquid-junction potential

$$E_{\text{cell I}} = \frac{RT}{nF} \ln {}_m\gamma_H + E_j \qquad (24)$$

Consequently, the knowledge of the medium effects for single ions would allow calculation of aqueous-nonaqueous liquid-junction potentials.

To summarize, there are now three major problems that can be solved with medium effects for single ions: 1)establishment of a solvent-independent electrode potential scale 2)establishment of universal ion-activity scales and 3) evaluation of liquid-junction potentials at aqueous-nonaqueous interfaces. The satisfactory solution to all three problems is dependent

on an accurate evaluation of medium effects for single ions. It must be pointed out that it is not necessary to measure the medium effect for every single ion individually. Once one single ion medium effect is available in any given solvent, all other medium effects for single ions become accessible through classical thermodynamic data. For instance, the difference in conventional standard potentials of the Ag/AgCl electrode between water and solvent s is related to the sum of the chloride ion medium effect, $\log {}_m\gamma_{Cl}$ in solvent s and the medium effect for the proton, $\log {}_m\gamma_H$ in solvent s:

$$\frac{{}_wE^o(Ag/AgCl,H_2O) - {}_sE^o(Ag/AgCl,s)}{2.303RT/nF} = \log {}_m\gamma_H + \log {}_m\gamma_{Cl} \qquad (25)$$

The medium effect for the proton appears in Equation 26 because all conventional standard potentials are differences between the absolute potentials of the electrode under consideration and the hydrogen electrode in the given solvent (see Equation 14). In a similar manner, thermodynamics can yield sums (or differences) of medium effects for other combinations of ions. For instance, the difference in conventional standard potentials of the silver electrode between water and

solvent s is related to the difference ($\log {}_{m}\gamma_{Ag} - \log {}_{m}\gamma_{H}$):

$$\frac{{}_{s}E^{\circ}(Ag/Ag^{+},s) - {}_{w}E^{\circ}(Ag/Ag^{+},H_2O)}{2.303RT/nF} = \log {}_{m}\gamma_{Ag} - \log {}_{m}\gamma_{H} \qquad (26)$$

Once one medium effect for one single ion is known, all other medium effects for single ions become accessible in a given solvent. If ${}_{m}\gamma_{H}$ in solvent s were known, ${}_{m}\gamma_{Cl}$ could be calculated using Equation 25 and the experimentally accessible quantities ${}_{w}E^{\circ}(Ag/AgCl,H_2O)$ and ${}_{s}E^{\circ}(Ag/AgCl,s)$. For this reason, anyone involved with methods for determining medium effects for single ions must also be involved with thermodynamic medium effects as well.

Electrochemical measurements in aqueous solutions are most abundant in the chemical literature and for this reason, the "universal" standard state most often chosen by investigators in the field of medium effects is the aqueous one. It is possible however, to choose the infinitely dilute solution in any other solvent as the standard state.

Thermodynamic medium effects.

Expressions for the activity of electrolytes.

The total free energy of an electrolyte is equal to the sum of the free energies of all of its ions (20). From the equation relating free energy to activity

$$G_i = G_i^o + RT \ln a_i \tag{27}$$

we get an expression for the activity of an electrolyte, a,

$$a = a_+^{\nu_+} a_-^{\nu_-} \tag{28}$$

where a_+ and a_- are the molar activities of the positive and negative ions, respectively, and ν_+ and ν_- are the number of moles of positive and negative ions contained in one mole of electrolyte. The molal activity of an ionic species, i, is given by

$$a_i = m_i \gamma_i \tag{29}$$

where m_i and γ_i are the molality and salt effect activity coefficient. Activity can also be defined using the molar or mole fraction scale. Ionic molalities of the positive (m_+) and negative (m_-) ions are related to the molality of the electrolyte, m, by the equations

$$m_+ = \nu_+ m \tag{30-a}$$

$$m_- = \nu_- m \tag{30-b}$$

Having in mind that ν is the total number of moles of ions in one mole of electrolyte

$$\nu = \nu_+ + \nu_- \tag{31}$$

an operational definition of activity can be written using Equations 28--30

$$a_{electrolyte} = \nu_+^{\nu_+} \nu_-^{\nu_-} \cdot m^{\nu} \gamma_+^{\nu_+} \gamma_-^{\nu_-} \tag{32}$$

To simplify Equation 32, a mean ionic activity coefficient, $\gamma_\pm$, can be defined

$$\gamma_\pm^{\nu} = \gamma_+^{\nu_+} \gamma_-^{\nu_-} \tag{33}$$

Equation 32 can now be written as

$$a_{electrolyte} = \nu_+^{\nu_+} \nu_-^{\nu_-} \cdot (m \gamma_\pm)^{\nu} \tag{34}$$

For a 1:1 electrolyte, the activity is given by

$$a_{1:1} = m^2 \gamma_\pm^2 \tag{35}$$

where $m^2 \gamma_{\pm}^2$ is the solubility (ion-activity) product of the electrolyte. For electrolytes of other types, Equation 34 can be used to arrive at expressions for activity.

For dilute solutions of neutral molecules, the activity can be very well approximated by concentrations (25).

Methods of determining medium effects.

The distribution method.

From the expression for the medium effect of solute i

$$ {}_m\gamma_i = \frac{a_i}{a_i^*} \qquad (6) $$

where a_i is the activity of the solute on the aqueous or any other "reference solvent" scale, and a_i^* is the activity of the solute in the same solution but on the scale in the given non-reference solvent, it can be seen that distribution methods can be used to evaluate medium effects for electrolytes and neutral molecules. In those few instances where two solvents are totally immiscible, the medium effect of a compound can be determined by studying its distribution between the solvents when they are in contact with one another. Since it is not possible to distribute a single ion between two phases, only medium effects for electroneutral compounds can be determined in this manner. In practice, the distribution method for determining medium effects has not been too useful because most solvents of interest are miscible with one another.

The solvation energy method.

By definition, the difference between aqueous and nonaqueous standard free energies of solvation is directly related to the medium effect:

$$ {}_{s}G_{i}^{o} - {}_{w}G_{i}^{o} = RT \ln {}_{m}\gamma_{i} \qquad (7) $$

This relationship suggests another method that can be used to determine thermodynamic medium effects for electrolytes. The standard free energy of solvation of species i can be determined in the solvents of interest and the medium effects can be computed from these values. Alternately, methods can be devised which give the difference between ${}_{s}G_{i}^{o}$ and ${}_{w}G_{i}^{o}$ directly. A major objection to the solvation energy method of determining medium effects is that the accuracy of the method is of the order of magnitude of the medium effects themselves unless the solvents involved have vastly differing solvating powers (4, 33).

The solubility method.

The solubility method is perhaps the most widely used method of determining thermodynamic medium effects. If an aqueous and nonaqueous solution is saturated with the compound of interest, the free energies of the saturated solutions will be

$$G(i,H_2O) = {}_wG_i^o + RT \ln (a_i)_{sat.} \qquad (36\text{-a})$$

$$G(i,s) = {}_sG_i^o + RT \ln (a_i^*)_{sat.} \qquad (36\text{-b})$$

where $(a_i)_{sat.}$ and $(a_i^*)_{sat.}$ are the activities of the saturated aqueous and nonaqueous solutions, respectively. If the solid crystals in contact with the aqueous and nonaqueous solutions are identical, the free energies of the solutions will be equal and, from Equations 36-a and 36-b:

$${}_sG_i^o - {}_wG_i^o = RT \ln \frac{(a_i)_{sat.}}{(a_i^*)_{sat.}} = RT \ln {}_m\gamma_i \qquad (37)$$

it can be seen that the medium effect for an electrolyte or an uncharged molecule can be determined by measuring its solubility in the solvents of interest. Again, it is important to note that the "reference solvent" does not have to be water.

There are various pitfalls to be watched for in

the solubility method. The first complication is that if crystal-solvates are formed, the free energies of the saturated aqueous and nonaqueous solutions will not be identical. In the general case of crystal-solvate formation, the expressions for the free energy of the solutions (Equations 360a and 36-b) must include the free energy change accompanying the transfer of solvent s from the pure solvent to the crystal-solvate

$$G = \nu RT \ln \frac{P_s}{P_{i \cdot x \cdot s}} \qquad (38)$$

Where P_s and $P_{i \cdot x \cdot s}$ are the vapor pressures of the solvent and the solvate, respectively. When corrections via Equation 38 are introduced into Equation 37 for the solvate $(i \cdot x \cdot s)$ and the hydrate $(i \cdot y \cdot H_2O)$, Equation 37 transforms into

$$ {}_sG_i^o - {}_wG_i^o - RT \frac{y}{x} \ln \frac{P_{H_2O}\, P_{i \cdot x \cdot s}}{P_s\, P_{i \cdot y \cdot H_2O}} = RT \ln \frac{(a_i)_{sat.}}{(a_i^*)_{sat.}} = \qquad (39)$$

$$= RT \ln {}_m\gamma_i$$

Another complication in the solubility method for determining medium effects for electrolytes is the possible association of ions in solvents of low dielectric constants. Where ion-pairing is appreciable, the activity of the electrolyte is no longer defined by Equation 29. The effective removal of ions from the

solution must be accounted for by including the degree of dissociation, α, in the expression for activity. For a uni-univalent electrolyte that is not completely dissociated, the activity becomes

$$a = m^2 \alpha^2 \gamma_{\pm}^2 \qquad (40)$$

Electrolytic conductance techniques are readily applied to determine the degree of dissociation.

A third problem that is often encountered when using the solubility method for determining medium effects is that of evaluating activity coefficients. In the case of dilute solutions of non-electrolytes, the activity coefficients are equal to unity (25). For electrolytes, activity coefficients have to be experimentally determined or calculated from a model. The Debye-Huckel model is useful for calculating activity coefficients of solutions of 1:1 electrolytes no more concentrated than 10^{-2} molar (32) in water and less than 10^{-2} molar for solutions in solvents with smaller dielectric constants than water. Experimental determinations of activity coefficients are desirable and possible in most instances.

The e.m.f. method.

Medium effects for electroneutral combinations of ions can be determined from e.m.f. measurements (34). The sums of the medium effects (in logarithmic form) of oppositely charged ions or the difference between the medium effects of ions of like charge are accessible.

The difference in standard free energies of solvation and hydration of species i corresponds to the transfer of species i from the aqueous to the nonaqueous standard states. The standard free energy for the hydration reaction

$$i(g) = i(w) \quad {}_wG_i^o \tag{41}$$

is ${}_wG_i^o$ and the standard free energy for the solvation reaction

$$i(g) = i(s) \quad {}_sG_i^o \tag{42}$$

is ${}_sG_i^o$. The transfer of i from aqueous to nonaqueous standard states corresponds to

$$i(w) = i(s) \quad {}_sG_i^o - {}_wG_i^o \tag{43}$$

and the energy of transfer is ${}_sG_i^o - {}_wG_i^o$. Standard free energies can be expressed in terms of standard potentials

via the equation

$$G_i^o = -nFE^o \qquad (44)$$

Thus, the medium effect for species i can be expressed in terms of standard potentials

$$\Delta E_i^o = -\frac{RT}{nF} \ln {}_m\gamma_i \qquad (45)$$

where ΔE_i^o is the standard potential corresponding to reaction 43. If standard free energies or solubility data are not available for a substance, its medium effect is still accessible through e.m.f. measurements. The experimental quantities that are available are differences in the standard potentials of species i and an arbitrary reference potential, usually that of hydrogen. In each solvent, the potential of hydrogen in that solvent is used as the reference potential. Thus, although the medium effect for a single ion, M^+, is not readily available through electrochemical measurements, the difference between the medium effects of M^+ and H^+ ions is accessible. The experimental aqueous standard potential of M^+ ion, ${}_wE^o(M,H_2O)$, in reality corresponds to the reaction

$$M^+(w) + \tfrac{1}{2} H_2 = M + H^+(w) \qquad {}_wE^o(H,H_2O) \qquad (46)$$

and in the nonaqueous solvent, the standard potential, ${}_sE^o(M,s)$, of M corresponds to

$$M^+(s) + \tfrac{1}{2}H_2 = M + H^+(s) \qquad {}_sE^o(M,s) \tag{47}$$

The difference between aqueous and nonaqueous standard potentials then corresponds to the reaction

$$M^+(w) + H^+(s) = M^+(s) + H^+(w) \tag{48}$$
$${}_wE^o(M,H_2O) - {}_sE^o(M,s)$$

and the difference ${}_wE^o(M,H_2O) - {}_sE^o(M,s)$ can be equated to the difference between the medium effects of M^+ and H^+ through Equations 43 and 45:

$${}_sE^o(M,s) - {}_wE^o(M,H_2O) = \frac{RT}{nF} \ln {}_m\gamma_i - \frac{RT}{nF} \ln {}_m\gamma_H \tag{49}$$

It should be noted again that ${}_sE^o(M,s)$ and ${}_wE^o(M,H_2O)$ are the conventional standard potentials that are experimentally accessible.

The difference between the conventional aqueous and nonaqueous standard potential of a divalent positive ion, Z^{+2} will correspond to this reaction

$$Z^{+2}(w) + 2H^+(s) = Z^{+2}(s) + 2H^+(w) \tag{50}$$
$${}_wE^o(Z,H_2O) - {}_sE^o(Z,s)$$

The difference, ${}_wE^o(Z,H_2O) - {}_sE^o(Z,s)$ can be equated to the difference between the medium effects of Z^{+2} and H^+ via Equations 42 and 44 :

$$ {}_sE^o(Z,s) - {}_wE^o(Z,H_2O) = \frac{RT}{2F} \ln {}_m\gamma_Z - \frac{RT}{F} \ln {}_m\gamma_H \qquad (51) $$

For an electrode reversible to a univalent negative ion, X^-, the conventional aqueous standard potential corresponds to the reaction

$$ X + \tfrac{1}{2}H_2 = X^-(w) + H^+(w) \quad {}_wE^o(X,H_2O) \qquad (52) $$

The conventional nonaqueous standard potential of X^- corresponds to

$$ X + \tfrac{1}{2}H_2 = X^-(s) + H^+(s) \quad {}_sE^o(X,s) \qquad (53) $$

The difference in standard potentials corresponding to the transfer of X^- and H^+ from water to the nonaqueous solvent is then

$$ X^-(w) + H^+(w) = X^-(s) + H^+(s) \qquad (54) $$
$$ {}_sE^o(X,s) - {}_wE^o(X,H_2O) $$

And from Equations 43 and 45, the medium effects of X^- and H^+ that correspond to the difference in standard

potentials of X^- are

$$ {}_wE^\circ(X,H_2O) - {}_sE^\circ(X,s) = \frac{RT}{F} \ln {}_m\gamma_X + \frac{RT}{F} \ln {}_m\gamma_H \qquad (55) $$

From the conventional standard potentials of a metal-metal ion electrode in water and in nonaqueous solvent, the difference between the medium effect of the metal ion and hydrogen can be calculated from Equations 49 or 51. From the conventional standard potentials of an anion electrode, the sum of the medium effects of the anion and hydrogen can be calculated from Equation 55. For the cases where divalent anions or trivalent anions and cations are involved, equations similar to 49, 51 and 55 can be derived. Only medium effects for electroneutral sums and differences of combinations of ions are experimentally accessible.

Medium effects for single ions.

Introductory remarks.

The solution to the three interrelated problems of establishing universal solvent-independent electrode potential scales and ion-activity scales, as well as of evaluating aqueous-nonaqueous liquid-junction potentials is dependent upon the evaluation of medium effects for single ions. For each solvent, only one single ion medium effect would have to be estimated and all others would then be accessible by rigorous thermodynamic methods. With medium effects for single ions, we could express all electrode potentials on a single scale with only one arbitrary zero point, $E_H^o = 0$ in water only; we could express all single ion activities on a single scale with only one standard state, the infinitely dilute aqueous solution; we could evaluate liquid-junction potentials at aqueous-nonaqueous interfaces.

Recently, there have been many extrathermodynamic methods proposed for evaluating medium effects for single ions. This particular branch of electrochemistry has become alive, so to speak with real valid attempts at solving the problems. The problem of the single ion medium effect would probably have remained academic if it weren't for the availability of many nonaqueous solvents in large scale quantities. Although there is probably

more known about aqueous electrochemistry than electrochemistry in all other solvents combined, the study of nonaqueous electrochemistry is developing at a rapid pace. More and more investigators are concerning themselves with nonaqueous chemistry and the importance and scope of medium effects for single ions has taken on new significance. Knowledge of medium effects for single ions will prove useful in the areas of study of electrode potential, liquid-junction potential, surface potential, solvation in pure and mixed solvents, of acid and base strengths, establishment of nonaqueous pH and other single-ion scales, theories of solvation, studies of hydrogen-bonding and other specific solute-solvent interactions, solubility product determinations, extraction theory and practice, and chromatographic theory and analysis. Nowadays, with our newly developed interests in nonaqueous chemistry, with the realization that chemistry does not have to be confined to aqueous media, the medium effect problem has reached a position of major importance.

Physical interpretation of medium effects for single ions.

Just mentioning the words "single ion" would be enough to disturb some thermodynamicists. In 1929, E. A. Guggenheim, the thermodynamicist, made his famous anti-single ion statement which for decades has deterred physical chemists from investigating energic properties of single ions. In Guggenheim's words (5):

> "The electric potential difference between two points in different media can never be measured and has not yet been defined in terms of physical realities; it is therefore a conception which has no physical significance."

This statement has done much more harm than good. It was probably intended to show that thermodynamics cannot give us exact values for certain properties of single ions. It does not mean, however, that energic properties of single ions can never be determined extrathermodynamically. Many investigators feel (4, 7, 8, 21, 32, 35) that non-thermodynamic properties of individual ions are not only physically significant but are accessible extrathermodynamically. There seems to be some sort of stigma on the field of single ion energetics due to Guggenheim's original statement and the number of investigators who blindly followed his lead and extended the original meaning of his statement until it was generally beleived that studies of single-ion properties are fruitless. On the contrary, studies of single-ion

energetics have proven to be extremely fruitful and useful. The pH scale and specific ion electrodes are just two areas in which single ion energetics have been successfully applied. There is no doubt that hydrogen-ion activities can be measured with more accuracy than many thermodynamic quantities (4, 12). The old beleif that only thermodynamic data are reliable is crumbling as investigators are discovering the wonderful usefulness of single ion quantities derived extrathermodynamically.

The widespread beleif that physical properties of single ions have no physical significance is absurd. This is just a myth that was started by the early thermodynamic purists and perpetuated until this day. It is obviously true that the whole is equal to the sum of its parts and thus, we can say that the free energy of a salt is equal to the sum of all the contributions to the free energy by the individual ions comprising the salt. Individual ions do exist, even though they are under each others influence. Alfenaar and DeLigny have said (21):

> "...knowledge of activity coefficients of individual ions is not only of academic interest, but can also contribute towards the understanding of intermolecular, and even intramolecular interactions. Hence, it may be concluded that activity coefficients of individual ions have physical significance."

and Strehlow has said (36):

> "If one accepts the view that the correct prediction of the outcome of an experiment and the correlation of experimental facts are the genuine aim of theoretical considerations, then 'single ion thermodynamics' is a legitimate branch of physical chemistry."

Other investigators feel that although single ion activities are thermodynamically inaccessible, they do have significance in that they offer an explanation for various phenomena. Frank (7) feels that the problem of single ion activities is one of accessibility only since there is no problem in defining a single ion activity in terms of a thought process. For example, one can think of a liquid-junction potential between solutions of different activity in two similar solvents as being due to the transport of ions across the junction.

For the past forty years, chemists have tacitly admitted the physical reality of single ion properties in their widespread use of the Debye-Huckel equations. Since the time of Pleskov (37) and Izmaylov (38), chemists have been actively seeking ways to measure experimentally medium effects for single ions.

There is an abundant amount of experimental evidence to support the physical reality of energic

properties of single ions. The success of the pH scale and other single ion scales is indisputable. As Popovych has said (4):

> "Conventional pa_H values are beleived to possess a definite meaning in terms of thermodynamic acid-base equilibria."

Strong acids are more tightly solvated by liquid ammonia than by water (36, 39). The difference in solvation energy of these acids between ammonia and water is about 25kcal/mole and almost wholly independent of the anion. Alkali salts of these acids have about the same solvation energy in water and liquid ammonia. Although circumstantial, this is good experimental evidence that protons are more tightly solvated by ammonia than by water whearas alkali-metal ions and anions do not prefer either solvent. From conductivity, transference, and viscosity measurements of solutions of silver nitrate in mixtures of acetonitrile and water, Strehlow and Koepp (88) determined that silver ions are preferentially solvated by CH_3CN as compared to water. It is difficult, if not impossible to discuss the thermodynamic properties of compounds without including some single ion interpretation.

Bockris and Reddy (32) ask the question "Is it meaningful to try to obtain experimental values of the heats of solvation of an individual ion?". In the

answer to this question, they cite proof that solvation enthalpies of single ions are meaningful. This can be seen by comparing the differences in hydration enthalpies between pairs of salts with only one varying ion. In Table 1, it is seen that there are almost constant differences in the heats of hydration of lithium and sodium halides and of sodium and potassium halides. Because in each pair of salts, the differing ions are Li--Na or Na--K, the differences in hydration energies of the salts must represent the difference in hydration energies of the individual cations.

In the opinion of this author, there is no question about physical significance of properties of single ions. This includes differences in those properties such as medium effects for single ions. The problem lies in the accessibility of those properties, not in their physical significance.

Table 1. Enthalpies of Hydration of Pairs of Alkali-Metal Salts with Common Anions (32).

Salt	$-\Delta H^{o}$ kcal/mole	Difference
LiF	245.2	27.4
NaF	217.8	
LiCl	211.2	27.4
NaCl	183.8	
LiBr	204.7	27.4
NaBr	177.3	
LiI	194.9	27.4
NaI	167.5	
NaCl	183.8	20.0
KCl	163.8	
NaBr	177.3	20.0
KBr	157.3	
NaI	167.5	20.0
KI	147.5	

Difference between "real" and "chemical" energies of solvation.

The process of solvation can be envisioned in a thought experiment. A particle in vacuum is brought across the vacuum-solution interface into the solvent where it is solvated. For an uncharged particle, the only energy involved is the energy of interaction between the particle and the solvent in the interior of the solution. There is no energy required to bring an uncharged particle across the surface of the solution. For a charged particle, however, there is an energy involved when the particle traverses this interface. This energy is given by $zF\psi$ where z is the charge on the particle, F the Faraday, and ψ the surface potential of the solvent. The energy term $zF\psi$ is opposite in sign for anions and cations. The total energy involved in bringing a particle from vacuum to its solvated state in solution is termed the "real" solvation energy. If medium effects for single ions were formulated using "real" solvation energies, they would include a term corresponding to the difference between the surface potentials of water and the nonaqueous solvent. This would be inconsistent with the definition of the medium effect as a measure of the difference between the standard free energies of hydration and solvation.

Alternately, a thought experiment can be devised for the solvation process in which the particle is discharged in vacuum, brought across the vacuum-solution interface, placed in the interior of the solvent, and then charged. In this process, the species crossing the double layer at the surface of the solution is uncharged regardless of its initial and final charge, so that the solvation energy derived from a process like this does not include the $zF\Psi$ term due to the surface potential of the liquid. Solvation energies derived from processes like these are called "chemical" energies of solvation and it is the difference between the "chemical" energies of solvation and hydration that exactly corresponds to the medium effect for an ion. For neutral molecules or electroneutral combinations of ions, the "real" and "chemical" energies of solvation are identical.

It is best to visualize the medium effect for a single ion as the energy corresponding to the following three thought processes; 1) two identical ions are discharged in vacuo 2) one ion is brought across the aqueous double layer, the other across the nonaqueous double layer 3) the ions are charged in their respective solvents.

Pleskov (37) was the first to emphasize the difference between "real" and "chemical" solvation energies. Following Pleskov's formulation, the "real"

energy of solvation for a cation, G_p is

$$G_p = G_x + zF_s\Psi_o \qquad (56\text{-a})$$

where G_x is the "chemical" solvation energy and $_s\Psi_o$ is the surface potential of the medium. For an anion, the "real" solvation energy, G_p is given by

$$G_p = G_x - zF_s\Psi_o \qquad (56\text{-b})$$

It is possible to measure the "real" solvation energies of single ions (40--43). It is only the "chemical" solvation energies that have proven to be experimentally innaccessible. With knowledge of "real" solvation energies and surface potentials, it would be possible to calculate "chemical" solvation energies. Alternately, with knowledge of "chemical" and "real" solvation energies, it would be possible to calculate surface potentials.

Randles (40, 41) devised a method to measure "real" hydration energies of ions. In his method, the potential difference is measured between a stream of mercury and a stream of electrolyte solution separated by inert gas such as N_2 or A. A jet of mercury is passed through the axis of a cylindrical tube down the sides of which is passing a stream of aqueous electrolyte.

A steady potential develops between the mercury and the solution. Cell II is a typical cell used by Randles

$$Hg\ jet\ /N_2\ gas\ /KCl(H_2O, flowing), Hg_2Cl_2, Hg \qquad \text{Cell II}$$

From the potential of Cell II and cells like it, Randles calculated the "real" solvation energy of alkali-metal and halide ions. As with medium effects, once the "real" solvation energy of one ion is known in any solvent, the "real" solvation energies of all other ions become accessible through thermodynamics. A difference between "real" and "chemical" solvation energies is that the "real" solvation energy of a single ion is a thermodynamic quantity to begin with. Since the surface potential of water is not yet known with any degree of accuracy, Randles' "real" single ion hydration energies cannot be used to calculate "chemical" hydration energies.

In another type of experiment, Case and Parsons (42, 43) estimated "real" free energies of transfer of individual ions from water to some organic solvents. They measured the e.m.f. in cells in which an air space separates an aqueous and a nonaqueous electrolyte solution. Identical electrodes are immersed in the two solutions and the "real" free energy of transfer of the

chloride ion is calculated from the e.m.f. of cells such as Cell III

$$Ag/AgCl/NaCl,solvent/air/NaCl,H_2O/AgCl/Ag \qquad \text{Cell III}$$

By combining Randles' data on "real" hydration energies with Case and Parson's data for "real" energies of transfer, "real" energies of solvation can be calculated. However, data on real solvation and hydration energies cannot be used to calculate medium effects until we have accurate values for the surface potential of all solvents involved.

Choice of water as a reference solvent.

So far in this thesis, the medium effect has been defined as a measure of the difference between the standard free energies of hydration and solvation. While this is by far the most common definition, it is a bit misleading since it implies that medium effects are involved only when water is one of the solvents. Although water is most often choosen as the "reference" solvent to which all nonaqueous activities and e.m.f.'s are referred, it need not necessarily be the case. Sometimes, experimental data are available for a series of solvents other than water. If a solvent-independent e.m.f. or ion-activity scale were to be set up using this data, the solvent for which the most data is available would be choosen as the "reference" solvent. In the most general sense, the medium effect can be defined as a measure of the difference between the standard free energy of solvation in a reference solvent and another solvent

$$ {}_{s}G_i^{o} - {}_{ref}G_i^{o} = RT \ln {}_{m}\gamma_i \qquad (57) $$

In this thesis, unless otherwise stated, it will be assumed that water is the reference solvent. There are actually many valid reasons for choosing water as the reference solvent. Water has been the most

frequently studied solvent. In the beginnings of chemistry, it was the only solvent available in quantity. It is easily purified, easy to obtain, and cheap. Its high dielectric constant (D = 78) makes it a good solvent for ionic compounds. It has a high boiling point and it is non-toxic. The author recommends retention of water as the "reference solvent".

Experimental inaccessibility of medium effects for single ions.

Medium effects for single ions are not directly accessible through the distribution, solvation energy, solubility, or e.m.f. methods. Since surface potentials of various solvents are not accurately known, knowledge of "real" chemical energies of solvation for single ions does not lead to knowledge of medium effects for single ions. Various thought experiments can be devised which would allow an investigator to work with single ions. In the ultimate experimental sense, an experiment can be devised in which a beam of single ions is directed at a solvent for the purpose of obtaining a chemical solvation energy. There are two important criticisms of an experiment like this. First of all, the observed solvation energy would be the "real" solvation energy rather than the "chemical" solvation energy because the ions would be passing through the vacuum-solution interface. The second criticism to this experiment is that once one ion entered the solution, the solution would develop a net charge. Because of this, the next ion would be entering a charged solution and this would give rise to an ion-solution repulsion energy which would have to be accounted for when calculating the single ion solvation energy. Each successive ion would see a solution that has a greater and greater

charge. The only way to counteract this difficulty is to have an equal number of oppositely charged ions enter the solution. In this case, the experimentally accessible quantity would be the solvation energy of the electrolyte, not of its individual ions. So far, no one has devised an experiment, practical or impractical which would allow direct measurement of the solvation energy of a single ion or the medium effect of a single ion. Apparantly, values of single ion solvation energies and medium effects for single ions must be arrived at via extrathermodynamic models and assumptions.

Extrathermodynamic methods for estimating medium effects for single ions.

Introduction.

The incentive for the evaluation of medium effects for single ions lies in trying to find a solution to the three interrelated problems of establishing a solvent-independent e.m.f. scale, solvent-independent ion-activity scales, and evaluation of aqueous-nonaqueous liquid-junction potentials. There have been more than twenty different extrathermodynamic approaches to the problem of evaluating medium effects for single ions. The results of the various approaches are not in good agreement. One of the major purposes of this section of this thesis is to review critically the existing methods for estimating the medium effects of single ions.

Basically, the methods can be divided into two broad categories: 1) those based on the assumption of negligible liquid-junction potential and 2) those based on relationships between the sizes of ions and their solvation energies. Among methods in the second group are extrapolation methods, calculations based on modified Born equations, and various empirical assumptions for reference solutes. In some methods, medium effects for single ions are estimated directly

whereas in others, solvation energies for single ions are estimated first and then the medium effects are calculated from their differences. It should be noted that it is not necessary to know the single ion solvation energies in order to calculate the corresponding medium effects.

There have been many reviews of methods for estimating medium effects for single ions (4, 8, 10, 12--14, 17, 18, 26--28, 36, 44--47). The review by Popovych (4) is by far the most comprehensive one.

The assumption of negligible liquid-junction potentials.

Introduction.

Methods for estimating medium effects based on the assumption of negligible liquid-junction potentials at the interface of two solvents make use of e.m.f. cells such as Cell I. If one assumes that the E_j in Cell I is negligible, the cell potential, E_{cell}, will be a direct measure of the medium effect of the proton. While the negligible E_j approach is primarily of historical interest only, Parker and Alexander (26) have recently revived this method. In aqueous electrochemistry, concentrated salt bridges have been used extensively (51) in cells with liquid-junction to minimize the junction potential. The basic requirement for the salt is that the mobility of its ions should be as equal as possible and that it carry most of the current. A natural extension of the use of concentrated salt bridges in aqueous electrochemistry was to use them for minimizing the liquid-junction potential between aqueous and nonaqueous solutions. In 1928, Koch (52) made use of $AgNO_3$ solutions to minimize the junction potential between an aqueous and a nonaqueous (acetonitrile) silver half-cell. Koch was not aware of the nature of the medium effect and he did not calculate medium effects for single ions from his data.

Bjerrum and Larsson.

Bjerrum and Larsson (9) were the first to propose an experimental method for the purpose of estimating medium effects for single ions. Their method was based on e.m.f. measurements of cells with liquid-junction and the assumption that aqueous--nonaqueous liquid-junction potentials could be suppressed with concentrated salt bridges. Cell IV is a typical cell used by them to estimate $\log {}_m\gamma_H$

$$Pt;H_2(g)/H^+,Cl^-/3.5N\ KCl\ (aq.)/Hg_2Cl_2(s);Hg;Pt \qquad \text{Cell IV}$$

Using an aqueous calomel electrode and a 3.5N aqueous KCl bridge, the standard potential of the cell was determined with an aqueous hydrogen electrode and with a nonaqueous hydrogen electrode. Assuming that the potential of the calomel electrode remained constant, Bjerrum and Larsson then calculated the medium effect for the proton using the equation

$$\ln {}_m\gamma_H = \frac{E^\circ(cell,H_2O) - E^\circ(cell,alc)}{RT/nF} \qquad (58)$$

where $E^\circ(cell,H_2O)$ and $E^\circ(cell,alc)$ are the standard potentials of Cell IV with an aqueous and a nonaqueous hydrogen electrode, respectively. The medium effects

for silver and benzoate ions were estimated in a similar manner. Bjerrum and Larsson estimated medium effects for single ions in ethanol--water mixtures and in 100 % ethanol. Some of their results are given in Table 76. In line with Bjerrum's notation (54) for the medium effect, Bjerrum and Larsson used "P" for "log $_{m}\gamma_{H}$".

Although Bjerrum and Larsson made experimental measurements on cells similar to Cell IV, Cell V would yield identical results

$$\mathrm{Pt;H_2(g,1\ atm);H^+(H_2O)/3.5N\ KCl\ (H_2O)/-}\ \overset{E_j}{}\ \mathrm{-H^+(nonaqueous);H_2(g,1\ atm);Pt} \qquad \text{Cell V}$$

The potential of Cell V with unit hydrogen ion activity in both half cells would be given by

$$E = {}_{w}E^{o}(H,s) - {}_{w}E^{o}(H,H_2O) + E_j \qquad (27)$$

The measured potential would be equal to the sum of the medium effect for the proton and the liquid-junction potential:

$$E = \frac{RT}{F} \ln {}_{m}\gamma_{H} + E_j \qquad (28)$$

Some criticisms of Bjerrum and Larsson's work are their failure to account for incomplete dissociation of electrolytes in ethanol and ethanol--water solvents and their use of Bjerrum's cube root formula

$$\log f = -k\sqrt[3]{C} \qquad (59)$$

for estimating activity coefficients. Bjerrum's formula is no longer accepted as a valid means of estimating activity coefficients.

Any method for estimating medium effects for single ions should yield values which are consistent with thermodynamic data. The experimental value of $\log {}_m\gamma_K - \log {}_m\gamma_H$ in 100 % ethanol, obtained by Dill, Itzkowitz, and Popovych (72) is +1.0. Bjerrum and Larsson's values of $\log {}_m\gamma_K$ and $\log {}_m\gamma_H$ are +4.1 and +2.5, respectively. These do not combine to give the experimentally observed value for $\log {}_m\gamma_K - \log {}_m\gamma_H$. There are other more glaring discrepancies in Bjerrum and Larsson's data. For instance, the experimental value of $\log {}_m\gamma_{NaBr}$ in 100 % ethanol as measured experimentally (31) is +2.43 whereas the sum of $\log {}_m\gamma_{Na}$ and $\log {}_m\gamma_{Br}$ as evaluated by Bjerrum and Larsson is +5.3.

Oiwa.

In an improvement over the method of Bjerrum and Larsson, Oiwa (55), using cells similar to Cell V, "corrected" the cell e.m.f. for liquid-junction potential using the Plank equation before calculating medium effects. However, the Plank equation (51) is an approximation which fails to account for the salt-effect activity coefficients of ions on both sides of the junction. Moreover, in the case of aqueous--nonaqueous junctions, Plank's equation also fails to account for the difference in standard free energy of solvation of ions on both sides of the junction. Actually, Oiwa realized the shortcomings of the Plank equation but without knowledge of medium effects for single ions, he could not correct for them.

Parker and Alexander.

Recently, Parker and Alexander (26) proposed that for cells of the following type:

$$\underset{\text{reference solvent}}{Ag/AgNO_3(0.01\ M)/Sat'd.Et_4N\ Pi/AgNO_3(0.01\ M)/Ag}\ \underset{\text{solvent s}}{}\qquad \text{Cell VI}$$

where both solvents are similar in type, the cell potential would be equal to $\log {}_m\gamma_{Ag}$. Both the reference solvent and solvent s have to be dipolar aprotic or, the reference solvent can be methanol if solvent s is water or formamide. The solvent used for the junction solution can be the reference solvent or solvent s.

All E_j assumptions are unsound. As will be shown in the next section, it is the medium effects of the ions in the junction solution and the solvent in the junction solution that determine the magnitude of E_j. Inclusion of a saturated salt bridge between aqueous and nonaqueous half-cells does not minimize the junction-potential.

The liquid-junction potential at an aqueous--nonaqueous interface is a function of medium effects for single ions.

Methods for estimating medium effects for single ions based on the assumption of negligible liquid-junction potential in cells such as Cells IV, V and VI are inherently invalid. A liquid-junction potential between solutions in two dissimilar solvents is due to transport of ions and solvent molecules across the aqueous--nonaqueous boundary. The contribution of ion transport to the junction potential is given by

$$E_j = -\frac{1}{F} \sum \frac{t_i}{z_i} \Delta G_i \qquad (60)$$

where t_i is the transference number of the ion, z_i its charge, and $\Delta G_i \equiv {}_sG_i - {}_wG_i$. The ΔG_i term is composed of a medium effect term, a molality term, and a salt-effect activity coefficient term:

$$\Delta G_i = {}_sG_i^o - {}_wG_i^o + RT \ln \frac{{}_sm_i}{{}_wm_i} + RT \ln \frac{{}_s\gamma_i}{{}_w\gamma_i} \qquad (61)$$

where the subscripts w and s refer to the aqueous and nonaqueous standard states, respectively. The term ${}_sG_i^o - {}_wG_i^o$ is equal to $RT \ln {}_m\gamma_i$, the medium effect of species i. Thus, the total liquid-junction potential between two solutions, E_j, consists of terms due to

1) the medium effects for the ions transported across the junction, $RT \ln {}_m\gamma_i$, 2) the inequality of the molalities in the two solutions, $RT \ln ({}_sm_i/{}_wm_i)$, 3) the difference in salt-effect activity coefficients in the two solutions, $RT \ln ({}_s\gamma_i/{}_w\gamma_i)$, and 4) the transport of solvent molecules across the junction, $E_{j\,solv}$ (53):

$$E_j = -\frac{1}{F}\sum\frac{t_i}{z_i}\left(\ln {}_m\gamma_i + RT\frac{{}_sm_i}{{}_wm_i} + RT \ln \frac{{}_s\gamma_i}{{}_w\gamma_i}\right) + E_{j\,solv} \quad (62)$$

The total liquid-junction potential is therefore the sum of an ionic contribution, E_j' and a solvent contribution, $E_{j\,solv}$:

$$E_j = E_j' + E_{j\,solv} \quad (63)$$

Equations such as the Henderson and Plank equations have been derived for the purposes of estimating liquid-junction potentials. These equations only account for that part of the liquid-junction potential due to concentration gradients across the junction (term 2, Eq. 62). They omit all activity coefficient terms including the medium effect and the term $E_{j\,solv}$. Thus, when evaluating liquid-junction potentials between two different media, equations such as Equation 64 (51)

$$E_j = -\frac{RT}{F}\int_1^2 \sum \frac{t_i}{z_i}\, d \log_m \gamma_i \qquad (64)$$

which is the general expression for a liquid-junction potential, have not proven to be useful.

Alfenaar, DeLigny, and Remijnse (53) evaluated the $E_{j\,solv}$ contribution to E_j using cells of the type:

$$\underset{H_2O}{Ag(s)/AgZ(s),MZ/MZ,AgZ(s)/Ag(s)} \qquad \underset{E_j}{\quad} \qquad \underset{CH_3OH--H_2O}{\quad} \qquad \text{Cell VII}$$

where MZ is an alkali halide. The concentration of MZ was kept low and equal in both half-cells thus eliminating the concentration and salt-effect activity coefficient terms from Equation 62. The liquid-junction potential of Cell VII is then

$$E_j = -\frac{t_M}{F}\Delta G_M^o + \frac{t_Z}{F}\Delta G_Z^o + E_{j\,solv} \qquad (65)$$

The e.m.f. of Cell VII is then

$$E = -\frac{t_M}{F}\Delta G_{MZ}^o + E_{j\,solv} \qquad (66)$$

In Equation 66, ΔG_{MZ}^o is the solvation energy change for a complete electrolyte which is a thermodynamic

quantity. Alfenaar, DeLigny and Remijnse were thus able to evaluate $E_{j\,solv}$ from experimental measurements on Cell VII. They found that $E_{j\,solv}$ is a function of the medium and of the electrolyte used, but it depends mostly on the composition of the medium.

Using previously determined values of medium effects for single ions (8), Alfenaar et al. were able to evaluate the overall E_j using Equation 65. According to their results, 10 - 25 % of the overall E_j is due to $E_{j\,solv}$ with the remainder attributable to E_j' which is due to the transport of ions across the junction. The average value of E_j in 100 % CH_3OH varied from +0.234v (for CsCl) to +0.272v (for NaCl). E_j using a saturated KCl junction was evaluated to be +0.268v. Clearly, the liquid-junction potential arising between solutions in water and methanol and methanol--water mixtures cannot be eliminated by using concentrated salt bridges. Alfenaar, DeLigny and Remijnse also found that the medium effects of the ions diffusing across the junction is the most important contribution to the aqueous--nonaqueous liquid-junction potential.

Components of solvation energy of an ion.

Due to the complexity of the structure of liquids and the nature of ion-solvent interactions, a rigorous mathematical treatment of the components of solvation energy has not yet been developed. Strictly speaking, any good theoretical treatment of solvation energies must include all the possible ion-solvent interactions.

The molecules adjacent to an ion are affected much more by the electric field surrounding the ion than molecules farther away. The ion "sees" those solvent molecules adjacent to it as individual molecules whereas the ion cannot distinguish between solvent molecules that are far away. The ion and the solvent molecules tend to get distorted due to their mutual interactions. In many instances induced-dipole and induced-quadrupole forces play a significant part in the total solvation energy of an ion.

Generally speaking, contributions to the solvation energy of an ion can be grouped into two categories, the electrostatic and the neutral, or non-electrostatic, contributions. The electrostatic contributions can be attributed to the interaction of solvent molecules with the electric field of the ion and these energies are generally functions of r^{-1}, where r is the ionic radius. Neutral contributions to the solvation energy of an ion include all those energies which would be

experienced by an uncharged particle of the same size and structure as the ion. In general, the formal division of solvation energy into an electrostatic and a neutral part becomes more appropriate as the ion gets larger. Solvent molecules adjacent to small ions line themselves up in the electric field of the ion. This is called dielectric saturation. In the absence of dielectric saturation, the neutral contribution to the solvation energy of an ion should exactly equal the solvation energy of an uncharged molecule of the same size and structure as the ion. The following is a discussion of various ion-solvent interactions which contribute to the solvation energy of an ion.

The Born charging energy, $G^{o}(\text{Born})$, represents the difference between the electrostatic free energy required to impart a charge, ze, to a spherical ion of radius r in a vacuum and in a solvent of uniform dielectric constant, D (57):

$$G^{o}(\text{Born}) = -\frac{z^2e^2}{2r}\left(1 - \frac{1}{D}\right) \qquad (67)$$

The Born charging energy is a function of r^{-1}. The Born model, the predictions based on it, and a critique of using it to estimate standard free energies of solvation will be discussed in section IV-C-2.

Ion-dipole forces are those which line up solvent

molecules in the electric field about an ion. The energy involved with ion-dipole forces depends on the angle between the dipole and the line joining the centers of the dipole and the ion, θ (56), and is given by $(-ze\mu n \cos\theta / r^2)$ (47, 56), where n is the solvation number and μ is the dipole moment of the solvent. Ion-dipole forces are functions of r^{-2}. They are short-range forces and for this reason, the dielectric constant does not appear in the expression because there are no solvent molecules between the dipole and the ion.

Dipole-dipole forces, which are also directional in character, have a maximum energy of $(2\mu_A\mu_B/r^3)$ when the dipoles are in line with each other. μ_A and μ_B are the dipole moments of the solvent and solute. These forces, which are functions of r^{-3}, would be greatest for large, highly polarizable ions.

Ion-quadrupole forces are functions of r^{-3} also. They are particularly important in aqueous solutions where water molecules close to the ion can be viewed as an assembly of four charges (the two protons and the two other $2sp^3$ oxygen orbitals being the centers of the quadrupole) rather than a dipole (32, 58). Ion-quadrupole energy has been formulated as $(ze\phi(3\cos^2\theta - 1)/2r^3)$ where ϕ is the quadrupole moment of the solvent and θ is the angle between

the quadrupole and the line joining the centers of the quadrupole and the ion (56). Very little is known about the magnitudes of quadrupole moments. However, they are opposite in sign for anions and cations. In recent mass spectrometric studies of gas phase equilibria between alkali-metal ions with water and halide ions with water (68, 69), Kebarle et al. have found that ion-quadrupole interactions are minimal and therefore it is difficult to distinguish between a positive and a negative ion of the same size on the basis of differences between their ion-quadrupole interaction energies.

Ion-(induced dipole) interaction energies are functions of r^{-4} (32, 56). These are important in aqueous solutions where water molecules adjacent to ions experience a distortion of their electronic cloud and an extra dipole moment is established in the water molecule over and above its regular dipole moment. The ion-(induced dipole) interaction is especially important for small ions and must be considered in any theory of solvation. This ion-(induced dipole) interaction occurs mainly between the ion and solvent molecules in the primary solvation sheath (32, 59) where solvent molecules are bound to the ion in one kinetic entity (20). For large ions, there is no permanently bound layer of water molecules

directly adjacent to the ion and so, there is no appreciable contribution to the solvation energy due to ion-(induced dipole) interactions.

Ion-(induced quadrupole) forces are functions of r^{-5} (60). These forces are probably quite small. Until now, they have always been neglected in solvation energy theories. Almost nothing is known about their magnitudes (56).

Dispersion forces are due to mutual polarization between ion and solvent. Dispersion forces are a function of r^{-6} (61).

Another contribution to the electrostatic part of the solvation energy for an ion is due to charge-transfer forces. These occur between two species that exist in a state of resonance between a non-bonded, AB, and a charge-transfer (bonded), A^+B^-, state. Charge-transfer forces are particularly strong when one of the species is electronegative and the other has a fairly low ionization potential. At present, only rough estimates of charge-transfer energies can be made. In a recent mass spectrometric study of gas phase equilibria of alkali-metal ions and water molecules (69), it has been found that the species $Li(H_2O)^+$ and $Na(H_2O)^+$ have a considerable degree of covalent character. Thus, for small ions, charge-transfer energies may play an important role in determining solvation energies.

Thus, the Born charging energy, ion-dipole energy, dipole-dipole energy, ion-quadrupole energy, ion-(induced dipole) energy, ion-(induced quadrupole) energy, and dispersion forces, which are functions of r^{-1}, r^{-2}, r^{-3}, r^{-3}, r^{-4}, r^{-5}, and r^{-6}, respectively, as well as charge-transfer energies, are contributors to the electrostatic free energy of solvation of ions.

Contributions to the neutral, or non-electrostatic component of solvation energy include dispersion interactions, energy of hole (cavity) formation, and a contribution due to change in standard state from gas to solution. As of now, there are no generally accepted methods which can be used to calculate dispersion interactions (4). Pierotti (133) and Alfenaar and DeLigny (8) beleive that dispersion interactions depend mainly on the polarizabilities per unit volume of the solute and solvent. For ions and atoms, the polarizability approximately equals the volume (83). Thus, ions and atoms of the same size should have the same polarizability. Alfenaar and DeLigny feel that polarizabilities and therefore dispersion interactions are only slightly dependent on radius. An excellent piece of supporting information is the fact that the free energy of transfer of the noble gases, CCl_4, ferrocene, $Sh(CH_3)_4$, and $Sn(C_2H_5)_4$ from water to methanol is a linear function of r^2 through

most of the range, where r is the radius of the uncharged molecule. Thus, it would appear that dispersion forces are proportional to the surface area of the particle and play a major role in the solvation of large particles.

Energy of hole or cavity formation is also a contributing factor to the neutral part of solvation energy (32). Placement of an ion in the bulk of the solvent involves disturbing the general structure of the solvent. For a highly structured solvent such as water, cavity formation involves the destruction of some hydrogen bonds (~ 5 Kcal/mole). For other less structured solvents, energy of cavity formation will include overcoming the solvent-solvent forces which must be disturbed for the ion to be included in the solvent. Energy of cavity formation is especially important for hydrogen-bonded solvents.

There is a neutral or non-electrostatic contribution to solvation energy due to the change in standard state from gas to solution. For comparisons between solvents, this contribution will be zero.

Several proposals have been made to formulate solvation energy in terms of a power series in r^{-1} (8, 58, 62). Rather than have an infinite series as Alfenaar and DeLigny (8) and Buckingham (58) formulated, it is more suitable to express solvation energy in terms

of a finite series where each parameter accounts for a specific energy contribution (62). With this in mind, an equation relating solvation energies of an ion, G_i^o, to a series in r^{-1} and a neutral contribution, $G_i^o(neut)$, can be written;

$$G_i^o = G_i^o(neut) + \frac{a}{r} + \frac{b}{r^2} + \frac{c}{r^3} + \frac{d}{r^3} + \frac{e}{r^4} + \frac{f}{r^5} + \frac{g}{r^6} \qquad (68)$$

a/r represents the Born charging term and is identical to Equation 67. The other terms on the right hand side of Equation 68 represent ion-dipole, dipole-dipole, ion-quadrupole, ion-(induced dipole), ion-(induced quadrupole), and dispersion forces. If specific chemical interactions occur between the ion and solvent, Equation 68 would have to be suitably revised. A term corresponding to charge-transfer energy does not appear in Equation 68 because it has not yet been given a mathematical formulation.

An exact solution to Equation 68 is not feasible at the present time because of our limited knowledge of the parameters in the equation. Thus, solvation energies for single ions cannot be predicted by compiling all of the interaction energies between ion and solvent.

Equation 68 can be written in terms of the

difference in solvation energy of an ion between a pair of solvents, ΔG_i^o:

$$\Delta G_i^o = \Delta G_i^o(\text{neut}) + \frac{a'}{r} + \frac{b'}{r^2} + \frac{c'}{r^3} + \frac{d'}{r^3} + \frac{e'}{r^4} + \frac{f'}{r^5} + \frac{g'}{r^6} \qquad (69)$$

In this equation, the terms on the right hand side represent differences in the various energy contributions from Equation 68.

The Born equation.

Estimating solvation energies and medium effects for single ions.

In 1920, Born (57) derived his equation relating the electrostatic contribution to the solvation energy of an ion to the radius and charge of the ion, and the dielectric constant of the medium. As stated previously, the Born charging energy, G_i^o(Born), given by Equation 67, represents the difference between the electrostatic free energy of charging the ion in vacuo (dielectric constant = 1) and in the solvent. Some authors (63) are inclined to speak of the Born charging energy as if it represented the entire electrostatic contribution to the free energy of solvation. Actually, it does not. As was shown in section IV-C-1, it is only one of seven (Equation 68) contributions to the total electrostatic free energy of solvation.

In the Born model, the ion "sees" a continuum of structureless solvent with a dielectric constant of D. The ion is viewed as a rigid, undistortable sphere. The Born model suggests a simple thought process that would represent the charging energy. The three steps in this experiment are 1) the ion is discharged in vacuo requiring energy equal to W_1 2) the uncharged sphere is slipped into the solvent, a process which requires

no electrostatic energy 3) the charge on the sphere is restored requiring energy equal to W_2. The Born charging energy would then be given by

$$G^{o}(\text{Born}) = W_1 + W_2 \qquad (73)$$

Thus, the Born charging energy is a "chemical" energy and not a "real" energy contribution to G^{o} because it does not include the energy required for a charged ion to cross the vacuum--solution interface. Some authors (32, 63) give the impression that $G^{o}(\text{Born})$ is a "real" energy of solvation.

For very small ions, where the electric field in the immediate vicinity of the ion is large, short range ion-solvent interactions that are functions of r^{-2} to r^{-6} undoubtedly play a major role in solvation. This would especially be true in the case of highly ordered solvents of high dielectric constant such as water. As the ion gets larger, the Born charging term will tend to predominate over the other electrostatic contributions to solvation energy. For very large ions, the Born charging energy is endorsed by this author as an excellent estimation of the electrostatic contribution to the solvation energy.

For one mole of ions, the Born equation becomes

$$G^{o}(\text{Born}) = -\frac{Nz^2e^2}{2r}\left(1 - \frac{1}{D}\right) \qquad (71)$$

And the Born charging contribution to the standard free energy of transfer of one mole of ions, i, from aqueous to nonaqueous solution, $\Delta G_i^{o}(\text{Born})$, is

$$\Delta G_i^{o}(\text{Born}) = {}_sG_i^{o}(\text{Born}) - {}_wG_i^{o}(\text{Born}) = \frac{Nz^2e^2}{2r_i}\left(\frac{1}{D_s} - \frac{1}{D_w}\right) \qquad (72)$$

where the subscripts s and w refer to the nonaqueous solvent and water, respectively. The Born contribution to the medium effect of an ion, ${}_m\gamma_i(\text{Born})$ is given by

$$\ln {}_m\gamma_i(\text{Born}) = \frac{Nz^2e^2}{2RTr_i}\left(\frac{1}{D_s} - \frac{1}{D_w}\right) \qquad (73)$$

At 25°C, $N = 6.02 \cdot 10^{23}$, $e = 4.80 \cdot 10^{-10}$ esu, $D_w = 78.3$, $R = 8.31$ joules deg^{-1} mole^{-1}, and $T = 298$ deg (12). Substituting numerical values into Equation 73, an expression for $\log {}_m\gamma_i(\text{Born})$ with water as the reference solvent is obtained:

$$\log {}_m\gamma_i(\text{Born}) = \frac{121.6z^2}{r_i}\left(\frac{1}{D_s} - 0.0128\right) \qquad (74)$$

Predictions based on the Born equation.

The Born equation has often been used as a starting point in formulating theories of solvation (32) and in estimating solvation energies for single ions. Bronsted (1) was using the Born equation in 1928 to predict changes in pKa's of acids from one medium to another. In effect, Bronsted was calculating medium effects using the Born equation.

Upon inspecting Equation 67, one sees that the

$$G^{o}(\text{Born}) = -\frac{z^2e^2}{2r}\left(1 - \frac{1}{D}\right) \qquad (67)$$

solvation energy of an ion due to Born charging decreases in absolute magnitude as the dielectric constant of the solvent decreases and as the radius of the ion increases. It also increases with the charge on the ion.

Table 2 is a listing of Born solvation energies for univalent ions covering a range of radii and solvents calculated using Equation 67. One can see that the solvation energy is more sensitive to the size of the ion than to the dielectric constant of the solvent. Solvation energies at $D = 24$, $D = 33$, and $D = 36$ are included in the table because these are the dielectric constants of ethanol, methanol, and acetonitrile, respectively.

Table 2. Solvation Energies, G_i°(Born), for Univalent Ions of Various Radii and Solvents of Various Dielectric Constants, in kcal/g-ion.

r, Å	D = 78	70	60	50	40	36	33	30	24	20	10
1	161.4	163.8	163.4	162.9	162.1	161.6	161.2	160.7	159.3	157.9	149.6
2	82.0	81.9	81.7	81.5	81.0	80.8	80.4	80.3	79.6	79.0	74.8
3	54.7	54.6	54.5	54.3	54.0	53.9	53.7	53.6	53.1	52.6	49.9
4	41.0	41.0	40.9	40.7	40.5	40.4	40.3	40.2	39.8	39.5	37.4
5	32.8	32.8	32.7	32.6	32.4	32.3	32.2	32.1	31.9	31.6	29.9
10	16.4	16.4	16.3	16.3	16.2	16.2	16.1	16.1	15.9	15.8	15.0

Table 3 is a listing of Born contributions to the medium effects of univalent ions of various radii in solvents of varying dielectric constants. The medium effects were calculated using Equation 75 where water is the reference solvent:

$$\log {}_m\gamma_i(\text{Born}) = \frac{2.303\, N z^2 e^2}{2\, RT\, r_i}\left(\frac{1}{D_s} - \frac{1}{D_w}\right) \qquad (75)$$

Born contributions to the medium effects are greatest for the smallest ions. In general, the Born part of the medium effect for an ion increases as the dielectric constant of the nonaqueous solvent decreases

Table 3. $\log_m \gamma_i$ (Born) for Univalent Ions of Various Radii and Solvents of Various Dielectric Constants. Water is Reference Solvent. 25°C.

r, Å	D = 70	60	50	40	36	33	30	24	20	10
1	0.178	0.468	0.873	1.481	1.819	2.126	2.494	3.508	4.521	10.601
2	0.089	0.234	0.437	0.741	0.909	1.063	1.247	1.754	2.261	5.301
3	0.059	0.156	0.291	0.494	0.606	0.709	0.832	1.169	1.507	3.534
4	0.045	0.117	0.218	0.370	0.455	0.532	0.624	0.877	1.130	2.650
5	0.036	0.094	0.175	0.296	0.364	0.425	0.499	0.712	0.904	2.120
10	0.018	0.047	0.087	0.148	0.182	0.213	0.249	0.351	0.452	1.060

Critique of the Born equation.

The Born equation gives only an approximation for the total solvation energy of an ion. For small ions, the short-range ion-solvent interaction energies must be taken into account when estimating solvation energies. For larger ions, the neutral, or non-electrostatic, contributions become increasingly important. The Born equation ignores all these as well as any specific ion-solvent interactions, charge transfer forces, etc.. The Born equation also fails to account for increase in ionic radius due to solvation and the dielectric saturation in the vicinity of the ion.

When the Born equation is used to calculate free energies of hydration of electrolytes, it is found that the calculated values are about 50 % higher than the observed ones (36, 64). Thus, the simple Born equation cannot be used effectively to estimate solvation energies or medium effects for single ions, at least not those of average sizes. However, Various attempts have been made to modify the original equation so that it would yield free energies of salts that are identical with experimental values.

Methods for estimating medium effects for single ions based on modified Born equations.

Introduction.

It was stated earlier that the Born equation yields values for solvation energies that are too high (36). The equation fails to account for dielectric saturation, short-range ion-solvent interactions and neutral contributions to solvation energy of an ion. The simple Born equation, which in most cases allows only qualitative predictions, has undergone many modifications (4) since it was first presented in 1920 (57). The parameters that have been adjusted in the various modifications are the ionic radius and the dielectric constant of the solvent. Usually, the crystallographic radius is used as a starting point and then various amounts are added to it to bring the solvation energy down to the observed value. In practice, the solvation energies of pairs of ions must be estimated because only those quantities are measurable. Once a correction has been applied to a pair of ions so that the predicted solvation energy equals the observed energy for the pair, the contribution of each individual ion (from the Born equation) becomes accessible.

The dielectric constant can also be adjusted so that predicted solvation energies give results in

agreement with experiment. In this case, the dielectric constant is decreased presumably to account for the expected decrease in dielectric constant in the vicinity of the ion due to orientation of the solvent dipoles in the electric field of the ion (dielectric saturation).

The Born equation for an electrolyte can be written as:

$$G_{\pm}^{o} = -\frac{z^2e^2}{2}\left(1 - \frac{1}{D}\right)\left(\frac{1}{r_+} + \frac{1}{r_-}\right) \qquad (76)$$

where r_+ and r_- are the radii of the cation and the anion, respectively. Consequently, the Born equation for medium effects of an electrolyte is

$$\ln {}_m\gamma_{\pm} = -\frac{z^2e^2}{2}\left(\frac{1}{D_s} - \frac{1}{D_w}\right)\left(\frac{1}{r_+} + \frac{1}{r_-}\right) \qquad (77)$$

where the subscripts w and s refer to water and the nonaqueous solvent, respectively.

Webb's approach.

Webb (65) made an attempt to improve the Born prediction of hydration energies by taking into account the decrease in dielectric constant for water in the vicinity of the ion and the energy of electrostriction (contraction of solvent resulting from attraction of water molecules by the ion) of the solution. Instead of using crystallographic radii, Webb used radii corresponding to the distance of closest approach between water molecules and the ions. From experimental values of hydration energy and partial molal volume for an electrolyte, the effective radii of the ions of the electrolyte can be obtained, and hence, individual ionic hydration energies.

Webb's approach was never expanded to nonaqueous solvents and so medium effects for single ions based on his method are not available.

Latimer, Pitzer, and Slansky's approach.

LPS model.

Latimer, Pitzer, and Slansky (66) proposed a radius correction term to the Born equation to account for the expected increase in ionic radius of the solvated ion. Their modified Born equation took the form :

$$G_{\pm}^{o} = -\frac{z^2e^2}{2}\left(1 - \frac{1}{D}\right)\left(\frac{1}{r_+ + R_+} + \frac{1}{r_- + R_-}\right) \qquad (78)$$

where R_+ and R_- are the empirical radius correction factors that are added to the crystallographic radii of the cation, r_+, and the anion, r_-, respectively, so as to make the calculated and the experimental value of $G_{\pm}^{o}$ equal. Latimer et al. were able to calculate hydration energies of alkali--halides to within a few kcal/mole. They found that for the alkali--halides, the best results were obtained by adding 0.1 Å to the Pauling crystallographic radii of the halides and 0.85 Å to the Pauling crystallographic radii of the alkali--metal ions. It should be noted that in this method, a constant amount is added to the crystallographic radii of all the alkali--metal ions and the same for the halide ions. No distinction is made between

ions of like charge as far as the radius correction goes. The radius correction presumably accounts for those ion-solvent interactions and neutral contributions to solvation energies not accounted for by the simple Born equation.

Work of Coetzee et al.

The modified Born equation of Latimer, Pitzer and Slansky (Equation 78) can be expanded to an equation for the free energy of transfer of a salt from water to a nonaqueous solvent. Since the radius correction term will assume different values in water and in the nonaqueous solvent, the modified Born equation for estimating $\Delta G_{\pm}^{o}$ for a salt becomes:

$$\Delta G_{\pm}^{o} \equiv {}_{s}G_{i}^{o} - {}_{w}G_{i}^{o} = -\frac{N e^2 z^2}{2}\left[\left(1 - \frac{1}{D_s}\right)\left(\frac{1}{r_+ + R_+(s)} + \frac{1}{r_- + R_-(s)}\right) - \left(1 - \frac{1}{D_w}\right)\left(\frac{1}{r_+ + R_+(w)} + \frac{1}{r_- + R_-(w)}\right)\right] \quad (79)$$

The free energy change associated with the transfer of a cation from water to solvent s, ΔG_{+}^{o}, can be identified with:

$$\Delta G_{+}^{o} = -\frac{N e^2 z^2}{2}\left[\left(\frac{1-1/Ds}{r_+ + R_+(s)}\right) - \left(\frac{1 - 1/Dw}{r_+ + R_+(w)}\right)\right] \quad (80)$$

and a similar equation can be written for ΔG_{-}^{o}.

Coetzee and Campion (67) felt that by using energy relationships for cations exclusively and determining the radius corrections $R_+(w)$ and $R_+(s)$ for double comparisons between pairs of solvents, an improvement

in the accuracy of the calculations of $R_+(s)$ and $R_+(w)$ results. They had available values of the differences between the free energies of transfer of alkali-metal ions and rubidium, $\Delta\Delta G^{\circ}_{(M-Rb)}$, defined by:

$$\Delta\Delta G^{\circ}_{(M-Rb)} = {}_s(G^{\circ}_M - G^{\circ}_{Rb}) - {}_w(G^{\circ}_M - G^{\circ}_{Rb}) = \quad (81)$$
$$= \Delta G^{\circ}_M - \Delta G^{\circ}_{Rb}$$

where M is an alkali-metal. ΔG°_M and ΔG°_{Rb} were expressed by equations similar to 80 and the radius correction terms, $R_+(w)$ and $R_+(s)$ were fitted directly into the difference between two such equations for two cations. It was assumed that $R_+(w)$ and $R_+(s)$ have the same value for all alkali-metal ions. Actually, it is the difference between the radius correction values, $\Delta R_+ = R_+(s) - R_+(w)$, rather than the individual values of $R_+(s)$ or $R_+(w)$ that is important in fitting calculated values of $\Delta\Delta G^{\circ}_{(M-Rb)}$ to the experimental quantities. Once values of $R_+(w)$ and $R_+(s)$ have been determined, Equation 80 could be used to evaluate solvation energy changes for single ions. It is interesting to note that the original value of 0.85 Å for $R_+(w)$ as determined by Latimer, Pitzer, and Slansky (66) has since been revised by Noyes (64) to 0.72 Å and again by Simon (63) to 0.65 Å. Rosseinsky (33) has a critical evaluation of values of $R_+(w)$ and $R_-(w)$ as

determined by different authors.

Coetzee and co-workers (15, 46, 63, 67) estimated medium effects for alkali-metal ions in seven dipolar aprotic solvents based on their modification of the Born equation. Values of $\Delta\Delta G^{\circ}_{(M-Rb)}$ were obtained from polarographic half-wave potentials of the alkali-metal ions in water and in the nonaqueous solvents. The half-wave potentials were referred to the half-wave potential of rubidium in the same solvent to obtain values for $\Delta_{w}E_{\frac{1}{2}(M-Rb)}$ and $\Delta_{s}E_{\frac{1}{2}(M-Rb)}$. From these ΔE°'s, values for $\Delta\Delta G^{\circ}_{(M-Rb)}$ were calculated. Half-wave potentials differ from standard potentials due to the effects of supporting electrolyte in the polarographic cell and the effects of amalgamation of the solvent-insoluble reduced species. Coetzee et al. feel that these effects cancel in their double comparisons and that $\Delta\Delta E_{\frac{1}{2}}$ closely approximates $\Delta\Delta E^{\circ}$. Medium effects for single ions in acetonitrile as determined by Coetzee et al. are given in Table 82.

The underlying assumption in this method for estimating medium effects for single ions is that the interaction between alkali-metal ions and the solvents studied is predominantly electrostatic and can be represented by the modified Born equation. The radius correction terms are supposed to account for short range ion-solvent interactions not directly accounted for by

the Born equation. By excluding anions from consideration, the dilemma of unequal ion-quadrupole interaction energies for oppositely charged ions has been avoided. However, any contributions to solvation energies due to non-electrostatic interactions have been ommitted from consideration in this method.

Work of Laidler and Pegis.

Laidler and Pegis (70) found the unmodified Born equation to be useful only as a first approximation for predicting hydration energies. Deviations of $G_{\pm}^{o}$ from experimental values are particularly significant for compounds containing small ions of high charge. Laidler and Pegis feel that drastic modifications of the radius term in the Born equation are unjustifiable and that drastic modifications are more properly made on the dielectric constant term.

The Born equation can be put in the form

$$G^{o}(\text{Born}) = \frac{z^2e^2}{2r_sD} - \frac{z^2e^2}{2r_v} \qquad (82)$$

where r_s and r_v are the radius of the ion in solution and vacuum, respectively. From Equation 82, it can be seen that the radius term in the Born equation is a composite of the radii of the ion in solution and in a vacuum. As a first modification to the Born equation, Laidler and Pegis recommend increasing the crystallographic radius of the ion by 25 % on the basis of expansion of the outer orbitals of the ion when it is in close proximity to solvent molecules. They then recommend that all remaining deviations between Born solvation energies and experimental solvation energies be accounted for by modifications in the dielectric

constant term of the Born equation. Increasing the crystallographic radii by more than 25 % or adding a constant radius increment to the radii of all alkali-metal or halide ions, is theoretically unjustified.

Laidler and Pegis have proposed an equation for the hydration energy of an ion

$$G^{o}(H_2O) = \frac{Nr^3}{2b} G(c) - \frac{Nz^2e^2}{2r} \qquad (83)$$

where G(c) is a complex double integral that takes into account variation of the dielectric constant of water in the electric field of the ion, b is an empirical quantity, and the other terms have their usual meaning. The equation yields results for $G^{o}(H_2O)$ that are in agreement with experimental values for compounds containing univalent ions larger than 1.3 Å. Laidler and Pegis' equation has never been expanded for nonaqueous solvents.

Stokes' modification.

For calculating free energies of solvation in water or partially aqueous solutions, Stokes (71) proposed a modified Born equation in which both the radius and the dielectric constant have been modified. The ions are assumed to be solvated by water molecules exclusively even in partially aqueous solvents. The effective dielectric constant in the immediate neighborhood of the hydrated ions (primary hydration layer) is given a value of 9 and the effective radius of the ion is set equal to the crystallographic radius plus a correction factor due to molecules in the primary hydration layer. The Stokes equation is:

$$G^{o} = \frac{N z^{2} e^{2}}{2}\left(\frac{2nr_w}{r_c(r_c + 2nr_w)D_{eff}} + \frac{1}{D(r_c + 2nr_w)}\right) \qquad (84)$$

where $2nr_w$ is the thickness of n layers of water molecules bound around the ion, r_c is the crystallographic radius, D the bulk dielectric constant, and D_{eff} the effective dielectric constant of the bound water. For univalent ions, $D_{eff} = 9$ and $2nr_w = 0$ for univalent anions and 2.8 Å for univalent cations in water. The Stokes equation is useful only in those situations where only water molecules are found in the primary hydration layer.

Hepler's modification.

Hepler's model.

In Stokes' modification of the Born equation (67), the dielectric constant of the solvent (water) changes from its saturated value to its bulk value along the imaginary line separating the primary hydration layer from the bulk of the solvent. A more sophisticated approach to the change in dielectric constant due to alignment of solvent molecules in the electric field of the ion was proposed by Hepler (73).

Hepler proposed a revision of the Born equation that takes into account variations in the dielectric constant of the solvent as a function of the distance from the ion:

$$G^{o} = \frac{N e^2}{2}\left[\int_{r_i}^{1.5} \frac{dr}{D_{sat} r^2} + \int_{1.5}^{4.0} \frac{dr}{(X_r - Y) r^2} + \int_{4.0}^{\infty} \frac{dr}{D_o r^2}\right] \qquad (85)$$

In this model, the region of dielectric saturation ($D_{sat} = 5$) exists for ions smaller than 1.5 Å. From a distance of 1.5 to 4.0 Å, the dielectric constant rises linearly to its bulk value, D_o, and is given by the expression $(X_r - Y)$ where $X = 0.4(D_0 - D_{sat})$, and $Y = (1.5X - D_{sat})$. After 4.0 Å from the center of the ion, the dielectric constant assumes its bulk value, D_o.

For ions having radii greater than 1.5 Å, the first integral in Equation 85 becomes zero and the lower limit of the second integral becomes r_i. For ions with radii of 4 Å or greater, the first two integrals become zero and the Hepler equation assumes the same form as the unmodified Born equation. The original limits on the integrals in the Hepler equation were assigned on the basis of aqueous solvation. They would have to be changed if the solvent is totally nonaqueous or if nonaqueous molecules participated in the primary hydration layer. Due to the limited amount of knowledge of dielectric saturation in nonaqueous solvents, it is difficult to apply the Hepler equation to purely nonaqueous systems.

Hepler has calculated standard free energies of transfer of some uni-univalent electrolytes from water to heavy water using Equation 85. Good agreement was found upon comparison with experimental values.

Changing the value of the dielectric constant of the solvent as a function of distance from the ion accounts for all the short-range ion-solvent interactions not accounted for by the simple Born equation. Hepler does not take into account any neutral contributions to the solvation energy of an ion.

Basicity effect of Bates et al.

Woodhead, Paabo, Robinson, and Bates (75) used the Hepler modified Born equation to calculate the free energy change for the reaction

$$RNH^+(s) + H^+(w) + RN(w) = RNH^+(w) + H^+(s) + RN(s) \qquad (86)$$

where s and w refer to 50 % methanol and water, respectively, RN is tris(hydroxymethyl) aminomethane, and the entire reaction represents the difference between the dissociation equilibria of RNH^+ in 50 % methanol and water. For reaction 86, $\left[p({}_sK) - p({}_wK)\right] =$ $=-0.254$ which corresponds to a free energy change of -1.45 kjoules/mole. Using the Hepler equation with values of 4.0 Å and 2.8 Å for the radii of RNH^+ and H^+, respectively, Woodhead, Paabo, Robinson and Bates calculated the electrostatic contribution to the free energy of reaction 86 as 0.48 kjoules/mole. The difference between the total observed free energy for transfer reaction 86 and the electrostatic free energy calculated via the Hepler modification of the Born equation was called the "basicity effect", ΔG_b^o:

$$\Delta G_b^o = \Delta G^o - \Delta G^o_{(Hepler)} \qquad (87)$$

In this case, the "basicity effect" is quite substantial at 2 kjoules/mole.

In a subsequent study (74), Paabo, Bates, and Robinson calculated the "basicity effect" for reaction 86 using ammonium ion instead of tris, The "basicity effect" is attributed to that part of the medium effect of the proton not already accounted for by the calculated (Hepler) electrostatic medium effect. Other calculations similar to these (4) have shown that in methanol--water solvents, the "basicity effect" increases up to 60 wt-% methanol and then decreases. This reflects the expected behavior of $\log {}_m\gamma_H$ in alcohol--water solvents (17, 76).

Bates et al. have attributed the "basicity effect" entirely to the proton. This does not seem reasonable since the Hepler modified Born equation does not satisfactorily account for all ion-solvent electrostatic interactions or for any neutral contributions to solvation energy of an ion.

Critique of Born equation modifications.

To calculate the solvation energy of an ion, all ion-solvent interactions--electrostatic and neutral--must be taken into account. Using the unmodified Born equation to account for solvation energies is entirely unsatisfactory. For small ions, short-range interactions are important contributors to solvation energies. For larger ions, neutral contributions become important. Thus, no matter what the size of the ion, the Born equation is not suitable for calculating the entire solvation energy.

Various modifications of the Born equation help correct its deficiencies. However, although there is theoretical justification for modifying the dielectric constant term in the Born equation, there seems to be little or no justification for modifying the radius term to fit Born solvation energies to experimental data (32, 36, 70, 77). Except for a small correction to account for expansion of outer orbitals (70), the radius correction terms have no physical significance (8).

In the case of small ions, the Born equation should be expanded into other terms to include interaction energies which are functions of higher orders of r than r^{-1}. Any solvation theory for small ions should also include a term for neutral contributions. It has been shown (69) that even for small ions such as Li^+ and Na^+

there is some covalent character (charge-transfer energy) involved in their interaction with water molecules.

In the case of large ions where there is no dielectric saturation and therefore, minimal short-range ion-solvent interactions, a solvation theory should include the Born charging energy and another term which is attributable to the neutral interactions. For large ions, the total solvation energy would be a composite of the Born charging energy and the neutral contributions

$$G^{o}_{(\text{large ion})} = G^{o}_{(\text{Born})} + G^{o}_{(\text{neutral})} \qquad (88)$$

There will be further discussion of Equation 88 in following sections.

Using modified Born equations to estimate differences in solvation energies for single ions between pairs of solvents leads to results that are accurate to 2 kcal/mole (33). It is then quite useless to use these values of ΔG^{o} to calculate medium effects because the medium effects themselves are often only 1 or 2 kcal/mole. So, even in cases where solvation energies are predominantly electrostatic in nature and solvation energies can be expressed in terms of modified Born equations, these equations do not allow accurate

evaluation of medium effects for single ions due to the inherent inaccuracy of the Born equation for estimating single ion solvation energies.

Non-electrostatic contribution to the solvation energy of ions.

Apportionment of medium effects into an electrostatic and a non-electrostatic component.

Aside from developing a method for estimating medium effects for single ions assuming negligible liquid-junction potentials for cells like Cell IV, Bjerrum and Larsson were also interested in defining the fundamental nature of the medium effect (9). They postulated that the "distribution coefficients", as they called the medium effects, consist of three components: 1) an electrostatic component, $_{m}\gamma_{(el)}$, 2) a non-electrostatic component, $_{m}\gamma_{(neut)}$, and 3) a solvation component, $_{m}\gamma_{(s)}$:

$$\log {}_{m}\gamma = \log {}_{m}\gamma_{(el)} + \log {}_{m}\gamma_{(neut)} + \log {}_{m}\gamma_{(s)} \qquad (89)$$

Bjerrum and Larsson considered the unmodified Born expression:

$$\log {}_{m}\gamma_{(Born)} = \frac{2.303\, N z^2 e^2}{2 RT r}\left(\frac{1}{D_s} - \frac{1}{D_w}\right) \qquad (75)$$

sufficient for estimating the electrostatic contribution to the solvation energy.

According to Bjerrum and Larsson, the neutral contribution to the medium effect for an ion could be equated to the medium effect for a structurally similar uncharged molecule, such as benzoic acid for the benzoate ion. The expression for the neutral component of the medium effect for a single ion is then given by

$$\log {}_{m}\gamma_{(neut)} = \log {}_{m}\gamma_{(molecular\ analog)} \qquad (90)$$

In the Bjerrum and Larsson formulation, the solvation component of the medium effect, ${}_{m}\gamma_{(s)}$, accounts for those ion-solvent interactions not accounted for by ${}_{m}\gamma_{(el)}$ and ${}_{m}\gamma_{(neut)}$. The simple Born equation does not account for solvation energy terms associated with ion-dipole, ion quadrupole, dipole-dipole, ion-(induced dipole), ion-(induced quadrupole) and dispersion interactions which are functions of r^{-2}, r^{-3}, r^{-3}, r^{-4}, r^{-5}, and r^{-6}, respectively. Thus, ${}_{m}\gamma_{(s)}$ accounts for all the components of ${}_{m}\gamma_{(el)}$ which are functions of r^{-n} (where $n = 2,3,4,5,6$) and any part of ${}_{m}\gamma_{(neut)}$ which is not accounted for by ${}_{m}\gamma_{(molecular\ analog)}$.

There have been formulations of the medium effect in terms of electrostatic and non-electrostatic components proposed by others. In 1930, Lannung (78) stated that the transference work for an electrolyte

can be split into two parts, an electrical part due to the charge on the ions and a "specific work" part which depends on the configuration of the ion. In 1964, Sager, Robinson, and Bates (79) apportioned the medium effects of cationic and uncharged acids in methanol--water solvents into an electrostatic and a non-electrostatic term. In this case, Sager et al. felt that the non-electrostatic term is constant for each particular solvent composition and it characterizes the acidity of the medium. DeLigny and Alfenaar (8, 110) feel that the non-electrostatic contribution to the medium effect for an ion is dependent on r^2 of the ion. They constructed plots of ΔG^o versus r^2 for the noble gases and other neutral molecules from which they were able to evaluate $\log {}_m\gamma_{(neut)}$ for ions of a given radius. These plots were linear over a large range indicating that the non-electrostatic contribution to the medium effect plays a large role especially in the case of large ions. Other authors have used medium effects of isoelectronic noble gases or molecular analogs to represent the neutral component of the medium effect for a single ion (8, 35, 60, 62).

Additivity of electrostatic and non-electrostatic components of solvation energy for large ions.

The electrostatic and neutral contributions to the change in standard free energy of solvation of an ion upon transfer from water to a nonaqueous solvent can be visualized with the aid of the following thought process: 1) the hydrated ion is discharged 2) the discharged ion is transferred from water to the nonaqueous solvent and 3) the ion is re-charged in the nonaqueous medium. The free energy corresponding to steps 1 and 3 corresponds to $\Delta G^{o}_{(el)}$ while the free energy change corresponding to step 2 corresponds to $\Delta G^{o}_{(neut)}$. The overall difference in the standard free energy of an ion between two solvents can be formulated in terms of $\Delta G^{o}_{i(neut)}$ and all the specific electrostatic interactions between the ion and the solvent:

$$\Delta G_i^{o} = \Delta G^{o}_{i(neut)} + \frac{a'}{r} + \frac{b'}{r^2} + \frac{c'}{r^3} + \frac{d'}{r^3} + \frac{e'}{r^4} + \frac{f'}{r^5} + \frac{g'}{r^6} \qquad (69)$$

If Equation 69 were to be applied in the case of a small ion, there would be a discrepancy between $\Delta G^{o}_{i(neut)}$ and $\Delta G^{o}_{(molecular\ analog)}$ because of dielectric saturation. The solvent structure around a small ion is different than the structure of the solvent around an uncharged molecular analog due to the short-range ion-

solvent interactions. For very large ions, this is not the case and the structure of the solvent around the ion is the same as that around an uncharged molecular analog. There have been various estimates about the range of dielectric saturation around monovalent ions. Alfenaar and DeLigny claim that it ceases to be appreciable in aqueous solution at a distance of 5 Å from the center of the ion (8). Hepler (73), Robinson and Stokes (20), and Conway and Desnoyers (81) set the range at 4 Å and Rosseinsky (33) gives a value of 3 Å. There are very few estimates of the ranges of dielectric saturation in nonaqueous solvents. For large ions with radii of 4 - 5 Å, the neutral component of solvation energy becomes equal to the solvation energy of an uncharged analog, at least in water. For large ions, the total medium effect would then be equal to the medium effect of an uncharged analog plus the medium effect due to the Born term:

$$\log {}_m\gamma_{(\text{large ion})} = \log {}_m\gamma_{(\text{neut})} + \log {}_m\gamma_{(\text{Born})} \qquad (91)$$

It should be emphasized that the validity of this relationship increases as the size of the ion increases. For small ions, effects of dielectric saturation will cause $\log {}_m\gamma_{(\text{neut})}$ as determined experimentally using molecular analogs, to be different than the neutral

contribution to the medium effect of the ion. Detailed arguments in support of Equation 91 can be found in the literature (4, 8, 62, 80). Grunwald, Baughman, and Kohnstam (80) were the first to report a successful test of Equation 91. They found that in dioxane--water mixtures, the observed values of $\log_m \gamma$ for tetraphenylphosphonium tetraphenylborate ($Ph_4P\ BPh_4$) were equal to the sum of $2\log_m \gamma$ of tetraphenylmethane (Ph_4C) determined experimentally and a simple Born term. However, this corroboration of Equation 91 pertains to incremental changes in solvent composition whereas medium effects usually involve more dramatic variations in the nature of the solvent.

"Zero-energy" versus "inert-gas" assumptions.

In much of the literature, the neutral contribution to the total medium effect of an ion is either ignored (the "zero-energy" assumption) or is accounted for by equating it to the medium effect of an inert gas of the same size or electronic structure (the "inert-gas" assumption).

The zero-energy assumption involves the opinion that for the transfer of a neutral molecule from its gaseous to its solution standard state, the energy change is solely attributable to the accompanying change in volume. According to this model, transferring a neutral molecule from one solvent to another involves no change in free energy. Another implication of the zero-energy assumption is that the structure of the solvent around an uncharged particle is identical to the structure of the bulk solvent. However, it is generally beleived that this is not the case (7, 59, 82). All proponents of modified Born equations have used the zero-energy assumption as have various investigators employing extrapolation procedures. At best, the zero-energy assumption is a poor convention.

The inert-gas assumption can involve using medium effects of isoelectronic inert gases or inert gas molecules of similar size as the estimate of the neutral contribution to the overall medium effect of an ion.

Bjerrum and Larsson (9) and Haugen and Friedman (35) have equated the medium effects of isoelectronic inert gases to the neutral components of the medium effects of the alkali-metal ions. Alfenaar and DeLigny (8) endorsed the inert-gas assumption but they preferred size to electronic structure as a criterion for assigning neutral analogs to alkali-metal and halide ions. From plots of ΔG^{o} versus r^{2} for the transfer of noble gases and other nonpolar solutes from water to methanol, Alfenaar and DeLigny interpolated values of $\Delta G^{o}_{(neut)}$ corresponding to the crystallographic radii of the ions. Needless to say, values of ${}_{m}Y_{(neut)}$ obtained from the two versions of the inert-gas assumption will not agree.

Since the solubilities and hence, the free energies of uncharged solutes vary with the solvent, it is obvious that the zero-energy assumption is nothing more than a convention. Although certain authors (15, 64) claim that some empirical relationships for solvation energy do better without a correction for ${}_{m}Y_{(neut)}$, there is no reason to beleive that the zero-energy assumption is credible.

The assumption of negligible medium effects for large ions.

Normal element method of Pleskov.

Pleskov (37) has shown that the change in the potential of an electrode from one solvent to another is directly related to the difference in solvation energy of the electrode-active ion in the respective solvents. Knowing this, Pleskov concluded that the best reference electrode would be one reversible to an ion which undergoes a negligible change in free energy of solvation from one solvent to another. The ion of such a "normal element" would have small solvation energies in as many solvents as possible. Hydrogen is naturally a poor choice as a reference electrode since the proton undergoes specific interaction with many solvents. Also, the solvation energy of the proton is expected to be smaller in more acidic solvents such as water and formic acid and larger in less acidic solvents such as ethanol and ammonia. The magnitude of the solvation energy of an ion is determined by its radius, charge, polarizability, and tendency toward specific interaction with the solvent. Thus, ions of the "normal element" should have a large radius, small charge, low polarizability, and a minimal tendency toward specific interaction with solvents.

According to the Born model, the solvation energy of an ion is inversely proportional to its radius. Thus, the "normal element" would require a large radius. A low charge and polarizability is required for the "normal element" so that short-range ion-solvent interactions are minimized. Specific interactions such as formation of complex ions and crystal solvates must also be minimal for the "normal element".

It is obvious that Pleskov had to choose an element whose ions are large as the "normal element". A cation is preferable because they are less polarizable than anions. The element should also be univalent. During his time, his choice was limited to Rb or Cs. The Rb^+ ion has a radius of 1.49 $\mathring{A}$ and the Cs^+ ion is 1.65 $\mathring{A}$ in radius (83). They are both univalent cations and their solvation energies are considerably lower than solvation energies of other metal ions. Neither ion forms complexes and their salts do not usually form crystal solvates. With this information, Pleskov assumed that the solvation energies of Rb^+ and Cs^+ would remain constant from one solvent to another and thus, the standard potentials of Rb^+ and Cs^+ would be superior to the standard potential of H^+ for the purposes of establishing a solvent-independent e.m.f. series. Cesium would have been the best choice for the "normal element" but standard potentials

of cesium were not reliably known during Pleskov's time, even in water. Therefore, Pleskov chose rubidium as his "normal element". It was a good first approximation to solving the problem of a solvent-independent e.m.f. scale. Actually, the standard potentials of rubidium and cesium are practically the same in all solvents that Pleskov had studied (H_2O, HCOOH, CH_3CN, NH_3, N_2H_4) which makes the choice of either of them equally good. Table 4 is a table of standard potentials obtained by Pleskov using the rubidium assumption, i.e., $E^o_{Rb} = 0$ in all solvents.

The standard potentials in any valid solvent-independent e.m.f. series should follow certain trends that would be expected from purely chemical considerations. The standard potential of hydrogen should be more negative in ammonia and hydrazine than it is in water reflecting the decrease in solvation energy of the proton from water to these solvents. In solvents more acidic than water, such as formic acid, one would expect the standard potential of hydrogen to be more positive than in water reflecting the expected increase of the solvation energy of the proton in acidic solvents. E^o's of the heavy metals such as copper, silver and mercury should be more negative in ammonia and hydrazine due to the formation of complex ions and crystal solvates of these heavy metals with the solvents. Standard potentials

Table 4. Standard Potential Series Obtained by Pleskov (37) Using the Assumption $E^{o}_{Rb} = 0$ in all Solvents. In Volts.

Element	H_2O	CH_3CN	HCOOH	N_2H_2	NH_3
Li	-0.09	-0.06	-0.03	-0.19	-0.31
Na	0.22	0.30	0.03	0.18	0.08
K	0.01	0.01	0.09	-0.01	-0.05
Rb	0	0	0	0	0
Cs	0.00	0.01	0.01	----	-0.02
Ca	0.16	0.42	0.25	0.10	0.29
Zn	2.17	2.43	2.40	1.60	1.40
Cd	2.53	2.70	2.70	1.91	1.73
H_2	2.93	3.17	3.45	2.01	1.93
Pb	2.80	3.05	2.73	2.36	2.25
Cu/Cu^{+}	3.45	2.79	----	2.23	2.34
Cu/Cu^{+2}	3.28	2.89	3.31	----	2.36
Hg/Hg^{+}	3.73	----	3.63	----	----
Ag	3.74	3.40	3.62	2.78	2.76
I	3.51	----	----	----	3.38
Br	4.01	----	----	----	3.76
Cl	4.29	----	----	----	3.96

of heavy metal ions should also be more negative in acetonitrile as compared to water reflecting complex formation in this solvent.

Looking at Table 4, one can see that Pleskov's solvent-independent standard potential series is in agreement with the above chemical considerations. In this series, the standard potential of rubidium is of course set equal to zero in all solvents studied. The standard potential of cesium is approximately constant and nearly zero (vs. rubidium) in all solvents studied. The standard potential of hydrogen varies from a low of +2.01 v in the basic solvent hydrazine to a high of +3.45 v in formic acid, thus indicating that hydrogen is a poor choice as a "normal element" if one assumes Pleskov's rubidium assumption is at least qualitatively correct.

In his paper (37), Pleskov concludes that a strict comparison of standard potentials in all solvents will not be possible until the liquid-junction potential at the interfaces between different solvents is known. He beleives that it will someday be possible to carry out a theoretical calculation of this potential when our knowledge of the structure of solutions is more complete. A list of medium effects for single ions in methanol based on Pleskov's "normal element" method is given in Table 79.

Although rubidium was the only element that Pleskov found suitable as a "normal element", its standard potential is not solvent-independent. Rubidium has a radius of 1.49 Å (83) and thus, there is considerable dielectric saturation of solvent around a rubidium ion due to short-range ion-solvent interactions. These interactions should vary with solvent depending on the dielectric constant, dipole moment, and polarizability of the solvent. If one calculates the Born contribution to the medium effect for rubidium ion in ethanol ($D = 24$) using the unmodified Born equation, it is found that $\log {}_m\gamma_{Rb(Born)} = +2.35$. This is just the Born contribution to $\log {}_m\gamma_{Rb}$.

Even though the "normal element" method may be useful as a first approximation for estimating medium effects for single ions in some solvents, the method has practical limitations. Standard potentials of rubidium are measured using rubidium amalgam electrodes. The amalgams are subject to corrosion, especially in acidic media. Although there are methods (85) which can be used to correct for these corrosion effects, it is doubtful whether corrections can be made with sufficient accuracy for acidic media.

It seems as if the Pleskov "normal element" method is not very accurate. It is now considered to be mainly of historical interest (4).

Strehlow's "modification" of Pleskov's normal element method.

Strehlow felt that Pleskov's "normal element" method of establishing solvent-independent e.m.f. series was useful as a first approximation but that the solvation energy of the Rb^+ ion was slightly different in different media. This difference in the solvation energy of Rb^+ ion is largely due to the Born charging and ion-dipole interactions of Rb^+ with solvent molecules. To account for the change in G^o_{Rb}, Strehlow and co-workers (36, 39, 87, 88) made use of the previously discussed radius-modified Born equations in which adjustable ionic radii were used.

Although Strehlow (36) refers to his work as a second approximation of the "normal element" assumption of Pleskov, in actuality, his studies involved use of solvation energies of alkali-halides and his solvent-independent e.m.f. scale was established in a manner analogous to Latimer, Pitzer and Slansky, and later of Coetzee et al.'s methods, but, completely different from Pleskov's e.m.f. scale.

After calculating solvation energies for individual ions in water and in nonaqueous solvents via Equations 76 and 77, Strehlow and his co-workers were able to calculate medium effects for single ions. Using these values, Strehlow was able to establish a solvent-independent e.m.f. series. Strehlow retained the standard

potential of the hydrogen electrode in water as an arbitrary zero point for his e.m.f. series on the basis of historical reasons and convenience since all aqueous electrochemical measurements are made using E_H^o as the zero point. Some of Strehlow's results including standard potentials of rubidium and hydrogen in various solvents are included in Table 5. Pleskov's values of E_H^o (on the $E_H^o = 0$ in H_2O scale) are also included in Table 5 for the sake of comparison. Pleskov's values for E_{Rb}^o were all constant and equal to -2.92 v in any solvent (referred to $E_H^o = 0$ in H_2O). Strehlow's results indicate that Rb^+ ion experiences a change in solvation energy upon transfer to nonaqueous solvents.

From Table 5, it is seen that the standard free energies of transfer of Rb^+ ion are orders of magnitude smaller than standard free energies of solvation. Thus, Strehlow's e.m.f. scale is based on calculated values of ΔG_i^o which are small differences between two large numbers. Even in the case of other alkali-metal and halide ions, standard free energies of transfer from water (D = 78) to methanol (D = 32) are less than 1 kcal/g-ion in the case of the alkali-metal ions and just a few kcal/ /g-ion for the halide ions. Table 6 is a listing of differences between standard free energies of solvation, ΔG^o, of single ions from water to methanol as estimated by Strehlow (36). According to Strehlow, the precision

Table 5. Standard Free Energies of Solvation for Rb^+ Ion and Standard Potentials of Rb^+ and H^+ Ions in Various Solvents According to Strehlow (36) and Pleskov (37). Standard Potentials are Referred to $E_H^o = 0$ in Water.

Solvent	R_+, Å	R_-, Å	$-G_{Rb}^o$ kcal/mole	$-\Delta G_{Rb}^o$ kcal/mole	E_{Rb}^o volts	E_H^o volts	E_H^o (Pleskov) volts
H_2O	0.85	0.25	71.0	0	-2.92	0	0
CH_3OH	0.80_7	0.37	71.1	+0.06	-2.93	+0.01	----
CH_3CN	0.72	0.61	73.5	+2.5	-3.03	+0.14	+0.24
HCOOH	0.78	0.38	72.3	+1.3	-2.98	+0.47	+0.52
$HCONH_2$	0.85	0.25	71.0	0	-2.92	-0.07	----

Table 6. Differences Between Standard Free Energies of Solvation of Single Ions From Water to Methanol at 25°C (36).

Ion	Na^+	K^+	Rb^+	Cs^+	Cl^-	Br^-	I^-
ΔG_i^o	-0.41	-0.03	+0.06	+0.15	+5.60	+4.95	+4.17

of the overall analysis for estimation of single ion standard free energies in water or methanol is 1 to 2 kcal/g-ion. With a precision of this magnitude, the values of ΔG^{o} are smaller than or approximately the same size as the experimental uncertainty. Strehlow also found that by varying the values of R_{+} and R_{-} in Equation 78, the values of G^{o} for single ions change by about 0.5 - 1 kcal/g-ion. He states (36) that while G^{o} is a sensitive function of R_{+} and R_{-}, ΔG^{o} is not. However, it should be noted that this added uncertainty in ΔG^{o} (due to uncertainty in R_{+} and R_{-}) is greater than the reported values of G^{o} of Na^{+}, K^{+}, Rb^{+}, and Cs^{+} ions between water and methanol. As Strehlow points out himself (36), it would be desirable to have other independent methods for the estimation of medium effects for single ions. A comparison of single ion medium effects in methanol obtained using Strehlow's method and other methods appears in Table 79.

Strehlow's method is empirical. There is no apparent chemical rationale for apportionment of $G_{\pm}^{o}$ between anions and cations on the basis of best-fit parameters for R_{+} and R_{-} for a series of alkali-halides. There is no chemical model of solvation inherent in Strehlow's method. However, it would not be fair to say that the Strehlow method is entirely useless. For solvents of similar dielectric constant, the Strehlow method and the

Pleskov "normal element" method might prove useful for intercomparisons of electrochemical date.

The assumption of equal medium effects for ion-molecule or ion-ion structural analogs.

Constancy of the standard potential of the ferrocene--ferricinium redox couple. Strehlow's $R_o(H)$ function.

Realizing that there are valid objections to estimating medium effects for single ions based on modified Born equations, and that the rubidium ion was not large enough, etc., Koepp, Wendt, and Strehlow (86) searched for a more suitable redox system to use in establishing solvent-endependent e.m.f. and ion-activity scales. A redox system whose standard potential could be assumed to be independent of the solvent had to be one in which the reduced form had a zero charge and the oxidized form a unit charge, so that electrostatic free energy changes from solvent to solvent would be minimized. For redox systems of similar size with a +2/+3 charge type, the calculated electrostatic free energy of solvation (Born equation) is five times greater than for the redox system of a 0/1 charge type. Other criteria which had to be met in choosing a redox couple whose potential is independent of solvent are 1) the oxidized and reduced species should have large radii 2) both species should be spherical with the charge on the oxidized species buried in the center of the molecule 3) equilibrium at a platinum electrode should be established

quickly 4) both oxidized and reduced forms should be sufficiently soluble in all solvents to be studied 5) the reduced and oxidized forms must be as similar in structure as possible 6) both forms must have minimal tendency toward specific interaction with solvents and 7) the standard potential of the redox couple must not be too positive so that solvents are not oxidized by the reduced species. These are very stringent requirements for any redox couple. Some of the criteria are contradictory. For example, a large species is not likely to establish a stable potential at a platinum electrode. Also, a large neutral molecule is expected to have a limited solubility in water.

After studying eighteen different redox systems, Koepp, Wendt, and Strehlow choose two which most closely fit the requirements listed above. The two redox systems chosen were 1) the ferrocene--ferricinium (Foc/Fic^+) couple (ferrocene is dicyclopentadienyl iron II) and 2) the cobaltocene--cobalticinium (Cob/Cib^+) couple (cobaltocene is dicyclopentadienyl cobalt II). Both couples are of the 0/+1 charge type. All species are large ($r_{Foc} = 3.8$ Å (8)) and spherical with the central charged atom buried in the center of the molecule. The reduced and oxidized forms are similar in structure, and all species have minimal tendency towards specific

interaction with solvents. The standard potential of the Foc/Fic^+ couple in water is +0.400±0.007 v (86) (DeLigny, Alfenaar, and vanDerVeen report +0.3923 v) and that of the Cob/Cib^+ couple in water is -0.918±0.010 v. Due to the limited solubility of the reduced forms, standard potentials of the couples have been determined polarographically using the assumptions that the half-wave potentials of the Foc/Fic^+ and Cob/Cib^+ couples are equal to the standard potentials of these couples.

Using the assumption of solvent-independence of the standard potential of Foc/Fic^+ and Cob/Cib^+, Strehlow then compared the standard potential of hydrogen in nonaqueous solvents to the aqueous value from the measured e.m.f. of cells like this :

$$Pt(s);H_2(g,1\ atm),H^+(a=1),Foc,Fic^+(1:1);Pt(s) \quad \text{Cell VIII-a}$$

$$Pt(s);H_2(g,1\ atm),H^+(a=1),Cob,Cib^+(1:1);Pt(s) \quad \text{Cell VIII-b}$$

The potentials of the above cells are measured in water, $E(H_2O)$, and in the nonaqueous solvent of interest E(s). If $a_H = 1$ in both solvents, the difference in potential of the aqueous and nonaqueous cells is equal to the medium effect for the proton in the nonaqueous solvent :

$$E(s) - E(H_2O) = {}_wE^o(H,s) - {}_wE^o(H,H_2O) = \frac{RT}{F} \ln {}_m\gamma_H \qquad (92)$$

On the basis of such e.m.f. measurements, Strehlow defined (36, 89) a redox function $R_o(H)$ which is a measure of hydrogen ion activity in nonaqueous solvents referred to the standard state in water:

$$R_o(H) = -\log a_H^* - \log {}_m\gamma_H \qquad (93)$$

The "o" in the redox function formulation refers to the charge of the reduced species, ferrocene, or cobaltocene. In practice, the potential of an all aqueous cell containing unit hydrogen ion activity is measured, E(1), and then the potential of the nonaqueous cell of unknown hydrogen ion activity is measured, E(X). Operationally, the redox function then becomes:

$$R_o(H) = \frac{F}{2.303\,RT}\quad E(X) - E(1) \qquad (94)$$

If the nonaqueous cell also has unit hydrogen ion activity, the redox function $R_o(H)$ becomes equal to the negative logarithm of the medium effect for the proton, $-\log {}_m\gamma_H$. Medium effects for other ions can be obtained using cells similar to Cell VIII.

For acid-base systems, the redox function $R_o(H)$ is supposed to follow the Hammett acidity function, H_o.

They have been shown to run parallel (89) in sulfuric acid--water mixtures. Hammett indicators are more susceptible to specific interaction with solvent than the redox couples used by Strehlow, and the species involved in the redox couples are larger than Hammett indicators which makes the basic assumption of constancy of E^{o}_{Foc/Fic^+} or E^{o}_{Cob/Cib^+} more plausible.

Actually, the magnitudes of the standard potentials of the Foc/Fic^+ and Cob/Cib^+ couples are probably quite independent of solvent. Both the oxidized and reduced forms of the systems are soluble in water and in the nonaqueous solvents and so the potentials of the couples is directly dependent on the solvation energies of the oxidized and reduced forms. The medium effects of the oxidized and reduced forms will affect the change in standard potentials of the redox couples from one solvent to another. The medium effects of the Fic^+ and Cib^+ ions will include an electrostatic and a neutral contribution :

$$\log {}_m\gamma_{Fic} = \log {}_m\gamma_{Fic(el)} + \log {}_m\gamma_{Fic(neut)} \qquad (95\text{-a})$$

$$\log {}_m\gamma_{Cib} = \log {}_m\gamma_{Cib(el)} + \log {}_m\gamma_{Cib(neut)} \qquad (95\text{-b})$$

The uncharged species, Foc and Cob, are excellent neutral analogs for the ions Fic^+ and Cib^+. It is

thus possible to equate the medium effects of Foc and Cob to the neutral component of the medium effect of the charged species :

$$\log {}_{m}\gamma_{Foc} = \log {}_{m}\gamma_{Fic(neut)} \qquad (96\text{-a})$$

$$\log {}_{m}\gamma_{Cob} = \log {}_{m}\gamma_{Cib(neut)} \qquad (96\text{-b})$$

The difference in standard potentials of the two redox couples in water and in the nonaqueous solvent can be equated to the medium effects of the species participating in the cell reactions. Having in mind Equations 95 and 96, we can write the expressions for the difference in standard potentials of the Foc/Fic^+ and Cob/Cib^+ couples in water and nonaqueous solvent :

$$ {}_{w}E^{o}(Foc/Fic^+,H_2O) - {}_{w}E^{o}(Foc/Fic^+,s) = \qquad (97\text{-a})$$

$$= \frac{2.303\,RT}{F}\left(- \log {}_{m}\gamma_{Fic(el)} + \log {}_{m}\gamma_{Fic(neut)} + \log {}_{m}\gamma_{Foc}\right)$$

$$ {}_{w}E^{o}(Cob/Cib^+,H_2O) - {}_{w}E^{o}(Cob/Cib^+,s) = \qquad (97\text{-b})$$

$$= \frac{2.303\,RT}{F}\left(- \log {}_{m}\gamma_{Cib(el)} + \log {}_{m}\gamma_{Cib(neut)} + \log {}_{m}\gamma_{Cob}\right)$$

Since Foc and Cob are reduced species and Fic^+ and Cib^+

are oxidized species, the medium effects of the reduced species will be expected to partially cancel with the medium effects of the oxidized species and the total change in standard potential of the two redox couples from aqueous to nonaqueous solvent will be equal to the electrostatic component of the medium effect for the charged species:

$$ {}_{w}E^{o}(Foc/Fic^{+},H_2O) - {}_{w}E^{o}(Foc/Fic^{+},s) = \qquad (98\text{-a}) $$

$$ = \frac{2.303\,RT}{F} \log {}_{m}\gamma_{Fic(el)} $$

$$ {}_{w}E^{o}(Cob/Cib^{+},H_2O) - {}_{w}E^{o}(Cob/Cib^{+},s) = \qquad (98\text{-b}) $$

$$ = \frac{2.303\,RT}{F} \log {}_{m}\gamma_{Cib(el)} $$

It is a blessing in disguise that the medium effects of Foc and Cob are included in the expressions for the standard potential differences of Cell VIII. In actuality, this ΔE^{o} is closely approximated by $\log {}_{m}\gamma_{Ox(el)}$ which itself is subject to estimation using the Born model. We can see that the E^{o}'s of the redox couples are not solvent-independent as originally assumed by Strehlow. The validity of the $R_o(H)$ function is dependent on the constancy of the E^{o} of the couples. Thus, the original redox function can be dismissed as

only a qualitative approximation.

If the redox function, $R_o(H)$, is modified to include the $\log {}_m\gamma_{Ox(el)}$ term, it would be an acceptable method for establishing universal e.m.f. and ion-activity scales. A modified function designated $R_o(H)_{mod}$ would take the following form:

$$R_o(H)_{mod} = -\log a_H^* - \log {}_m\gamma_H + \log {}_m\gamma_{Ox(el)} \qquad (99)$$

This modified function would then yield pa_H values on the aqueous scale, regardless of the solvent.

Medium effects for the proton derived from Strehlow's work, and Pleskov's rubidium assumption are presented in Table 7. As can be seen by inspecting Table 7, the values of $\log {}_m\gamma_H$ determined by various methods can differ considerably. Apparantly, there is still a need for new methods of estimating medium effects for single ions that yield more consistent and satisfying results.

The ferrocene assumption of Strehlow is inherently better than the rubidium assumption ("normal element" assumption) of Pleskov. The idea that the difference in solvation energy of any ion in water and a nonaqueous solvent could be negligible appears inplausible as a generality. However, the ferrocene assumption with a correction term for $\log {}_m\gamma_{Ox(el)}$ included should

Table 7. Medium Effects for the Proton, $\log {}_{m}\gamma_{H}$, Based on the Assumptions of Pleskov and Strehlow. 25°C, Molal Scale.

	Assumptions			
Solvent	Pleskov $E^{o}_{Rb} = 0$	Modified Born (36)	Strehlow Foc/Fic^{+} (36)	Cob/Cib^{+} (36)
CH_3OH	0.3	0.07	-0.3	-0.3
CH_3CN	4.2	2.3	2.4	2.6
HCOOH	9.0	8.1	---	---
$HCONH_2$	---	1.2	-2.5	-2.4

prove to be quite a satisfactory method for estimating medium effects for single ions.

There are some weak points in the modified ferrocene assumption. First, ferrocene has a radius of 3.8 Å (8). Thus, it is probably not quite large enough to completely escape the effects of dielectric saturation even in water. The solvent structure in the vicinity of the ferrocent molecule might be different than the solvent structure around the ferricinium ion. In other words, the medium effect of the ferrocene molecule may not be equal to the neutral component of the medium effect of ferricinium. Another weak point of the Foc/Fic^+ or Cob/Cib^+ assumptions is that the standard potentials of these couples are always determined polarographically. This is necessary because of the limited solubility of ferrocene in water and the reluctance of the couple to reach a stable potential at a platinum electrode (36). Cobaltocene is rather unstable in solution so measurement of the $E_{\frac{1}{2}}$ of Cob/Cib^+ is the most convenient method of estimating standard potentials for this couple. Because of the presence of supporting electrolyte and the possible inequality of the diffusion constants of the oxidized and reduced forms, the half-wave potentials are not necessarily equal to the standard potentials. Coetzee, McGuire and Hedrick (84) observed that $E_{\frac{1}{2}}$'s are dependent on the supporting electrolyte used.

Most measurements of $E_{\frac{1}{2}}$ are determined using a saturated calomel electrode (SCE) as reference. In many studies, the assumption is made that the liquid-junction potential between the solution and the SCE is reproducible and constant regardless of supporting electrolyte used. Kolthoff (44) recommends that in future polarographic studies, a reference electrode composed of silver-silver perchlorate be used. To keep the liquid-junction potential small and reproducible, the perchlorate ion concentrations in both half-cells would be kept small and as close as possible. A perchlorate salt bridge in the same solvent would be used.

The difference between the standard potentials of Foc/Fic^+ and Cob/Cib^+ couples in aqueous solution is 1.33 v and, within experimental error, independent of solvent (36). We would expect this condition if all species in both redox couples were the same size and, if the effects of dielectric saturation were negligible or equal for both redox systems. However, the difference between the standard potentials of ferrocene and rubidium are also nearly independent of solvent which implies that either the constancy of $E^o(Foc/Fic^+)$ and $E^o(Cob/Cib^+)$ or $E^o(Rb)$ is in doubt. I believe that $E^o(Rb)$ is not solvent-independent but $E^o(Foc/Fic^+)$ and $E^o(Cob/Cib^+)$ corrected for ${}_m\gamma_{Ox(el)}$ might be.

There has been a great deal of attention given to

the ferrocene and cobaltocene assumptions. Aside from Strehlow's work, Coetzee and his co-workers (84) and Kolthoff and Thomas (97) have studied the Foc/Fic^+ couple in water and acetonitrile, Kuwana, Bublitz, and Hoh (91) have done chronopotentiometric studies of ferrocene and some other dicyclopentadienyl compounds, and the Foc/Fic^+ assumption has been used to estimate solvation energies in DMSO (92) and sulfolane (93). In this research, medium effects for Foc were evaluated in ethanol--water solvents and values for $\log {}_m\gamma_{Fic}$ were calculated using Equation 95-a. A list of these values is given in Table 50.

Substituted ferroin assumptions.

In the Foc/Fic$^+$ and Cob/Cib$^+$ assumptions, the medium effects of the oxidized form (a cation) and a corresponding reduced form (an uncharged molecule) are equal. Similar assumptions have been proposed for estimating medium effects or liquid-junction potentials in which two structurally similar cations which comprise a redox couple are assumed to have equal medium effects.

Iwamoto and co-workers (94--96) have investigated the usefulness of various large-ion redox couples for evaluating changes in liquid-junction potentials in voltammetric studies. They were seeking a redox couple whose standard potential would be independent of the solvent. They chose the tris(4,7-dimethyl-1,10-phenanthroline)iron(II)/tris(4,7-dimethyl-1,10-phenanthroline)iron(III) (ferroin) couple as having a standard potential that varies least with solvent composition. This is a +2/+3 couple and there are strong objections to using a couple of this charge type as a reference whose E^o is solvent-independent. The Born equation predicts a five-fold increase in the medium effect for the ions in this couple as compared with the ions in a 0/+1 couple such as Foc/Fic$^+$. Specific solvation effects are generally greater with ions of +2 or +3 charge than with uncharged molecules

or +1 ions. Coetzee and Campion (67) claim that the open structure of the iron (II) and iron (III) complexes makes them quite susceptible to specific interactions with solvents.

Kolthoff and Thomas (97) found use for the tris (o-phenanthroline)iron(II)/tris(o-phenanthroline) iron(III) redox couple as a couple whose standard potential is independent of solvent. On the basis of the assumed constancy of this redox couple, they determined the standard potentials of various electrodes in acetonitrile on the water scale. The same objections that were raised to the work of Iwamoto et al. apply here. The constancy of the standard potentials of couples composed of ion-ion structural analogs does not seem reasonable.

Three assumptions of Parker et al.

Parker and co-workers have proposed three assumptions for estimating medium effects for single ions based on the assumed equality of the medium effects of ion-molecule structural analogs (26, 30). The tetraphenylborate--tetraphenylmethane (Ph_4B^---Ph_4C) assumption proposed by Parker and Alexander (26) states that the medium effect of the BPh_4^- ion is equal to the medium effect of the neutral molecule Ph_4C. Parker and Alexander applied this assumption to solvents of similar dielectric constant. It is by no means a generally applicable method for estimating medium effects for single ions. The medium effect of BPh_4^- ion should differ from the medium effect of Ph_4C by an electrostatic contribution for which Parker and Alexander fail to correct.

In the iodine--triiodide (I_2--I_3^-) assumption, the medium effect of iodine is assumed to be equal to the medium effect of the triiodide ion. The potential of the I_2/I_3^- couple is then assumed to be solvent independent. There are definite differences in specific solvation and size between I_2 and I_3^- and this assumption does not appear to be valid even for solvents with similar dielectric constants. Alexander, Ko, Parker, and Broxton (30) applied the I_2--I_3^- assumption in water and some dipolar aprotic solvents.

The drastic changes in dielectric constants and solvent type involved in these studies render them dubious.

In the SN-transition state assumption, Parker and Alexander (26) assume that the change in solvation energy of the transition state complex for aromatic nucleophilic substitution reactions of 4-nitrophenyl or 2,4-dinitrophenyl halides is equal to the change in solvation energy of the aromatic halides themselves. For reactions of the type:

$$Ag^+Y^- + ArX = ArY + Ag^+X^- \qquad (100)$$

where X = halide and Y = N_3^-, SCN^-, or Cl^-, the ratio of the rate constants in a dipolar aprotic solvent, k_s, and methanol, k_m, would be equal to the medium effect of Y if the SN-transition state assumption is correct:

$$\log \frac{k_s}{k_m} = \log {}_m\gamma_{ArX} - \log {}_m\gamma_{ArXY}^{\ddagger} + \log {}_m\gamma_Y = \log {}_m\gamma_Y \qquad (101)$$

In Equation 101, $ArXY^{\ddagger}$ is the transition state complex which is similar in structure to ArX. The SN-transition state assumption sets $\log {}_m\gamma_{ArXY}$ equal to $\log {}_m\gamma_{ArX}$. This is also an ion-molecule assumption in that the medium effect of an ion is set equal to the medium effect of its uncharged analog. The same objections that apply to Parker's BPh_4^---Ph_4C and I_2--I_3^-

assumptions will apply here.

Extrapolation procedures.

Izmaylov's methods.

Izmaylov, along with his co-workers was the most prolific worker in the field of medium effects for single ions (38, 47, 49, 98--105). His methods for estimating medium effects with the aid of an extrapolation procedure will be discussed in this section.

Izmaylov felt that methods for apportioning the free energy of solvation between the two ions of an electrolyte should not be based on any hypothesis about the structure of the solvent. He proposed a method (100,101) for estimating free energies of solvation of single ions by graphical extrapolation of sums and differences of G^{o}'s of a given ion in combination with other ions of varying radius, r, vs. i/r, to $1/r = 0$. When determining the free energy of solvation for a given ion, three plots would be constructed: 1) a plot of $(-G_i^{o} + G_X^{o})$ (where i = ion of interest and X = halide ion) versus $1/r_X$ 2) a plot of $(G_M^{o} - G_i^{o})$ (where M = alkali-metal ion) vs. $1/r_M$ and 3) a plot of $(-G_i^{o} + (G_M^{o} - G_X^{o})/2)$ vs. 1/r (where r is the average radius of X and M). All three plots are extrapolated to a common intercept, G_i^{o}, the solvation energy of a single ion.

Izmaylov assumed that all the components of solvation energy of an ion were functions of $1/r^n$ where n could assume values of 1, 2, 3, 4, and 6. Thus, the

solvation energy of an infinitely large ion would be zero. Implicit in Izmaylov's approach is the cancellation of that part of the free energy of solvation of G_X^o and G_M^o which in reality does not decrease as 1/r approaches zero. Thus, although Izmaylov ignored the neutral contribution to solvation energy (he considered it negligible for ions below 10 Å in size) this contribution can be assumed to be equal for infinitely large ions of opposite charge, and in theory, Izmaylov's intercepts might very well represent single ion energies of solvation. In application, however, Izmaylov's method yields results which are not entirely satisfactory. The thermodynamic solvation energies employed in the extrapolation are determined via Born-Haber cycles using electron affinities, ionization potentials, sublimation energies, dissociation energies, and heats of reaction as well as e.m.f. and solubility data. Izmaylov claims an accuracy of ± 0.5 kcal/mole for his thermodynamic solvation energies. This value seems to be a bit optomistic considering all the steps necessary in determining the solvation energies. Noyes (106) who uses an extrapolation procedure similar to Izmaylov's to estimate free energies of hydration for single ions, hopes for an accuracy of no more than ± 2 kcal/mole. Thus, the magnitudes of many medium effects for single ions will usually be no larger than the uncertainty of the method. There is also a lack of internal

consistency in Izmaylov's values of medium effects for single ions. The sum of estimated ionic medium effects should be equal to the experimentally observed values for any electroneutral combination of ions. For example, the observed value (72) of ($\log {}_m\gamma_K - \log {}_m\gamma_H$) in 100 % ethanol is 1.0 but Izmaylov's values of $\log {}_m\gamma_K$ and $\log {}_m\gamma_H$ are +4.0 and +3.9 respectively.

In cases of extreme solvation energy changes (large medium effects), Izmaylov's extrapolation method does yield results that are in agreement with chemical considerations. For example, $\log {}_m\gamma_H$ in formic acid is +10.0, a value that indicates that protons are solvated far less strongly in formic acid than in water. Izmaylov's value for $\log {}_m\gamma_H$ in ammonia is -15.8 which indicates that protons are more strongly solvated in this solvent as compared to water. This author endorses Izmaylov's method only when semi-quantitative results are desired and only in those instances where the medium effects for single ions are greater in magnitude than the inaccuracies of the method.

In a modification of his original method (102, 103), Izmaylov plotted sums and differences of ionic solvation energies as a function of $1/n^2$ where n is the principle quantum number of the lowest vacant orbital of the ion. In this connection, Izmaylov states that the major

portion of solvation energy can be attributed to the energy of formation of complexes between ions and solvent molecules. This energy of complex formation depends on the energic properties of the vacant orbitals of the ions. The ionic radius was only an indirect measure of this energy. Izmaylov assumed that for isoelectronic pairs of alkali-metal (M) and halide (X) ions, the solvation energy differences would approach zero as $1/n^2$ approached zero. He therefore plotted the function $(-G_i + (G_M^o - G_X^o)/2)$ versus $1/n^2$ for $n = 3$, 4, 5, and 6 (corresponding to NaF, KCl, RbBr, and CsI) and extrapolated to $1/n^2 = 0$ to obtain the energy of solvation for a single ion, G_i^o. The solvation energies obtained from this extrapolation were, on the average, 1.0 - 1.5 kcal/mole lower in absolute values for cations and higher by the same amount for anions compared to values from Izmaylov's original 1/r extrapolation procedure. Izmaylov considered solvation energies for single ions estimated by this new method more reliable than those obtained from the 1/r method because solvation energies of both cations and anions could be expressed as a single function of $1/n^2$. All of Izmaylov's medium effects reported in this thesis will be those obtained using his $1/n^2$ method.

Having estimated solvation energies for single ions

in ten solvents, Izmaylov was able to calculate medium effects for single ions using Equation 7. Table 8 lists these medium effects for single ions in ethanol, methanol, and acetonitrile and the hydration energies of single ions in water.

Izmaylov's results indicate that, in general, both positive and negative ions are preferentially solvated in water as opposed to ethanol, methanol and acetonitrile with the exception of cases where there is specific ion-solvent interaction such as the Ag^+ ion in acetonitrile.

Izmaylov's medium effects for single ions in ethanol, methanol, and acetonitrile are compared with those of other investigators in Tables 76, 79 and 82.

Table 8. Medium Effects, $\log {}_m\gamma$, and Hydration Energies, ${}_wG^o$, of Single Ions According to Izmaylov (102). 25°C, Molal Scale.

Ion	Solvent CH_3OH	CH_3CN	C_2H_5OH	$-{}_wG^o$ kcal/g-ion
H^+	3.1	5.5	3.9	256.5
Cl^-	1.0	8.0	1.2	74.5
Br^-	1.0	5.0	1.2	69.0
I^-	0.0	2.3	0.8	60.5
Li^+	1.6	1.8	2.9	117.0
Na^+	1.8	2.5	4.2	94.0
K^+	2.0	1.4	4.0	77.0
Rb^+	2.8	1.6	4.6	72.5
Cs^+	2.7	1.1	3.8	63.0
Ag^+	3.5	-3.0	3.7	110.0
Ca^{+2}	---	7.8	---	371.0
Zn^{+2}	5.4	7.7	7.7	492.5
Cd^{+2}	5.0	6.2	7.6	428.0

Linear extrapolation of Feakins et al.

Feakins and Watson (107) devised a method for estimating medium effects for single ions based on Izmaylov's original 1/r extrapolation in which free energies of solvation of electroneutral combinations of one ion and alkali metal or halide ions were plotted as a function of 1/r of the varying ion. However, instead of estimating free energies of solvation for single ions in individual solvents, Feakins and Watson estimated their differences for single ions, ΔG°, directly. The differences in standard free energies of solvation of the hydrogen halides ($\Delta G_H^{\circ} + \Delta G_X^{\circ}$) were fitted to a linear equation as a function of 1/r of the halide ion:

$$(\Delta G_H^{\circ} + \Delta G_X^{\circ}) = \Delta G_H^{\circ} + a(r_X)^{-1} \qquad (102)$$

where the intercept is ΔG_H° and r_X is the crystallographic radius of the halide ion. In a similar manner, the standard free energies of transfer of LiCl, NaCl, and KCl, ($\Delta G_{Cl}^{\circ} + \Delta G_M^{\circ}$) were espressed as a linear function of 1/r of the alkali-metal ion

$$(\Delta G_{Cl}^{\circ} + \Delta G_M^{\circ}) = \Delta G_{Cl}^{\circ} + b(r_M)^{-1} \qquad (103)$$

where the intercept is ΔG_{Cl}° and r_M is the radius of

the alkali-metal ion. The slopes, a and b in Equations 102 and 103 are opposite in sign and an order of magnitude greater than the slopes predicted from the Born equation.

Of course, once any one medium effect for a single ion is determined, all other medium effects for single ions become accessible. Feakins and Watson were able to calculate the medium effects for a variety of ions from the values of ${}_{m}\gamma_{H}$ and ${}_{m}\gamma_{Cl}$ obtained directly from their extrapolation. However, values of ${}_{m}\gamma$ for the same ion derived from ${}_{m}\gamma_{H}$ and ${}_{m}\gamma_{Cl}$ were found to differ by as much as 1.5 kcal/g - ion. For this reason, an average value of ${}_{m}\gamma_{Cl}$ was used in calculating medium effects for other single ions.

Feakins and co-workers (108) estimated medium effects for single ions in some dioxane--water and acetic acid--water mixtures (108) and in the entire range of methanol--water solvents (109). According to the results in methanol, cations are preferentially solvated in this solvent as compared to water and anions are preferentially solvated by water.

Although the above linear extrapolation is similar to Izmaylov's 1/r method, it gives values of medium effects for single ions that are often of different magnitude and opposite in sign to those determined by Izmaylov. There is some doubt about the linear

dependence of ΔG_t^o on r^{-1} (4). Izmaylov's extrapolations are curved. For small ions, short-range ion-solvent interactions that are functions of r^{-2}--r^{-6} are important contributions to G^o. If solvation energies of RbCl and CsCl were included in Equation 103, the linear relationship would not be evident at all. As in Izmaylov's method, the extrapolations are long and, as Feakins points out (108), graphs of $\Delta G_{\pm}^o$ versus 1/r are usually concave or convex to the r^{-1} axis rather then linear. Feakins states that the neutral component of the medium effect for a small ion cannot be approximated by the corresponding free energy change of an isoelectronic noble gas due to effects of dielectric saturation. However, this does not seem to be a reasonable explanation of why the neutral contribution is ignored entirely in his method.

Medium effects for single ions in methanol as determined by Feakins et al. are compared with those from other methods in Table 79.

Method of DeLigny et al.

DeLigny and Alfenaar (110) proposed an improvement of the existing extrapolation methods for estimating medium effects for single ions based on the subtraction of a neutral component from ΔG^{o} before such an extrapolation is performed. As in the method of Feakins, the solvation-energy changes rather than the solvation energies for single ions, are estimated directly. Thermodynamic values of ΔG^{o} for the halogen acids and for the proton minus alkali-metal ion were corrected by subtracting a $\Delta G^{o}_{(neut)}$ term corresponding to the free energy of transfer of an uncharged molecule of the same dimensions as the halide or the alkali-metal ions. This corrected ΔG^{o} was plotted as a function of r^{-1} of the varying ion for both series of ΔG^{o}'s and the resulting curve extrapolated to infinite radius of the varying ion to give ΔG^{o}_{H}. Extrapolations were performed for methanol--water solvents and pure methanol.

DeLigny and Alfenaar apportion the standard free energy of transfer of an ion between an electrostatic and a neutral component:

$$\Delta G_i^{o} = \Delta G^{o}_{i(el)} + \Delta G^{o}_{i(neut)} \qquad (104)$$

For a large ion, the neutral component would be equivalent to the change in standard free energy of an

uncharged molecule having the same dimensions as the ion. If the ion is large enough, the major contribution to the electrostatic component would be estimated from the Born equation (Equation 67). The latter approaches zero as the radius of the ion approaches infinity.

For large particles, the $\Delta G^{\circ}_{(neut)}$ term is proportional to the surface area of the particle (r^2), so that it increases with increasing radius. It is for this reason, that before extrapolating ΔG° to $1/r = 0$, $\Delta G^{\circ}_{(neut)}$ must be subtracted from the total ΔG°. To determine $\Delta G^{\circ}_{(neut)}$ for the alkali-metal and halide ions, DeLigny and Alfenaar employ a plot of ΔG° versus r^2 for the noble gases, methane, and other nonpolar solutes and interpolate values of $\Delta G^{\circ}_{(neut)}$ corresponding to the ionic radii of the ions. These $\Delta G^{\circ}_{(neut)}$ values are then combined with the thermodynamic sums ($(\Delta G^{\circ}_H + \Delta G^{\circ}_X)$ where $X = Cl^-$, Br^-, I^-) and differences ($(\Delta G^{\circ}_H - \Delta G^{\circ}_M)$ where $M = Li^+$, Na^+, K^+, Rb^+, Cs^+) of standard free energies of transfer to obtain the free energy terms useful for extrapolation. These terms are really $(\Delta G^{\circ}_H + \Delta G^{\circ}_{X(el)})$ and $(\Delta G^{\circ}_H - \Delta G^{\circ}_{M(el)})$:

$$\Delta G^{\circ}_H + \Delta G^{\circ}_{X(el)} = \Delta G^{\circ}_H + \Delta G^{\circ}_X - \Delta G^{\circ}_{X(neut)} \qquad (105\text{-a})$$

$$\Delta G^{\circ}_H - \Delta G^{\circ}_{M(el)} = \Delta G^{\circ}_H - \Delta G^{\circ}_M + \Delta G^{\circ}_{M(neut)} \qquad (105\text{-b})$$

For the actual extrapolation, $(\Delta G_H^o + \Delta G_{X(el)}^o)$ and $(\Delta G_H^o - \Delta G_{M(el)}^o)$ are plotted versus $1/r$ of the varying ion. Both curves are extrapolated to a common intercept at $1/r = 0$. In the region between $1/r = 0$ and $1/r = 0.1$ ($r = 10$ Å), the effects of dielectric saturation and short-range ion-solvent interactions in the methanol--water solvents studied were considered negligible and the plots were linear having a slope predicted by the Born equation. Values of ΔG^o at $1/r = 0$ were taken as the standard free energy of transfer for the proton.

The extrapolations to $1/r = 0$ are long and somewhat arbitrary. Mean values of ΔG_H^o from water to various methanol--water solvents have 90 % probability intervals of from ± 2.7 % to ± 15 % based on extrapolations performed independently by nine different people (110). Using this extrapolation procedure, DeLigny and Alfenaar arrive at a value of -0.88 for $\log {}_m\gamma_H$ in 100 % methanol at 25°C. All indications are (4) that liquid methanol is less basic than water and thus, $\log {}_m\gamma_H$ should be positive in 100 % methanol. It is highly likely that for the small ions involved in this study, the neutral component of the medium effect cannot be accurately approximated by the medium effect of an uncharged analog.

In another method for estimation of medium effects

for single ions, DeLigny and Alfenaar (8) again considered ΔG^{o} to be composed of an electrostatic part and a neutral part. The neutral part, $\Delta G^{o}_{(neut)}$, was set equal to the ΔG^{o} of an uncharged solute of the same dimensions as the ion and the electrostatic part, $\Delta G^{o}_{(el)}$, was set equal to a power series in $1/r$:

$$\Delta G_i^{o} = \Delta G^{o}_{i(neut)} + \frac{a}{r} + \frac{b}{r^2} + \frac{c}{r^3} + \cdots \qquad (106)$$

where a is given by the Born equation, r is the crystallographic radius of the ion, and b, c, etc., are empirical coefficients. In the case of small ions, the short-range ion-solvent interactions and the difference between $\Delta G^{o}_{(neut)}$ for the small ion and ΔG^{o} of an uncharged molecule of the same size are supposed to be accounted for by the terms proportional to the higher order terms in r^{-1}.

To estimate the medium effect for the proton in methanol and methanol--water solvents, the following two series were used:

$$\Delta G_H^{o} + \Delta G_X^{o} - \Delta G^{o}_{X(neut)} = \Delta G_H^{o} + \frac{a}{r_X} + \frac{b}{r_X^2} + \frac{c}{r_X^3} + \cdots \qquad (107\text{-a})$$

$$\Delta G_H^{o} - \Delta G_M^{o} + \Delta G^{o}_{M(neut)} = \Delta G_H^{o} + \frac{a}{r_M} + \frac{d}{r_M^2} + \frac{e}{r_M^3} + \cdots \qquad (107\text{-b})$$

The quantities on the left hand side of Equations 107-a and 107-b and the radii of the varying ions are the necessary data. Values for ΔG_H^o and b, c, d, e, ... are evaluated by the method of least squares. Both of the functions have a common intercept, ΔG_H^o. To increase the available number of data points, the ferrocene--ferricinium couple was employed and the following equation used :

$$\Delta G_H^o - \Delta G_{Fic}^o + \Delta G_{Foc}^o = \Delta G_H^o + \frac{a}{r_{Foc}} + \frac{f}{r_{Foc}^2} + \frac{g}{r_{Foc}^3} + \cdots \qquad (108)$$

In this case, ΔG_{Foc}^o equals $\Delta G_{Fic(neut)}^o$. Since the entire quantity on the left hand side of the above equation is determined polarographically, it was not necessary to evaluate ΔG_{Foc}^o separately.

As noted earlier, the values of $\Delta G_{(neut)}^o$ for the alkali-metal and halide ions were estimated via the "inert-gas" assumption in which $\Delta G_{(neut)}^o$ is equated to the observed ΔG^o of an uncharged molecule of the same size as the ion. Values of ΔG^o of the inert gases, CH_4, CCl_4, Foc, $Sn(CH_3)_4$, and $Sh(C_2H_5)_4$ were plotted versus r^2 and values of $\Delta G_{(neut)}^o$ for halide and alkali-metal ions were interpolated using the crystallographic radii of the ions. DeLigny and Alfenaar

found that values of ΔG^{o} for the inert solutes studied were linear functions of the mole fraction of methanol and could be interpolated for any solvent composition. The graph of ΔG^{o} versus r^{2} for the inert solutes in methanol is linear from $r^{2}=4$ to $r^{2}=25$. Some values of ΔG^{o}'s, medium effects, and crystallographic radii of the inert solutes in methanol are given in Table 9. From the values of the medium effects of neutral molecules in methanol, (see Table 9), it can be seen than the neutral contributions to the total medium effect do not play an insignificant role as proponents of the "zero-energy" assumption would have us believe.

This extrapolation method of DeLigny and Alfenaar is an improvement over their first method in which values of $\log {}_{m}\gamma_{(el)}$ were estimated using the simple Born equation. The power series in r^{-1} accounts for ion-dipole, dipole-dipole, ion-(induced dipole), ion-quadrupole, ion-(induced quadrupole) and dispersion forces which, collectively, are probably appreciable for small ions. Still, the above extrapolation method does have some drawbacks. The extrapolations are quite long. The curve representing $(\Delta G_{H}^{o} + \Delta G_{X}^{o} - \Delta G_{X(neut)}^{o})$ is fitted to three points only. The values of $(\Delta G_{H}^{o} - \Delta G_{Fic}^{o} + \Delta G_{Foc}^{o})$ which fall closest to the Y-axis are determined polarographically and are thus

Table 9. ΔG°, Medium Effects, and Crystallographic Radii of Neutral Molecules in Methanol, 25°C, Molal Scale (8).

Molecule	ΔG° cal/mole	$\log_m \gamma$	r
He	930 ± 20	0.682	1.29 ± 0.05
Ne	1019 ± 20	0.747	1.60 ± 0.03
Ar	1314 ± 20	0.963	1.92 ± 0.03
Kr	1473 ± 70	1.080	1.98 ± 0.03
Rn	2075 ± 70	1.521	2.3 ± 0.1
CH_4	1667 ± 50	1.222	2.1 ± 0.1
CCl_4	3912 ± 34	2.868	3.6 ± 0.1
Foc	4360 ± 150	3.196	3.8 ± 0.2
$Sn(CH_3)_4$	5380 ± 80	3.944	4.2 ± 0.1
$Sn(C_2H_5)_4$	6803 ± 166	4.987	4.7 ± 0.2

subject to errors due to the nonequivalency of $E_{\frac{1}{2}}$ with E°. Values of ΔG_H° are especially sensitive to the values of $(\Delta G_H^{\circ} - \Delta G_{Fic}^{\circ} + \Delta G_{Foc}^{\circ})$. DeLigny and Alfenaar claim that the overall precision of the ΔG_H° values ranges from a high of 0.7 % (for 10wt-% methanol) to a low of 17.7 % (for 100wt-% methanol). This seems reasonable since the maximum error involved in determining $\Delta G_{(neut)}^{\circ}$ was reported to be ~10 %.

A major criticism of DeLigny and Alfenaar's method is that the ion employed in the extrapolation are small and values for $\Delta G_{(neut)}^{\circ}$ obtained from plots of ΔG° versus r^2 for inert gases and other nonpolar solutes will not correspond exactly to $\Delta G_{(neut)}^{\circ}$ for the ions due to effects of dielectric saturation. Thus, although DeLigny and Alfenaar were certainly right in subtracting values of $\Delta G_{(neut)}^{\circ}$ from ΔG° before performing the extrapolations, their method is still at fault because of the small sizes of the ions employed. The "inert-gas" assumption works best for large particles where the structure of the solvent surrounding the particles is the same as the structure of the solvent around an ion of similar size.

Values of medium effects for single ions and their corresponding neutral components in 100 % methanol as determined by DeLigny and Alfenaar by their second

extrapolation method are given in Table 9-a. DeLigny and Alfenaar's results are also compared with those from other investigators in Table 79.

Medium effects for single ions determined by this method differ from those determined by DeLigny and Alfenaar's first extrapolation method where $_{m}\gamma_{(el)}$ was estimated using the Born equation. For $\log {}_{m}\gamma_{H}$, the new value in 100 % methanol is -1.45, even less satisfying than the first value obtained by DeLigny and Alfenaar of -0.88.

Table 9-a. Medium Effects for Single Ions, $\log {}_m\gamma_i$, and for Their Neutral Components, $\log {}_m\gamma_{i(neut)}$, in Methanol According to DeLigny and Alfenaar (8). 25°C, Molal Scale.

Ion	$\log {}_m\gamma_i$	$\log {}_m\gamma_{i(neut)}$
Cl^-	+5.69	-0.84
Br^-	+5.31	-1.00
I^-	+4.56	-1.30
H^+	-1.45	----
Na^+	-1.34	-0.65
K^+	-0.90	-0.68
Rb^+	-0.89	-0.72
Cs^+	-0.94	-0.77

Salomon's extrapolation procedure.

Salomon (60, 111) proposed an extrapolation method for estimating free energies of solvation of single ions that is almost identical with Izmaylov's 1/r method. Salomon first plots experimentally observable energy combinations $(G_M^o - G_H^o)$ versus 1/r (M = alkali-metal ion) and $(G_X^o + G_H^o)$ versus 1/r (X = halide ion). By interpolation, he gets values of these combinations at identical values of 1/r. He proposes that for oppositely charged ions of equal radii, all terms contributing to the standard free energy of solvation of an ion will cancel except for ion-quadrupole interactions. He assumes that the ion-quadrupole energies are small. Salomon plots the difference between interpolated values of $(G_M^o - G_H^o)$ and $(G_X^o + G_H^o)$ which he calls $d\Delta G_{i\,\text{conventional}}^o$:

$$d\Delta G_{i\,\text{conventional}}^o \equiv G_M^o - G_X^o - 2G_H^o \qquad (109)$$

versus r^{-1} and extrapolates to $r^{-1} = 0$ to obtain values for G_H^o.

This is essentially the same method as Izmaylov's average plot. The extrapolations are still quite long although due to the inclusion of interpolated values of $(G_M^o - G_H^o)$ and $(G_X^o + G_H^o)$, Salomon's figures contain more points than Izmaylov's. Salomon obtained solvation

energies for single ions in methanol (111), 20 % dioxane in water (111), and propylene carbonate (60). Table 10 gives medium effects for single ions in methanol based on Salomon's work along with Izmaylov's medium effects based on his $1/n^2$ method. The results of both methods differ quite drastically. According to Salomon's value of -2.1 for $\log {}_m\gamma_H$ in 100 % methanol, methanol is a stronger base than water. Izmaylov's results are chemically more acceptable than Salomon's.

Salomon made use of e.m.f. data, free energies of formation, ionization potentials, electron affinities, and solubility data to evaluate $d\Delta G_{i\,\text{conventional}}^{o}$. Many of the energy values reported in his papers are precise to 1 - 2 kcal/mole which is of the same order of magnitude as the medium effects for single ions. A major criticism of his method is that values of G_H^o are dependent on the values of crystallographic radii used. Using values of radii from Pauling (83) or Gourary and Adrian (112), Salomon reports G_H^o can differ by as much as 2 kcal/g - ion.

Table 10. Medium Effects for Single Ions, $\log_m \gamma_i$, in Methanol, According to Salomon (111) and Izmaylov (103).

Ion	$\log_m \gamma_i$ (Salomon)	$\log_m \gamma_i$ (Izmaylov)
H^+	-2.1	+3.1
Li^+	-2.8	+1.6
Na^+	-2.1	+1.8
K^+	-1.4	+2.0
Rb^+	-3.0	+2.8
Cs^+	-2.0	+2.7
Cl^-	+6.2	+1.0
Br^-	+6.0	+1.0
I^-	+4.5	0.0

A critique of the extrapolation methods.

In all of the extrapolation methods except those of DeLigny and Alfenaar, the "zero-energy" assumption was made for the non-electrostatic component of the medium effect. Now we know that it is only the electrostatic component of the medium effect that approaches zero as the radius of an ion approaches infinity. The neutral components of solvation energy play an increasingly more important role as the radius of the ion increases. In the methods of Izmaylov, Feakins, and Salomon, the extrapolated function is $(G_H^o + (G_X^o - G_M^o)/2)$ and in this case, the neutral components of X and M may tend to cancel at $r^{-1} = 0$. It is interesting to note that in Izmaylov's $1/r$ and $1/n^2$ extrapolations, the two functions $(G_H^o - G_M^o)$ vs. r^{-1}, and $(G_H^o + G_X^o)$ vs. r^{-1}, have the same intercept as the average function. This does not seem reasonable since in the separate functions, the neutral component of the medium effect of the varying ion should approach infinity as r^{-1} approaches zero.

There are theoretical objections to extrapolations described above. In the small-ion region, where r is less than 4 Å, the components of solvation energy that are functions of higher powers of r^{-1} make important contributions to the total solvation energy. Thus, for small ions, plotting G^o as a function of r^{-1} is an oversimplification, and particularly when a straight

line if forced upon the data points, as in Feakin's extrapolation (8). Conway and Salomon (113) object to plotting solvation energies as a function of crystallographic radius, because they believe that some of the ion-solvent interaction energies are functions of the radius of the solvated ion.

All of the extrapolations discussed are long and based on insufficient number of points covering a narrow range of ionic radii. Often only three or four points are available. From the available data, which are always those for small ions, the extrapolation is extended into the region of very large ions which are likely to be governed by completely different types of relationships with the solvents. Thus, the input data in the extrapolation methods are not precise enough to abstract small quantities from them. Izmaylov's most optomistic estimate of the accuracy of the thermodynamic solvation energies necessary for the extrapolations is 0.5 kcal/mole (101). Most other estimates place the uncertainty in $\Delta G_{\pm}^{o}$ at 2 kcal/mole (4, 33, 106). Medium effects, which are usually of the order of 1 or 2 kcal/mole themselves are not reliable when derived from data whose uncertainty is of the same order of magnitude as the medium effects.

In Izmaylov's $1/n^2$ extrapolation, there is not enough evidence to justify the assumption that the major

portion of the solvation energy of an ion is proportional to the number of the lowest unoccupied energy level. In reality, this number is a label, a bookkeeping number. As an example, in the case of NaF, it is highly unlikely that the ion-solvent interactions of Na^+ and F^- ions are identical or even that the structure of the solvent around both ions is similar. This method may be suitable for very large ions provided more attention is paid to the quantitative aspects of the quantum numbers describing the lowest available energy levels.

In Salomon's extrapolation method, the assumption of cancellation of short-range ion-solvent interactions for positive and negative ions of the same size is not alltogether a valid assumption. For the solvents studied, the solvent structure around oppositely charged small ions will differ considerably (50, 59, 82).

DeLigny and Alfenaar's extrapolation procedures appear to be the most theoretically sound. By making use of the inert-gas assumption and a power series in 1/r, they should be avoiding or compensating for all the effects of the neutral component of solvation energy and short-range ion-solvent interactions. However, DeLigny and Alfenaar are still abstracting medium effects from information that has an uncertainty of the same order of magnitude as the medium effects. Also, their

uncertainties are compounded due to uncertainties in estimating $\Delta G^{o}_{(neut)}$ from the inert-gas assumption. A major criticism of DeLigny and Alfenaar's results is that they are not chemically satisfying. Their medium effects for methanol are positive for anions and negative for cations. Most other methods give positive values for medium effects of anions and cations in methanol.

In conclusion, it seems that extrapolation procedures are capable of yielding reliable values of medium effects for single ions only in cases where there are drastic differences in solvation energies of those ions. None of the extrapolation methods discussed appear to be universally applicable. Too many of the results (such as those of Salomon and Izmaylov's $1/n^2$ extrapolations) are contradictory. Other, more reliable methods for estimating medium effects for single ions must be sought.

Use of proton exchange constants in evaluating medium effects for single ions.

N. A. Izmaylov, one of the major contributors to the field of estimating medium effects for single ions, based his first approach to the problem (38, 49) on the fact that strong acids exhibit the same change in standard free energy of solvation on transfer from water to a given solvent. On this basis, Izmaylov made the assumption that the log of the medium effect for the strong acid, $\log {}_m\gamma_{HX}$, could be apportioned equally between the proton and the anion:

$$\tfrac{1}{2} \log {}_m\gamma_{HX} = \log {}_m\gamma_H = \log {}_m\gamma_X \qquad (110)$$

In effect, Izmaylov said that the solvation energies and medium effects of the proton and strong-acid anions are equal. Izmaylov's first approach to the problem is totally empirical and mainly of historical interest. Izmaylov proposed no model as a basis for his apportioning the medium effects of strong acids. There is experimental evidence to indicate that the major portion of the medium effect of strong acids can be attributed to the proton. For hydrogen and halide ions, specific solute-solvent interactions are certainly present in many solvents (14, 27, 36, 46, 50). Another sound criticism of Izmaylov's first approach

is the probable unequal solvation energies of hydrogen and strong acid anions due to differences in their radii. If, for the sake of discussion, this method were adopted, it could not be applied to aprotic solvents because of homoconjugation. Aprotic solvents such as acetonitrile are weak hydrogen bond donors. Interactions between undissociated acid molecules and their anions are stronger in these solvents than solvent-anion interactions.

Results from more reasonable methods (4) indicate that the medium effects for the proton and halide ions usually differ. Using Izmaylov's method, they would be equal.

In an attempt to improve on his first approach for estimating medium effects for single ions, Izmaylov (98, 99, 104) considered the medium effect of an acid, HA, as composed of an electrostatic term, $2 \log {}_{m}\gamma_{(el)}$, which could be apportioned equally between the proton and the anion, and a basicity term, $2 \log {}_{m}\gamma_{(basic)}$, which was attributable to the proton:

$$\log {}_{m}\gamma_{HA} = 2 \log {}_{m}\gamma_{(el)} + 2 \log {}_{m}\gamma_{(basic)} \qquad (111)$$

In terms of this formulation, the medium effect for the proton, $\log {}_{m}\gamma_{H}$, is given by:

$$\log {}_{m}\gamma_{H} = 2 \log {}_{m}\gamma_{(basic)} + \log {}_{m}\gamma_{(el)} \qquad (112)$$

Izmaylov obtained values for the $\log {}_{m}\gamma_{(basic)}$ term using proton exchange constants, K_r, which are equilibrium constants for the proton exchange reaction between water and solvent SH :

$$SH_2^+ + H_2O = SH + H_3O^+ \qquad (113)$$

$\log {}_{m}\gamma_{(basic)}$ is then given by :

$$\log {}_{m}\gamma_{(basic)} = \tfrac{1}{2} \log K_r + \frac{a^*_{H_2O}}{a^*_{SH}} \qquad (114)$$

where $a^*_{H_2O}$ and a^*_{SH} are the activities of water and solvent SH referred to infinitely dilute solution of water in SH and pure SH, respectively. Izmaylov obtained the $\log {}_{m}\gamma_{(el)}$ term from the relationship :

$$\log {}_{m}\gamma_{(el)} = \tfrac{1}{2} \log {}_{m}\gamma_{HA} - \log {}_{m}\gamma_{(basic)} \qquad (115)$$

Thus, Izmaylov was able to estimate the medium effect for the proton from thermodynamic values of $\log {}_{m}\gamma_{HA}$ and values for proton exchange constants, K_r.

The constant, K_r, is determined from e.m.f.,

conductance, indicator, and catalytic measurements made in solvent SH before and after addition of small amounts of water (12, 24, 45). Ideally, K_r should be the constant for reaction 113 in vacuo.

There have been several objections to Izmaylov's approach (4, 114). There is no apparent reason why the electrostatic term should be equal for the proton and the anion. According to Izmaylov's formulation, the medium effect of the anion is composed of an electrostatic contribution only. No account is made for the "neutral component" of the medium effect for the anion (zero-energy assumption). Izmaylov's use of K_r determined in a mixed solvent also leaves something to be desired. Since water is present as a dilute solution and solvent SH as an almost pure liquid, it is difficult to agree that K_r would represent the relative proton affinities of the two solvents (4, 114). Popovych (4) cites mass-spectrometric studies according to which the relative proton affinities of water and methanol molecules disagree with those based on the values of K_r derived from measurements in mixed solvents.

According to Franks and Ives (114), proton exchange constants are not comparable between solvents. If it is desired to use values of K_r determined in more than one solvent, a suitable unvarying standard state must be choosen for all solvent compositions. In terms of

standard free energies of solvation for reactants and products in Equation 113, K_r is defined as:

$$\ln K_r = -\frac{{}_sG^o}{RT} \qquad (116)$$

where ${}_sG^o$ is the standard free energy for reaction 119 in solvent S. This standard free energy, ${}_sG^o$, is in turn dependent on the standard state chosen and on the medium effects for the reactants and products in reaction 119. If the aqueous standard state is chosen,

$$ {}_sG^o = {}_wG^o + RT \ln {}_m\gamma_{H_3O} + RT \ln {}_m\gamma_{SH} - \qquad (117)$$
$$ - RT \ln {}_m\gamma_{SH_2} - RT \ln {}_m\gamma_{H_2O} $$

Thus, for each solvent, ${}_sG^o$ will vary in a manner dependent on the medium effects of the reactants and products in the proton exchange reaction. Thus, proton exchange constants are not constant over any solvent composition range and are a poor measure of the relative basicities of water and nonaqueous solvents (114).

Grunwald's activity postulate.

Grunwald and co-workers (115--117) proposed an original method for estimating medium effects for single ions in ethanol--water solvents based on a relationship between Δ pK's of organic acids, the medium effect for the proton, and two empirical constants. The Δ pK of uncharged acid HA can be defined in terms of the medium effects for the acid, HA, the conjugate base, A^-, and the proton:

$$\Delta pK(HA) = \log {}_m\gamma_H + \log \frac{{}_m\gamma_A}{{}_m\gamma_{HA}} \qquad (118)$$

In a dimilar manner, Δ pK for a cationic acid, BH^+, can be written as

$$\Delta pK(BH^+) = \log {}_m\gamma_H + \log \frac{{}_m\gamma_B}{{}_m\gamma_{BH}} \qquad (119)$$

Grunwald's approach is based on the assumption that the terms $\log({}_m\gamma_A/{}_m\gamma_{HA})$ and $\log({}_m\gamma_B/{}_m\gamma_{BH})$ in the above two equations can be related to a parameter, $\bar{m}$, which is a function of the structure of the acid, and another parameter, Y, which is dependent on the solvent and charge type of the acid. "Activity postulates" can then be written for the uncharged and cationic acids. For the uncharged acid, HA, the activity postulate takes the form:

$$\log \frac{m\gamma_A}{m\gamma_{HA}} = \bar{m}_{HA} Y_- \qquad (120)$$

and for the cationic acid, BH^+, the activity postulate is

$$\log \frac{m\gamma_B}{m\gamma_{BH}} = \bar{m}_{BH} Y_o \qquad (121)$$

The subscripts "$_-$" and "o" refer to the charge type of the conjugate base.

By arbitrarily assigning values to Y_o and Y_- of -1.00 and +1.00, respectively, Grunwald was able to evaluate $\bar{m}_{HA}$ and $\bar{m}_{BH^+}$ from experimental values of Δ pK(HA) and Δ pK(BH^+). Then, using the relationships

$$\Delta \text{pK(HA)} = \log {}_m\gamma_H + \bar{m}_{HA} Y_- \qquad (122)$$

$$\Delta \text{pK}(BH^+) = \log {}_m\gamma_H + \bar{m}_{BH^+} Y_o \qquad (123)$$

he was able to calculate medium effects for the proton.

Grunwald believes that the empirical division of the medium effect ratios of the conjugate acid-base pairs into a solvent-dependent term, Y, and an acid-dependent term, $\bar{m}$, is significant because he derives the same values for $\log {}_m\gamma_H$ from Equations 122 and 123. Actually, all this means is that his method for estimating

medium effects for single ions yields internally consistent values. In fact, the ratio $\log({}_{m}Y_{A}/{}_{m}Y_{HA})$ should be roughly equal to $\log {}_{m}Y_{A(el)}$ since $\log {}_{m}Y_{HA}$ is approximately equal to $\log {}_{m}Y_{A(neut)}$. Similarly, the ratio of $\log({}_{m}Y_{B}/{}_{m}Y_{BH})$ should be roughly equal to $-\log {}_{m}Y_{BH(el)}$. Thus, the activity postulates actually mean:

$$\bar{m}_{HA}\, Y_{-} = \log {}_{m}Y_{A(el)} \tag{124}$$

$$\bar{m}_{BH^{+}}\, Y_{o} = -\log {}_{m}Y_{BH(el)} \tag{125}$$

The terms $\bar{m}_{HA}\, Y_{-}$ and $\bar{m}_{BH^{+}}\, Y_{o}$ can be envisioned formally as the product of a solvent-dependent--acid-independent parameter (a dielectric constant term) and a solvent-independent--acid-dependent parameter (a radius term). But, if this were the case, the solvent-dependent parameter would have to be the same for all acids regardless of charge type. On the other hand, Grunwald differentiates between the solvent-dependent parameters Y_{-} and Y_{o} on the basis of charge type of conjugate base.

Some values of the medium effect for the proton in ethanol--water solvents as obtained by Grunwald are compared with values from other methods in Table 74.

The Hammett acidity functions.

Hammett and Deyrup (118, 119) used an indicator approach to establish a solvent-independent acidity scale. An acidity function, H_o, was defined in terms of the acidity constants K_{HIn^+} of uncharged indicator bases, In. From the dissociation of the acid form:

$$HIn^+ = H^+ + In \tag{126}$$

an equation relating pK_{HIn^+} to hydrogen ion activity is derived via the mass action expression:

$$K_{HIn^+} = \frac{a_H a_{In}}{a_{HIn}} = \frac{a_H m_{In} \gamma_{In}}{m_{HIn} \gamma_{HIn}} \tag{127}$$

and

$$pK_{HIn^+} = -\log \frac{a_H m_{In} \gamma_{In}}{m_{HIn} \gamma_{HIn}} \tag{128}$$

where m_{In} and m_{HIn} are the molalities, γ_{In} and γ_{HIn} are the activity coefficients of the indicator and protonated indicator, respectively, and the pK's and a's are referred to aqueous standard states. The Hammett function, H_o, is then defined in terms of a_H and the ratio of the activity coefficients of indicator and protonated indicator:

$$pK_{HIn^+} = H_o - \log \frac{m_{In}}{m_{HIn}} \tag{129}$$

and

$$H_o \equiv - \log \frac{a_H \gamma_{In}}{\gamma_{HIn}} \tag{130}$$

The activity coefficients γ_{In} and γ_{HIn} are the products of the salt effect and medium effect activity coefficients because of aqueous standard state

$$\gamma_{In} = s^{\gamma}In \, m^{\gamma}In \tag{131}$$

$$\gamma_{HIn} = s^{\gamma}HIn \, m^{\gamma}HIn \tag{132}$$

In practice, the ratio $(\gamma_{In}/\gamma_{HIn})$ is generally assumed to be unity which makes H_o equal to $- \log a_H$. To determine the value of H_o, one has to know pK_{HIn^+} of the protonated indicator and the concentration ratio (In/HIn). In aqueous solution, the following relationship can be written assuming $s^{\gamma}In = s^{\gamma}HIn$:

$$H_o = pK_{HIn^+} + \log \frac{m_{In}}{m_{HIn}} = pa_H \tag{133}$$

The Hammett function is a direct measure of pa_H

only for dilute solutions in water. In more concentrated aqueous solutions, the activity coefficients of the In and HIn^+ species have values less than unity. Unless γ_{In}/γ_{HIn} is unity, H_o does not equal pa_H. In nonaqueous solutions, the activity coefficients of the species In and HIn^+ include the medium effect and the Hammett function assumes the form:

$$H_o = -\log a_H - \log \frac{s\gamma_{In}}{s\gamma_{HIn}} - \log \frac{m\gamma_{In}}{m\gamma_{HIn}} \qquad (134)$$

where the subscripts s and m refer to salt effect and medium effect, respectively. Thus, unless the two activity coefficient ratios cancel or are equal to unity, H_o as it is measured operationally via Equation 133, is not equal to pa_H. For large indicator species, the ratio $({}_m\gamma_{HIn}/{}_m\gamma_{In})$ would be approximately equal to ${}_m\gamma_{HIn(el)}$ which can be estimated via the Born equation or some modification of it.

The application of the Hammett function in nonaqueous media requires knowledge of medium effects for In and HIn^+ or, at the least, knowledge of the electrostatic component of the medium effect of HIn^+. Hammett functions seem most useful in aqueous or partially aqueous media. In nonaqueous media, the problem of the inequality of ${}_m\gamma_{In}$ and ${}_m\gamma_{HIn}$ becomes important.

The reference-electrolyte method.

Introduction.

Of the methods for estimating medium effects for single ions discussed so far, only the extrapolation procedures of DeLigny and Alfenaar (8, 110) appear to be theoretically sound. However, even in these methods, the results are questionable due to the small sizes of the ions employed in the extrapolation. Fortunately, another method is available for estimating medium effects for single ions that is more credible than any method proposed to date. This is the reference-electrolyte method.

A reference electrolyte is a 1:1 electrolyte composed of large ions as identical as possible in size, geometry, and other physico-chemical properties which determine interactions with solvents. In the reference-electrolyte method, the assumption is that the medium effect for the electrolyte can be apportioned equally between the anion and cation

$$\log {}_m\gamma_{\text{cation}} = \log {}_m\gamma_{\text{anion}} = \tfrac{1}{2} \log {}_m\gamma_{\substack{\text{reference} \\ \text{electrolyte}}} \qquad (135)$$

Once the medium effects of the reference cation and anion are known in a given solvent, medium effects for all other single ions become accessible. In this

research, medium effects for single ions were determined in ethanol, ethanol--water mixtures, methanol, and acetonitrile using two reference electrolytes : tetraphenylphosphonium tetraphenylborate (Ph_4P BPh_4), and tetraphenylarsonium tetraphenylborate (Ph_4As BPh_4). The results were compared with those obtained earlier by Popovych and Dill (17) who used triisoamyl-n-butylammonium tetraphenylborate (TAB BPh_4).

The idea of apportioning measurable properties of an electrolyte between its ions is not new. In 1933 Bernal and Fowler (48) first stated the assumption that ions of equal radii have equal energies of solvation. In 1949, Kraus (120) proposed using tetrabutylammonium triphenylfluoroborate (Bu_4N Ph_3FB) as a reference electrolyte in conductance studies. Kraus proposed that since the ions of Bu_4B Ph_3FB have approximately equal size, low charge density, and since they have the same geometry and do not undergo specific solvation, the limiting equivalent conductance of the electrolyte could be equally apportioned between the two ions :

$$\lambda_o Bu_4N = \lambda_o Ph_3FB = \tfrac{1}{2}\Lambda_o Bu_4N\ Ph_3FB \qquad (136)$$

In 1958, Fuoss, Berkowitz and Hirsch (121) proposed using tetrabutylammonium tetraphenylborate as a reference electrolyte for conductance studies. This

was thought to be a great improvement over Kraus' choice of Bu_4N Ph_3FB since the tetraphenylborate ion is symmetrical (122). In the conductance field, Coetzee and Cunningham proposed tetraisoamylammonium tetraisoamylborate as a reference electrolyte in 1965 (122). There has been a great deal of interest in the use of reference electrolytes to determine limiting ionic equivalent conductances especially in those solvents where accurate transference data are not available.

The first use of a reference electrolyte to estimate free-energy changes for ions was in 1960. In that year, Grunwald, Baughman and Kohnstam (80) reported on the use of the reference electrolyte Ph_4P BPh_4 to estimate free energy changes experienced by single ions upon incremental changes in dioxane--water composition centering around 50 % dioxane with the 50 % dioxane--water as a reference solvent. However, Grunwald, Baughman, and Kohnstam's measurements were performed in solvents of very similar composition. Popovych (18) was the first to propose the use of a reference electrolyte for estimating medium effects for single ions, i.e. for free-energy changes involved on the "transfer" of ions from water to nonaqueous solvents. Popovych first used the reference electrolyte triisoamyl-n-butylammonium tetraphenylborate (TAB BPh_4)

to determine medium effects in methanol and in the "ASTM medium", which consists of 50.0 % toluene, 49.5 % isopropanol, and 0.5 % water, by volume. Later, Popovych and Dill (17) used TAB BPh_4 to estimate medium effects for single ions in anhydrous ethanol and ethanol--water mixtures. Other investigators (26, 31, 44) have made use of Ph_4As BPh_4 as a reference electrolyte for estimating medium effects in dipolar aprotic solvents using methanol as a reference medium.

There is a sound theoretical basis for the reference-electrolyte method for estimating medium effects for single ions. The reference ions are large ($r > 4$ Å), have small surface charge densities, low polarizabilities, do not interact specifically with solvent molecules, and are as similar in size and structure as possible. Their large size helps to minimize the effects of dielectric saturation and other short-range ion-solvent interactions. Ion-quadrupole energies, which are functions of r^{-3} and are of opposite sign for cations and anions, are at an absolute minimum due to the large size of the reference ions. The major contribution to the medium effects of these large reference ions is from the neutral component (4). Being that both the anion and the cation are structurally similar, the neutral contributions to their solvation energies are expected

to be identical. The electrostatic contribution to the solvation energies of the large reference ions are also expected to be equal. The major portion of the electrostatic contribution to the solvation energy is the Born charging energy which is proportional to r^{-1} of the ion. Ions of equal size have equal Born charging energies. However, the equality of solvation energies is not of utmost importance for the reference ions. The major consideration is that the <u>difference</u> in solvation energy between water and a nonaqueous solvent be identical for both ions. This is exactly what is theoretically predicted for our large reference ions.

Medium effects for Ph_4P BPh_4, Ph_4As BPh_4, and TAB BPh_4 have to be determined in order to apply the reference-electrolyte assumption from which we evaluate the medium effects for single ions. The reference ions are not electrode-active and because of this, it is necessary to determine medium effects of the reference electrolytes by the solubility method. The reference electrolytes are insoluble in water ($\sim 10^{-7}$ M) and somewhat unstable at such low concentrations in solvents containing water. Fortunately, medium effects are differences between standard free energies of solvation and hydration which allows the medium effect of a compound to be determined from medium effects of other

compounds containing the ions of interest. For example, in the case of $Ph_4P\ BPh_4$, the medium effects, $\log {}_m\gamma$, of $Ph_4P\ Pi$, $KBPh_4$, and KPi can be combined to give the medium effect for the reference electrolyte :

$$\log {}_m\gamma_{Ph_4P\ BPh_4} = \log {}_m\gamma_{Ph_4P\ Pi} + \log {}_m\gamma_{KBPh_4} - \log {}_m\gamma_{KPi} \quad (137)$$

This is actually the method used in this research for determining $\log {}_m\gamma_{Ph_4P\ BPh_4}$. Similarly, the medium effect of $Ph_4As\ BPh_4$ is determined using the relationship

$$\log {}_m\gamma_{Ph_4As\ BPh_4} = \log {}_m\gamma_{Ph_4As\ Pi} + \log {}_m\gamma_{KBPh_4} - \log {}_m\gamma_{KPi} \quad (138)$$

and for $TAB\ BPh_4$:

$$\log {}_m\gamma_{TAB\ BPh_4} = \log {}_m\gamma_{TAB\ Pi} + \log {}_m\gamma_{KBPh_4} - \log {}_m\gamma_{KPi} \quad (139)$$

Once the medium effects have been determined for the reference electrolytes, medium effects can be estimated for the reference ions by applying the reference-electrolyte assumptions :

$$\log {}_{m}\gamma_{Ph_4P} = \log {}_{m}\gamma_{BPh_4} = \tfrac{1}{2} \log {}_{m}\gamma_{Ph_4P\ BPh_4} \qquad (140)$$

$$\log {}_{m}\gamma_{Ph_4As} = \log {}_{m}\gamma_{BPh_4} = \tfrac{1}{2} \log {}_{m}\gamma_{Ph_4As\ BPh_4} \qquad (141)$$

$$\log {}_{m}\gamma_{TAB} = \log {}_{m}\gamma_{BPh_4} = \tfrac{1}{2} \log {}_{m}\gamma_{TAB\ BPh_4} \qquad (142)$$

Medium effects for other single ions can be calculated using the medium effects for the reference ions in combination with those of complete electrolytes. For example, the medium effect for potassium ion can be calculated from the medium effects of the BPh_4^- ion and that of $KBPh_4$:

$$\log {}_{m}\gamma_{K} = \log {}_{m}\gamma_{KBPh_4} - \log {}_{m}\gamma_{BPh_4} \qquad (143)$$

Once the medium effect for potassium has been evaluated, the medium effect for the chloride ion can be calculated, e.g. :

$$\log {}_{m}\gamma_{Cl} = \log {}_{m}\gamma_{KCl} - \log {}_{m}\gamma_{K} \qquad (144)$$

The medium effect for the proton can be calculated using $\log {}_{m}\gamma_{Cl}$ and $\log {}_{m}\gamma_{HCl}$:

$$\log {}_{m}\gamma_{H} = \log {}_{m}\gamma_{HCl} - \log {}_{m}\gamma_{Cl} \qquad (145)$$

Equations 143-145 are representative of the many paths that can be used to estimate medium effects for single ions once the medium effects for the ions of the reference electrolyte become available.

In this research, medium effects for single ions were estimated in anhydrous ethanol, ethanol--water solvents, acetonitrile, and methanol. Medium effects for reference electrolytes and single ions were evaluated at intervals of 10 wt.-% in the ethanol--water solvent system. Medium effects for a varied array of ions in ethanol--water solvents, methanol and acetonitrile have been calculated using available literature data for thermodynamic medium effects for complete electrolytes or other electroneutral combinations of ions.

In this research, thermodynamic solubility products of Ph_4P Pi and Ph_4As Pi have been determined in water, ethanol, ethanol--water mixtures, methanol, and acetonitrile. Solubilities and solubility products of TAB Pi, $KBPh_4$, and KPi have been recalculated and in some cases, reevaluated from the data of Dill and Popovych (139). The thermodynamic solubility products of $RbBPh_4$ and $CsBPh_4$ have been determined in water, ethanol, and methanol, and the solubilities of

ferrocene and TlCl have been determined in water, ethanol, and all the ethanol--water solvents. Tetraphenylmethane (Ph_4C), tetraphenylsilane (Ph_4Si), and tetraphenylgermane (Ph_4Ge) have been purified and their absorptivities and solubilities determined in methanol, acetonitrile, and ethanol--water mixtures from 60 to 100 wt.-%. Differential thermal analysis was performed on all the solute-solvent mixtures studied in this work in order to check for the formation of crystal solvates.

In order to determine the thermodynamic solubility products of the compounds studied, solubilities, activity coefficients, and degrees of dissociation were measured or calculated for each compound in each solvent. Solubilities were carefully determined by exposing a slurry of the compound in the solvent to ultrasonic waves for a short ($\sim$ 30 minutes) period and then equilibrating the slurry by shaking it at constant temperature until two successive analyses produced identical results (usually between 3 and 6 days). Activity coefficients were evaluated by the method of Bronsted and LaMer (123) in which the solubility of the compound is studied at varying ionic strengths. Degrees of dissociation were evaluated from studies of electrolytic conductance as a function of concentration.

Reference electrolytes studied in this research effort.

Tetraphenylphosphonium tetraphenylborate, $Ph_4P\ BPh_4$.

Historically, the first reference electrolyte to be used for the purpose of estimating medium effects for single ions was tetraphenylphosphonium tetraphenylborate, $Ph_4P\ BPh_4$. Grunwald, Baughman, and Kohnstam (80) shose $Ph_4P\ BPh_4$ because of the equality of the Ph_4P^+ and BPh_4^- radii (4.2 Å based on molecular models), the general similarity in structure of the two ions, the small surface charge density of the two ions ($\sim$ +0.18 unit of charge per phenyl group for the Ph_4P^+ ion and less for the BPh_4^- ion) and the fact that the dissimilar atoms of the two ions are buried within the phenyl ring structure. Grunwald and co-workers estimated medium effects for single ions in dioxane--water mixtures centering around 50 wt.-% dioxane. They used 50 wt.-% dioxane as a reference solvent. Thus, the variations in the medium involved in their study was confined to a narrow range.

Two other estimates of the radius of BPh_4^- ion are available. In an article by Friedman (124), a figure is presented in which the ionic radius of various ions is plotted as a function of ΔH^o from water to propylene carbonate. Using this figure, the radius of BPh_4^- is found to be 5.5 Å. Coetzee and Cunningham (122) give

a value of 4.8 Å for the radius of the BPh_4^- ion. If one takes the view that the radii of Ph_4P^+ and BPh_4^- should differ by an amount equal to the difference in radii of the central atoms, than BPh_4^- and Ph_4P^+ would differ by 0.22 Å. Phosphorus has a covalent radius of 1.10 Å (83) and boron has a covalent radius of 0.88 Å (83). The BPh_4^- ion can be thought of as being slightly larger than molecular models predict due to its negative charge. Similarly, the Ph_4P^+ ion might be slightly smaller than the size predicted by molecular models due to its positive charge. The effects of the charges on the ions tends to counteract the differences in the sizes of the central atoms and Ph_4P^+ and BPh_4^- are probably very nearly equal in size.

The structural similarities of Ph_4P^+ and BPh_4^- ions are of utmost importance. Both ions consist of a central atom buried underneath four phenyl groups. Any surface charges or deformities should be very similar for both ions. Both ions are large enough so that short-range ion-solvent interaction energies are not significant contributors to their solvation energies. Neither ion is expected to form complexes in solutions of water, alcohols, or dipolar aprotic solvents. Tetraphenylphosphonium tetraphenylborate appears to be an excellent reference electrolyte.

Tetraphenylarsonium tetraphenylborate, $Ph_4As\ BPh_4$.

In 1967, Alexander and Parker (28) recommended using $Ph_4As\ BPh_4$ as a reference electrolyte. Their choice of $Ph_4As\ BPh_4$ was based on reasoning similar to Grunwald, Baughman and Kohnstam's for $Ph_4P\ BPh_4$. The Ph_4As^+ ion is approximately the same size as the BPh_4^- ion (124). Both Ph_4As^+ and BPh_4^- are large, have low surface charge densities, have their central atom buried under four phenyl groups, and both ions are structurally similar.

Alexander and Parker used the $Ph_4As\ BPh_4$ assumption to estimate medium effects for single ions in methanol, water, and some dipolar aprotic solvents. They chose methanol as a reference solvent because some of their supporting data such as the solubility of $AgBPh_4$ were not available or were inaccurate for solutions in water. All of the medium effects based on the $Ph_4As\ BPh_4$ assumption reported by Parker and his co-workers (27, 28, 30) were calculated from concentration solubility products with no corrections for incomplete dissociation or activity coefficients. Also, some of their calculations are based on values for the solubility of $AgBPh_4$, a rather unstable salt in many solvents for which reliable K_{sp} values in water and methanol have not been determined until recently (31). As has been pointed out (36), when comparing solubility products in dissimilar solvents

for the purpose of determining medium effects, activity coefficients cannot be neglected. Values of medium effects for single ions in acetonitrile and in methanol based on the work of Parker and his associates are given in Tables 79 and 82.

In 1966, Arnett and McKelvey (125) had used the assumption that enthalpies of transfer, ΔH^{o}, of Ph_4As^+ and BPh_4^- ions are equal for transfer from water to dimethylsulfoxide (DMSO). The same assumption was also used by Arnett and McKelvey and Friedman (124). Krishnan and Friedman (126) also used the Ph_4As BPh_4 assumption to estimate enthalpies of transfer for single ions from water to propylene carbonate and DMSO.

Kolthoff and Chantooni (31) have used the Ph_4As BPh_4 assumption to estimate medium effects for single ions in water, acetonitrile, dimethylsulfoxide, and dimethylformamide using methanol as a reference solvent. These authors endorse the reference-electrolyte methods in general on the basis of the agreement of medium effects for single ions as derived from these methods with chemical reasoning. Kolthoff and Chantooni do correct for incomplete dissociation and the (salt effect) activity coefficients although their method for estimating activity coefficients is somewhat ambiguous. Some of their results are reported in Tables 79 and 82.

Springer, Coetzee and Kay (127) determined transference

numbers of $(CH_3)_4N^+$ and ClO_4^- ions in acetonitrile and thus were able to calculate limiting equivalent ionic conductances of various ions that seemed suitable for use as reference ions in this solvent. The limiting equivalent ionic conductances of Ph_4As^+ and BPh_4^- ions were found to be 55.8 and 58.3, respectively, in acetonitrile. These values differ by 4.4 %. While the limiting equivalent ionic conductances of Ph_4As^+ and BPh_4^- ions in acetonitrile are not identical, the use of $Ph_4As\ BPh_4$ as a reference electrolyte in acetonitrile seems plausible especially when the large, similar sizes of the ions are considered. Similarity of limiting equivalent ionic conductance is not the best criterion for choosing reference ions and can be used only as an indication that the ions of a reference electrolyte will experience equal changes in solvation energies between solvents under consideration.

Triisoamyl-n-butylammonium tetraphenylborate, TAB BPh_4.

Popovych (18) was the first to use TAB BPh_4 as a reference electrolyte. His choice of TAB BPh_4 was based on the equality of the Stokes radii of TAB^+ and BPh_4^- ions in water (128) and methanol (129). Later, it was shown that these ions have equal Stokes radii in acetonitrile as well (122). Popovych estimated medium effects for single ions in methanol and ASTM (50.0 % toluene, 49.5 % isopropanol and 0.5 % water). Popovych and Dill (17) estimated medium effects for single ions in ethanol and ethanol--water solvents based on the TAB BPh_4 assumption.

TAB BPh_4 does not appear to be as good a reference electrolyte as Ph_4P BPh_4 or Ph_4As BPh_4. The BPh_4^- ion is closer in structure and chemical type to the tetraphenyl cations Ph_4P^+ and Ph_4As^+ than it is to TAB^+. In this research, medium effects for single ions in ethanol and ethanol--water solvents were re-evaluated from the data of Popovych and Dill (17, 139) and compared to medium effects for single ions based on the Ph_4P BPh_4 and Ph_4As BPh_4 assumptions.

A critique of the reference-electrolyte method.

The ions of a reference electrolyte should be large, have a low polarizability, small surface charge density, and minimal tendency towards specific interaction with solvent. Compounds containing the reference ions that are used in determining medium effects by the solubility method should form no crystal solvates with the solvents being studied.

There has been some criticism of the reference-electrolyte method, about the specific ions involved and not about the theoretical soundness of the method.

Grunwald, Baughman and Kohnstam (80) have criticized the Ph_4P BPh_4 assumption on the basis of possible inequality of surface charge densities for the two ions based on resonance structures that can be written for the Ph_4P^+ ion in which the positive charge is on the ortho- and para- positions of the phenyl rings. Although small, this difference appears to be valid. More information about the sizes, polarizabilities, and surface charges of the reference ions is required.

Parker and Alexander (26) have criticized the reference electrolytes by suggesting that tetraphenylborates may form crystal solvates. One of the goals of this research was to check whether the compounds whose medium effects were determined via the solubility method in this study do not form crystal solvates. When

alternate paths are available for calculating the medium effect for any single ion, they should be taken. If results differ by more than the experimental error, there is a possibility that one or more of the compounds used forms crystal solvates.

Salomon (60) points out that the reference ions may be subject to micelle formation in organic solvents. However, Grunwald, Baughman and Kohnstam (80) cite evidence that for large-ion salts such as $(n\text{-}Bu)_4N\ BPh_4$ and $Ph_4P\ BPh_4$, where several groups are attached to the center of ionic charge, the critical micelle concentration is usually quite high. Fuoss, Berkowitz, Hirsch, and Petrucci (121) found $(n\text{-}Bu)_4N\ BPh_4$ to be a normal electrolyte in a variety of organic solvents.

Coetzee and Sharpe (130) have argued that water, methanol, ethanol, acetonitrile, DMSO, and sulfolane differentiate between Ph_4As^+, Ph_4P^+, and BPh_4^- ions in terms of specific solvation. Their conclusions are based on NMR data. They reported molar chemical shifts of $NaBPh_4$, $Ph_4P\ Cl$ and $Ph_4As\ Cl$ studied as a function of concentration from 0.1 to 0.4 M in ethanol, methanol, and water. The molar chemical shifts of these compounds decrease in absolute value as concentration decreases. No data is available for 10^{-5}--10^{-3} molar solutions but upon extrapolation of Coetzee and Sharp's reported values, the difference in molar chemical

shifts between the tetraphenyl ions at low conentration would be negligible. Medium effects are properties of infinite dilution and all studies carried out in the present research made use of solutions no more concentrated than 10^{-3} M. It should be borne in mind, however, that it is difficult to translate NMR shifts in terms of energetics and that appreciable shifts may be associated with negligible free-energy changes. Moreover, NMR measurements are made on relatively concentrated solutions, where the large tetraphenyl ions constitute an appreciable volume fraction of the solution, leading to a pertubation of the solvent structure which may not occur at the extreme dilutions at which medium effects are typically determined. From a practical view point, the question is not the existence of such differentiating interactions per se, but rather their magnitudes relative to the experimental error in the Δ pK values or similar data from which the medium effects are calculated. Results of this study show that any differentiation between the solvent-solute interactions for the Ph_4As^+ and the Ph_4P^+ ions is at the most of the order of magnitude of experimental errors in the Δ pK's, but it can only be inferred that the same is true for the BPh_4^- ion.

Although there are some valid criticisms of the reference electrolytes used in this research, the

reference-electrolyte method for estimating medium effects for single ions is undoubtedly the only method proposed to date that is widely applicable in a wide variety of solvents. The reference electrolytes were chosen to fit the criteria for reference electrolytes as closely as possible.

Studies of the medium effects of Ph_4C, Ph_4Si, Ph_4Ge.

Another major goal of this research is to find out if the observed medium effects of the reference ions will equal the sum of a calculated electrostatic component, $\log {}_mY_{(el)}$, and an experimental neutral component, $\log {}_mY_{(neut)}$. In section IV-C-4-b, it was shown that, theoretically, for large ions which do not undergo specific interactions with the solvent, ${}_mY_{(el)}$ can be estimated via the Born equation and ${}_mY_{(neut)}$ will be equal to the medium effect of a structurally similar uncharged molecule:

$$\log {}_mY_{\substack{\text{reference}\\\text{ion}}} = \log {}_mY_{(\text{Born})} + \log {}_mY_{\substack{(\text{neutral}\\\text{analog})}} \qquad (88)$$

It is proposed that the medium effects of the molecules tetraphenylmethane (Ph_4C), tetraphenylsilane (Ph_4Si), and tetraphenylgermane (Ph_4Ge) will make excellent neutral components for the medium effects of the reference ions Ph_4P^+, Ph_4As^+, BPh_4^-, and possibly, TAB^+. Ph_4C, Ph_4Si, Ph_4Ge and all the reference ions are tetrahedral, they are all approximately equal in size, and all but TAB^+ are tetraphenyl species.

The compound Ph_4C has been used successfully by Grunwald, Baughman, and Kohnstam (80) as a neutral analog for the Ph_4P^+ and BPh_4^- ions. These authors verified

the validity of Equation 88 in dioxane--water mixtures but only for incremental changes in solvent composition centering on 50 wt.-% dioxane. From molecular model considerations, Grunwald, Baughman, and Kohnstam found the radii of Ph_4P^+, BPh_4^-, and Ph_4C to be 4.2 Å, 4.2 Å, and 4.05 Å, respectively. In an independent method, using the molar volume of Ph_4C (287 ml. at 20°C), they found the radius of Ph_4C to be 4.02 Å. Thus, Ph_4C is a fairly good neutral analog for Ph_4P^+ and BPh_4^-. Here, it is proposed that Ph_4Si and Ph_4Ge as well as Ph_4C will, collectively, make suitable neutral analogs for all the reference ions. The larger radii of Si (1.17 Å) and Ge (1.22 Å) as compared to C (0.77 Å) will make Ph_4Si and Ph_4Ge larger compared to Ph_4C and this will compensate for the smaller radius of Ph_4C compared to Ph_4P^+ or BPh_4^-. The three elements, C ($r = 0.77$ Å), Si ($r = 1.17$ Å) and Ge ($r = 1.22$ Å) have crystallographic radii corresponding to B ($r = 0.88$ Å), P ($r = 1.10$ Å), and As ($r = 1.18$ Å). Although all species have a different central atom, these atoms are buried in the interior. The perimeter of the species exposed to the solvent will be the same for all the tetraphenyl molecules and ions, except for a small surface charge which will distinguish the ions from the uncharged molecules. Our objective is to determine whether adding a calculated (Born) electrostatic medium effect

to the experimental medium effects for Ph_4C, Ph_4Si, and Ph_4Ge, will result in the observed medium effects of Ph_4P^+, Ph_4As^+, BPh_4^-, and TAB^+.

Properties of single ions have often been arrived at by measuring the desired properties of structurally similar molecules and then adjusting these measurements to account for the charge on the ion. Ferrocene has been used as the neutral analog for ferricinium ion (36, 90, 110), OsO_4 has been used as the neutral analog for ReO_4^- (35), and many investigators have used inert gases as neutral analogs for isoelectronic and equal-size ions ("inert-gas" assumption). Parker (26, 27) has gone so far as to say that $\log {}_m\gamma_{Ph_4C} = \log {}_m\gamma_{BPh_4}$ (the Ph_4C--BPh_4^- assumption), i.e., he neglected even the Born charging contribution to the medium effects of reference ions.

In this work, the validity of Equation 88 will be checked in ethanol--water solvents, methanol, and acetonitrile.

Experimental.

Preparation of solvents.

Ethanol--water solvents.

Purified U.S.P. 95 % ethanol was used to prepare ethanol--water mixtures containing less than 95 wt.-% ethanol. The starting material was purified by slow distillation using a 30-cm vigreux column. The distillation flask was charged with about five liters of the U.S.P. alcohol having a specific conductivity of 60 to 200×10^{-8} mho/cm. The rate of distillation was about 0.2 liter/hour. The first 1.5 liters was rejected and the middle fraction (about 2.5 liters) was collected for use. In this manner, ethanol having a specific conductivity of 5 to 25×10^{-8} mho/cm was collected. The conductivity of the ethanol was not decreased by additional distillation. The percentage composition of the distillate and all other ethanol--water solvents used in this study was determined by interpolation using density-versus-wt.-% ethanol data available in the literature (131). The composition of the freshly distilled U.S.P. 95 % ethanol varied from 92 to 94 wt.-% in ethanol.

Ethanol--water mixtures were prepared volumetrically with approximate amounts of distilled ethanol and distilled or de-ionized water. The density of the

mixtures was determined gravimetrically using calibrated 100-ml volumetric flasks. Pentuplicate density determinations were performed on all ethanol--water mixtures used in this study. Appendix A-1 contains a listing of densities of ethanol--water mixtures from the paper of Osborne, McKelvey, and Bearce (131).

U.S.P. 200 proof ethyl alcohol (Publicker Industries Co.) was used as starting material in the preparation of 100 wt.-% ethanol. Five liters of the 200-proof alcohol were refluxed over magnesium ethoxide for 24 hours while passing a slow stream of nitrogen through the charge. The alcohol was then distilled through a 30-cm vigreux column. The first 1.5 liters were rejected, and the middle 2.5 liters collected. The middle fraction had a specific conductance of 0.6 to 13×10^{-8} mho/cm and a density of about 0.7851g/ml at 25°C which compares favorably with the available literature values of 0.7850g/ml (132) and 0.7851g/ml (131).

Before use, all solvents were de-aerated with a stream of helium passed through a fritted glass bubbler containing the given solvent.

Methanol.

Matheson Coleman and Bell spectroquality grade methanol was used without further purification.

Acetonitrile.

Matheson Coleman and Bell spectroquality acetonitrile was refluxed for 24 hours over CaH_2 and then distilled slowly through a 30-cm vigreux column. Out of a charge of 5 liters, the first liter was rejected and the middle three liters were collected for use.

Preparation and purification of materials.

KPi.

Potassium picrate was prepared in hot 1:1 aqueous methanol by neutralization of picric acid with potassium hydroxide (both Baker analyzed). On cooling, large needles of KPi separated. These were filtered, washed with water, and recrystallized four times from distilled water. The crystals were dried in vacuo at 80°C for 24 hours.

$RbBPh_4$, $CsBPh_4$.

$RbBPh_4$ and $CsBPh_4$ were prepared by metathesis of $NaBPh_4$ (Fisher Certified) and the corresponding alkali-metal chloride (Alfa Inorganics). $NaBPh_4$ dissolved in hot distilled water was slowly added to an equimolar amount of RbCl or CsCl dissolved in hot distilled water. A milky white precipitate of $RbBPh_4$ or $CsBPh_4$ was formed which was filtered, washed with a large quantity of distilled water, and recrystallized three times from a 3:1 acetone--water mixture. The resulting crystals were dried in vacuo at 80°C for 24 hours.

Ph_4P Pi, Ph_4As Pi.

Ph_4P Pi and Ph_4As Pi were prepared by combining hot equimolar ethanolic solutions of picric acid (Baker analyzed reagent) and Ph_4As Cl or Ph_4P Cl (or Ph_4P Br) (Alfa Inorganics), respectively. Water was added to incipient cloudiness, followed by dissolution with a minimum of hot ethanol. The crystals which separated upon cooling were washed with water, purified by double recrystallization from ethanol--water mixtures, and dried *in vacuo* at 80°C for 24 hours. The electrolytes were recrystallized once more prior to the determination of their conductances.

LiCl, TlCl.

Mallinckrodt LiCl (reagent grade) and Alfa Inorganics TlCl (ultrapure) were used without further purification.

Ph_4P BPh_4.

Ph_4P BPh_4 was prepared by mixing hot equimolar aqueous solutions of Ph_4P Cl and $NaBPh_4$. The resulting white precipitate was filtered, washed with hot water, and recrystallized once from pure acetone. The crystals were dried *in vacuo* at room temperature for 2 weeks.

Ph_4C, Ph_4Si, Ph_4Ge.

Ph_4C, Ph_4Si, and Ph_4Ge from Alfa Inorganics were purified by triple sublimation. The purity of the snow-white sublimates was monitored by uv spectrophotometry as their complex spectra and especially the peak-height ratios are very sensitive to the presence of impurities and to decomposition. A sample was considered sufficiently pure when successive sublimations produced no spectral change.

Ferrocene.

Ferrocene from Alfa Inorganics was purified by double recrystallization from U.S.P. 200-proof ethanol. The ferrocene was dissolved in hot ethanol, the solution was filtered while hot, and then water was added to incipient cloudiness, followed by dissolution with hot ethanol. Upon cooling, crystals of ferrocene separated. The procedure was repeated once more and the ferrocene was dried *in vacuo* at room temperature for two weeks.

Solubility studies of electrolytes.

Introduction.

Medium effects of Ph_4P Pi, Ph_4As Pi, KPi, $RbBPh_4$, $CsBPh_4$, and TlCl were determined by the solubility method. These compounds have intermediate solubilities in the range of 10^{-3} to 10^{-5} M. This allows evaluation of their ion-activity products without complications of the sort that would arise if their solubilities were much larger. It was impractical to determine the medium effects of the reference electrolytes directly due to their low solubilities ($\sim 10^{-7}$ M) in water-rich solvents.

The solubilities of Ph_4P Pi and Ph_4As Pi were determined in water, ethanol, methanol, acetonitrile, and in ethanol--water solvents at intervals of about 10 wt.-% ethanol. The solubility of potassium picrate was determined at 10 and 90 wt.-% ethanol. $RbBPh_4$ and $CsBPh_4$ solubilities were determined in water, ethanol and acetonitrile. The solubility of TlCl was determined in water, ethanol, and ethanol--water solvents at intervals of about 10 wt.-% ethanol.

Solubilities of electrolytes were determined by the usual procedure of shaking salt with solvent in a thermostatted flask until the concentration no longer changed. A significant improvement was made in the

method of preparing the salt-solvent mixtures for shaking. This consisted of subjecting the suspensions to the dispersing action of an ultrasonic generator (the Maxomatic from the L & R Manufacturing Co.) for a period of about two hours prior to their equilibration on the shakers at 25.00°C. The use of the ultrasonic generator reduced the time needed for equilibration from 2 - 4 weeks (16) to an average of 3 days.

After exposure in the ultrasonic generator, the salt-solvent mixtures were placed in water-jacketed shaker flasks. Water from a 25.00°C constant temperature bath was circulated through the shaker flasks. The bath water temperature was kept constant at 25.00 $\pm$ 0.02°C with the aid of a Yellow Springs Instrument Company model 72 proportional temperature controller. The water temperature was checked periodically with an NBS $\pm$ 0.01°C certified thermometer. Solutions were considered saturated when successive analyses several days apart differed by no more than 0.6 % which is the precision of the spectrophotometric analysis employed for picrates and tetraphenylborates.

Solutions of picrates and tetraphenylborates were analyzed spectrophotometrically on a Cary model 14 recording spectrophotometer. An aliquot of the solution was removed from the shaker flask, diluted to the proper concentration, and a spectrum recorded.

All dilutions were made using solvent equilibrated to 25°C in a constant temperature bath. Spectra were taken immediately after preparation of the solutions to minimize temperature changes. Molar absorptivities of picrates and tetraphenylborates throughout the ethanol--water solvent system were available from the data of Dill and Popovych (16). These are given in Table 11. The absorptivities were found to be independent of cation (11, 19). Molar absorptivity of Pi^- ion in water was re-determined with $Ph_4P\,Pi$ and found to have the same value as Dill and Popovych report. Molar absorptivities of the picrate maximum at 369nm in acetonitrile was determined on solutions of KPi, $Ph_4As\,Pi$, and $Ph_4P\,Pi$ with resulting values of $1.69_5 \times 10^4$, $1.69_6 \times 10^4$, and $1.68_9 \times 10^4$, respectively. An average value of 1.693×10^4 was used for molar absorptivity of Pi^- in acetonitrile. Similarly, using solutions of $RbBPh_4$ and $CsBPh_4$ in acetonitrile, molar absorptivities of 3203 and 2082 were obtained for the BPh_4^- peaks at 266nm and 274nm, respectively, reproducible to about 2 - 3 ppt. Beer's law was obeyed throughout.

It was found that when a large excess of solid was present, equilibration was complete in a shorter period of time. All solutions were deaerated with helium gas that was first bubbled through a gas-saturating tower filled with the given pure solvent.

Table 11. Molar Absorptivity of Picrate and Tetraphenylborate Ions in Ethanol--Water Solvents (16), Methanol (19), and Acetonitrile at 25°C.

wt.-% ethanol	Picrate $\epsilon \times 10^{-4}$ at 355nm	Tetraphenylborate $\epsilon \times 10^{-3}$ 266nm	274nm
0.0	1.43	3.23	1.99
10.0	1.43	3.21	2.02
20.0	1.45	3.19	2.05
30.0	1.48	3.18	2.06
40.0	1.51	3.16	2.08
50.0	1.54	3.15	2.08
60.0	1.55	3.13	2.09
70.0	1.56	3.11	2.09
80.0	1.57	3.08	2.09
90.0	1.58	3.03	2.10
100.0	1.60	2.97	2.10
CH_3OH	1.56	3.00	2.12
CH_3CN	1.69	3.20	2.08

Samples of solution were carefully withdrawn from the shaker flasks in such a manner as to exclude all solid particles from the sample. If it was impossible to withdraw a clear sample free from even minute particles, the solutions were filtered through a well-washed ($\sim$ 50ml of solvent) 25mm Millipore filter with a pore size of 2 microns. It was found that at least five millileters of solvent had to be passed through the 2.5cm filters to clear them of all loose material. In the case of acetonitrile solutions, special filters were available that are inert in this solvent.

Aqueous thallium chloride solutions were analyzed using the method of Merritt, Hershenson, and Rogers (134). A known volume of TlCl colution was placed in a 100-ml. volumetric flask containing 50-ml of concentrated hydrochloric acid. The solution was diulted to 100ml with water. A spectrum of the $TlCl_6^{-5}$ complex ($\lambda_{max} = 245nm$) was then recorded on a Cary 14 recording spectrophotometer. The reference solution consisted of 50ml of concentrated HCl diluted to 100ml with water. The absorbance of the complex at 245nm was used to calculate the concentration of Tl^+ in the original solution. Molar absorptivities were determined using prepared TlCl solutions of known concentration. This method is suitable for determining Tl^+ concentrations on the order of $10^{-6}M$.

Nonaqueous TlCl solutions were analyzed by the same method as the aqueous solutions. The volume of nonaqueous solvent in each solution was adjusted so that both the standard (known) and unknown solutions contained the same solvent composition. Reference solutions for the nonaqueous analysis contained that specific solvent composition used in the particular analysis.

Solubility studies of the neutral compounds.

Ph_4C, Ph_4Si, Ph_4Ge.

Solutions of Ph_4C, Ph_4Si, and Ph_4Ge were particularly sensitive to decomposition. In order to determine their solubilities, special precautions had to be taken. All the neutral compounds had low solubilities ($\sim 10^{-5}$M) in solvents containing more than 30 wt.-% water which madi it quite difficult to determine their molar absorptivities.

Solubilities of Ph_4C, Ph_4Si, and Ph_4Ge were determined the same way as solubilities of electrolytes except for two additional precautions. First, light was excluded from all solutions by wrapping the shaker flasks with aluminum foil. Second, the compound-solvent mixtures were not exposed to ultrasonic dispersion due to the tendency of the solutions to decompose. Saturation was generally acheived in 6 - 10 days. Every 3 - 4 days, portions of the solutions were withdrawn, filtered through well-washed 0.2 micron Millipore filters if necessary, and their uv spectra recorded. The suspensions were repeatedly deaerated following each withdrawal. A solution was considered saturated when two successive analyses at 3 - 4 day intervals indicated no change in concentration. If changes in the peak-height ratios were detected in the uv spectra,

indicating possible decomposition, the sample was discarded. Eight replicate solubility determinations were performed for each solute-solvent combination.

Ultraviolet spectra of Ph_4C, Ph_4Si, and Ph_4Ge are benzene-like exhibiting peaks (e.g. in 100 % ethanol) at 272nm, 262n, and 255nm (Ph_4C), 272nm, 265nm, 261nm, 254nm (Ph_4Si), 269nm, 265nm, 263nm, 259nm, 253nm, and 247nm (Ph_4Ge). Molar absorptivities for each compound were determined at each wavelength. Separate absorptivity determinations were performed at least three times for each compound-solvent combination and usually, they were performed five times. On the average, these absorptivities were reproducible to about $\pm$1.5 %. Absorptivities were determined in ethanol, ethanol--water mixtures, methanol, and acetonitrile. In ethanol--water solvents containing less than 80 wt.-% ethanol, such minute quantities of solid had to be used ($\sim$ 10 - 15 mg/2 liters) that the absorptivities were considered questionable. As a result, the average values of absorptivity in 100 % and 93 % ethanol were employed in the calculations for the entire ethanol--water system. Molar absorptivities of Ph_4C, Ph_4Si, and Ph_4Ge in ethanol, ethanol--water solvents, methanol, and acetonitrile appear in Tables 12 - 14.

Table 12. Molar Absorptivities of Tetraphenylmethane, Ph_4C, in Ethanol--Water Solvents, Methanol, and Acetonitrile at 25°C.

wt.-% ethanol in water	absorptivity x 10^{-3} 272nm	262nm	255nm
100.0	1.01	1.64	1.80
93.0	0.999	1.62	1.80
80.4	0.936	1.50	1.67
CH_3OH	0.897	1.35	1.36
CH_3CN	0.894	1.46	----

Table 13. Molar Absorptivities of Tetraphenylsilane, Ph_4Si, in Ethanol--Water Solvents, Methanol, and Acetonitrile at 25°C.

wt.-% ethanol in water	absorptivity $\times 10^{-3}$			
	272nm	265nm	261nm	254nm
100.0	1.05	1.34	1.37	1.01
92.6	1.06	1.35	1.37	1.02
80.4	1.02	1.29	1.34	0.988
CH_3OH	0.986	1.26	1.29	0.944
CH_3CN	1.06	1.37	1.39	1.03

Table 14. Molar Absorptivities of Tetraphenylgermane, Ph_4Ge, in Ethanol--Water Solvents, Methanol, and Acetonitrile at 25°C.

wt.-% ethanol in water	absorptivity x 10^{-3}					
	269nm	265nm	263nm	259nm	253nm	247nm
100.0	0.624	1.00	0.891	1.23	0.927	0.593
93.0	0.616	1.01	0.890	1.24	0.927	0.576
80.4	0.594	0.968	0.865	1.20	0.907	0.574
CH_3OH	0.610	0.993	0.888	1.23	0.925	0.592
CH_3CN	0.670	1.04	0.970	1.29	0.991	-----

Ferrocene.

The solubility of ferrocene was also determined in the same manner as that of the electrolytes. The small value of ϵ ($\sim$ 100) coupled with the low solubility in water-rich solvents ($\sim 10^{-5}$M) made it necessary to use a special slidewire on the Cary 14 spectrophotometer that had a full-scale deflection of 0.1 absorbance units. Molar absorptivities were determined from 40 to 100 wt.-% ethanol. In ethanol, ferrocene has two broad absorbance bands centering on 400nm and 325nm, respectively. As the water content of the solvent increases, the absorbance band at 325nm flattens out and eventually (at $\sim$ 20 % ethanol) becomes indistinguishable from the surrounding flat part of the spectrum. Molar absorptivities of ferrocene in ethanol and ethanol--water solvents are reported in Table 15. The absorptivities in solvents containing less than 40 wt.-% ethanol were extrapolated graphically from a large-scale plot of absorptivity versus wt.-% ethanol.

Table 15. Molar Absorptivities of Ferrocene in Ethanol--Water Solvents at 25°C.

wt.-% ethanol in water	absorptivity 440nm	325nm
100.0	90.9	50.3
92.6	91.0	50.9
80.4	91.7	50.5
70.5	91.7	50.4
60.7	91.9	50.5
51.2	92.2	50.8
38.9	93.0	51.9
30.0*	93.7	----
20.0*	94.4	----
10.0*	95.2	----
0.0*	96.0	----

* Determined by extrapolation on a large-scale plot of ϵ_{440nm} versus wt.-% ethanol.

Electrolytic conductance studies.

Conductance measurements were performed using a Wayne-Kerr model B-221 Universal Bridge and a conductance cell with bright platinum electrodes having a cell constant of 0.00993323 cm^{-1}. The Wayne-Kerr bridge measures conductance directly and is accurate to 0.1 %.

All solutions were prepared gravimetrically, correcting to weights in vacuo. The molarity of each solution was calculated from the weight of stock solution used and the weight of the final solution. Volumes of solutions were determined using the density of the pure solvent.

The conductance cell used was of the pipet type. It was sealed at the bottom by a water-tight ground glass cap. A short piece of rubber tubing was connected to the top of the cell to facilitate closing (with a pinchcock clamp) and filling (with a rubber bulb). During measurements, the cell was immersed in a 25.00 $\pm$ 0.01°C water bath. The absolute temperature of the bath was determined to $\pm$ 0.01°C with a National Bureau of Standards certified thermometer and controlled by a Yellow Springs Instrument Company model 72 proportional temperature controller. The same thermometer was used to check temperatures during solubility and activity coefficient determinations.

The stirrer in the constant temperature bath was of the variable speed type. The stirring speed had no effect on the measured conductance of the solutions.

Before a conductance run, the cell was rinsed a minimum of twenty times with pure solvent and allowed to stand overnight filled with the pure solvent. All conductance runs were preformed in a continuous time period (usually 12 hours) to minimize effects of decomposition of Ph_4P Pi or Ph_4As Pi (none was observed) and effects of change in conductance due to absorption of atmospheric CO_2. All precautions were taken to expose the solutions as little as possible to air. The conductance of the least concentrated solutions was determined first to minimize effects of desorption of salt from the electrodes. The electrodes were equilibrated with two or three fresh portions of solution. The final value for conductance was adopted when successive readings taken at fifteen minute intervals agreed to about 0.05 %.

Tables 16 - 18 list conductances and concentrations of Ph_4P Pi, Ph_4As Pi, and TlCl in those ethanol--water solvents in which association is appreciable at 25°C. The $\Delta\Lambda$ column lists differences between measured equivalent conductances and equivalent conductances calculated from the Shedlovsky equation (Equation 155).

To determine the cell constant, conductances of

accurately known solutions of KPi in spectroquality methanol were compared with the data of Coplan and Fuoss (129). A cell constant of 0.0099332 cm^{-1} was determined based on the 0.01 demal KCl standard of Jones and Bradshaw (138).

To determine the precision of the conductance experiments, the Λ_o of Ph_4P Pi in 93.4 wt.-% ethanol was determined two times using ten solutions each time. Values of $\Lambda_o Ph_4P$ Pi from these two determinations were within one ppt of each other.

Table 16. Conductances of Ph_4P Pi in Ethanol--Water Solvents at 25°C.

10^4C	Λ	$\Delta\Lambda$	10^4C	Λ	$\Delta\Lambda$
100 wt.-% ethanol			82.5 wt.-% ethanol		
$k_o = 8.4 \times 10^{-8}$ mho/cm			$k_o = 44.6 \times 10^{-8}$ mho/cm		
5.4028	41.95	-0.02	4.6938	31.16	+0.01
7.2791	41.07	-0.01	6.2320	30.769	-0.006
9.9467	40.04	+0.03	8.6242	30.26	-0.01
12.651	39.14	+0.03	11.037	29.830	-0.007
15.566	38.25	-0.01	13.258	29.484	+0.009
18.777	37.43	-0.02	15.940	29.085	+0.004
93.4 wt.-% ethanol			72.3 wt.-% ethanol		
$k_o = 4.0 \times 10^{-8}$ mho/cm			$k_o = 27.5 \times 10^{-8}$ mho/cm		
13.927	34.032	-0.008	4.2852	27.457	-0.003
15.751	33.652	-0.003	5.9259	27.180	+0.007
18.376	33.153	+0.006	7.5240	26.90	-0.03
21.022	32.691	+0.008	9.1755	26.75	+0.05
24.307	32.161	0.000	11.024	26.44	-0.02
27.500	31.693	-0.008			

Table 17. Conductances of Ph_4As Pi in Ethanol--Water Solvents at 25°C.

10^4C	Λ	$\Delta\Lambda$
100 wt.-% ethanol		
$k_o = 10.9 \times 10^{-8}$ mho/cm		
1.7095	41.95	-0.02
3.5510	40.731	-0.005
4.8798	40.031	+0.001
6.5954	39.247	-0.005
8.4456	38.56	+0.04
10.337	37.89	+0.01
12.014	37.363	+0.004
13.613	36.901	-0.007
15.486	36.427	+0.007
17.554	35.91	-0.03
93.0 wt.-% ethanol		
$k^o = 21.9 \times 10^{-8}$ mho/cm		
3.8406	36.600	+0.002
5.4203	36.02	+0.03
6.8059	35.48	-0.05
8.3362	35.075	+0.002
9.9778	34.65	+0.02

10^4C	Λ	$\Delta\Lambda$
80.9 wt.-% ethanol		
$k_o = 8.9 \times 10^{-8}$ mho/cm		
9.9795	29.22	-0.01
12.026	28.91	+0.02
14.948	28.468	-0.005
18.080	28.073	+0.007
20.317	27.795	-0.006
68.8 wt.-% ethanol		
$k_o = 6.4 \times 10^{-8}$ mho/cm		
7.5055	26.35	+0.04
9.4022	26.106	-0.005
10.995	25.94	-0.02
13.079	25.74	-0.03
14.802	25.62	-0.02
16.904	25.47	-0.01
19.058	25.37	+0.05

Table. 18. Conductances of TlCl in Ethanol--Water Solvents at 25°C.

10^5C	Λ	$\Delta\Lambda$
100 wt.-% ethanol		
$k_o = 1.01 \times 10^{-7}$ mho/cm		
0.685	52.33	-0.08
1.007	52.17	+0.05
1.269	52.0	+0.1
1.820	51.4	-0.1
2.274	51.05	-0.09
2.575	51.0	+0.1
2.853	50.71	-0.02
92.0 wt.-% ethanol		
$k_o = 1.24 \times 10^{-7}$ mho/cm		
2.631	52.33	+0.06
3.644	51.87	+0.06
4.593	51.3	-0.1
5.343	51.0	-0.1
6.122	50.84	+0.08
7.144	50.36	-0.01
7.959	50.16	+0.09
8.891	49.72	-0.03
10.06	49.350	+0.001

10^4C	Λ	$\Delta\Lambda$
80.5 wt.-% ethanol		
$k_o = 8.34 \times 10^{-7}$ mho/cm		
0.2203	48.0	-0.2
0.5812	47.7	+0.1
0.8460	47.25	+0.07
1.195	46.79	+0.07
1.567	46.29	+0.01
1.832	45.96	-0.01
2.144	45.70	+0.06
2.448	45.31	-0.01
2.733	45.047	-0.000
3.008	44.73	-0.06
3.475	44.35	-0.02
70.2 wt.-% ethanol		
$k_o = 1.28 \times 10^{-7}$ mho/cm		
0.6567	49.072	+0.001
1.630	48.32	+0.04
2.307	47.81	-0.01
2.805	47.499	-0.000
3.691	46.96	-0.02
4.233	46.66	-0.02
4.974	46.26	-0.04
5.801	46.0	+0.1
6.646	45.4	-0.1
7.342	45.1	-0.1
8.193	44.9	+0.1
61.2 wt.-% ethanol		
$k_o = 1.87 \times 10^{-7}$ mho/cm		
1.527	51.033	-0.004
2.397	50.53	-0.07
3.684	50.02	-0.01
5.154	49.48	+0.02
6.444	49.97	-0.02
7.665	48.6	+0.06
8.783	48.28	+0.05

Table 18. (Continued)

10^4C	Λ	$\Delta\Lambda$
61.2 wt.-% ethanol (continued)		
10.29	47.84	+0.05
11.69	47.42	+0.02
12.99	47.10	+0.05
14.51	46.5	-0.1
51.2 wt.-% ethanol		
$k_o = 6.02 \times 10^{-7}$ mho/cm		
1.448	54.6	-0.1
2.004	54.50	-0.04
3.641	54.07	+0.03
4.922	53.71	+0.02
6.512	53.5	+0.2
8.143	52.95	+0.01
9.529	52.72	+0.08
11.61	52.27	+0.03
13.39	51.89	-0.01
14.88	51.5	-0.1
16.79	51.30	-0.02
39.2 wt.-% ethanol		
$k_o = 8.64 \times 10^{-7}$ mho/cm		
6.690	60.44	+0.06
8.474	60.05	-0.03
10.50	59.75	+0.01
12.51	59.40	-0.04
14.30	59.12	-0.05
17.10	58.82	+0.03
18.67	58.584	+0.003
21.64	58.23	+0.02

10^4C	Λ	$\Delta\Lambda$
30.2 wt.-% ethanol		
$k_o = 3.65 \times 10^{-7}$ mho/cm		
5.914	69.38	-0.03
8.851	68.79	-0.04
11.72	68.35	+0.02
14.64	68.0	+0.1
17.69	67.35	-0.04
20.83	66.93	-0.01
23.19	66.67	+0.05
27.01	66.131	+0.004
29.94	65.72	-0.05
20.7 wt.-% ethanol		
$k_o = 5.0 \times 10^{-7}$ mho/cm		
2.498	85.37	-0.03
6.946	84.43	+0.04
11.59	83.48	-0.07
13.81	83.13	-0.06
16.17	82.9_6	+0.1
19.37	82.5_2	+0.2
21.27	81.9_5	-0.2
23.64	81.76	-0.03
9.9 wt.-% ethanol		
$k_o = 1.62 \times 10^{-6}$ mho/cm		
2.793	115.1	-0.2
5.560	114.2	-0.2
8.727	113.58	+0.08
12.33	112.7	+0.1
16.78	111.66	+0.03

Table 18. (Continued)

$10^4 C$	Λ	$\Delta\Lambda$
9.9 wt.-% ethanol (continued)		
21.22	111.1	+0.3
29.82	109.17	+0.01
35.10	108.28	+0.01
37.51	107.8	-0.1
42.58	107.04	-0.08
0.0 wt.-% ethanol		
$k_o = 1.34 \times 10^{-6}$ mho/cm		
8.559	153.6	-0.1
12.91	152.0	-0.1
16.78	150.80	-0.05
21.62	149.6	+0.3
26.28	148.1	+0.1
30.45	146.85	-0.03
35.23	145.7	+0.1
38.94	144.6	-0.1
44.06	143.4	-0.1

Determination of activity coefficients in ethanol--water solvents.

Activity coefficients were determined experimentally for Ph_4P Pi and Ph_4As Pi throughout the entire ethanol--water solvent system at intervals of approximately 10 wt.-% ethanol by studying the variation in solubility of these salts with varying ionic strength. Ionic strengths were varied with LiCl. Stock solutions of LiCl were prepared gravimetrically and then diluted to proper concentration volumetrically. All solutions were equilibrated at 25°C before final dilution. A large excess of solid salt was mixed with the LiCl solutions and the solubilities determined. Ten solutions of varying ionic strengths were prepared for each electrolyte-solvent mixture.

The apparatus used for determining activity coefficients is the same as the one used for determining solubilities.

Differential thermal analysis.

The purified solids $KBPh_4$, $RbBPh_4$, $CsBPh_4$, TAB BPh_4, Ph_4P Pi, Ph_4As Pi, KPi, Ph_4C, Ph_4Si, Ph_4Ge, and TlCl were individually equilibrated with water, methanol, acetonitrile, and 50 wt.-% ethanol (with the exception of Ph_4C, Ph_4Si, and Ph_4Ge in water) under identical conditions as used for their solubility determinations. The suspensions were filtered and the solids, dried by suction in air. The wetted samples were analyzed in air in a Du Pont 900 Differential Thermal Analyzer. Glass beads were used as a reference material. The thermocouple reference junctions were placed in an ice--water bath. Thermograms were obtained over the range of 20 - 240°C at the most sensitive ΔT setting of 0.2°C/inch. Temperature was varied at the rate of 20°C/minute.

Experimental results and discussion.

Solubility of electrolytes.

Ethanol--water solvents.

The solubilities of Ph_4P Pi, Ph_4As Pi, and TlCl in ethanol--water solvents are reported here for the first time. Experimental values of solubilities of these compounds are given in Tables 19 - 21.

The solubilities of Ph_4P Pi and Ph_4As Pi vary in an almost identical manner throughout the range of ethanol--water solvents (Figure 2). Both compounds have low solubilities in water and reach a maximum solubility in $\sim$ 80 wt.-% ethanol. The solubility of TlCl decreases steadily from water to 100 % ethanol.

The solubility of KPi in 10.2 wt.-% ethanol was determined to be 1.78×10^{-2} M. Solubilities of $RbBPh_4$ and $CsBPh_4$ in water were determined to be 5.42×10^{-5} M ($\pm$ 2 %) and 4.01×10^{-5} M ($\pm$ 4 %), respectively. Pflaum and Howick (143) have previously determined the solubility of $RbBPh_4$ and $CsBPh_4$ in water to be 2.33×10^{-5}, and 2.79×10^{-5} M, respectively. Solubilities of $KBPh_4$, TAB Pi, and KPi which were required for the calculation of medium effects for the reference electrolytes were available in the literature (139).

Table 19. Solubilities of Ph_4P Pi in Ethanol--Water Solvents. 25°C, Molar Scale

wt.-% ethanol	Solubility M x 10^5
0.0	4.51
10.0	7.62
19.0	16.0
31.2	54.5
39.3	118.
50.7	242.
61.0	399.
70.6	511.
80.8	572.
93.2	470.
100.0	344.

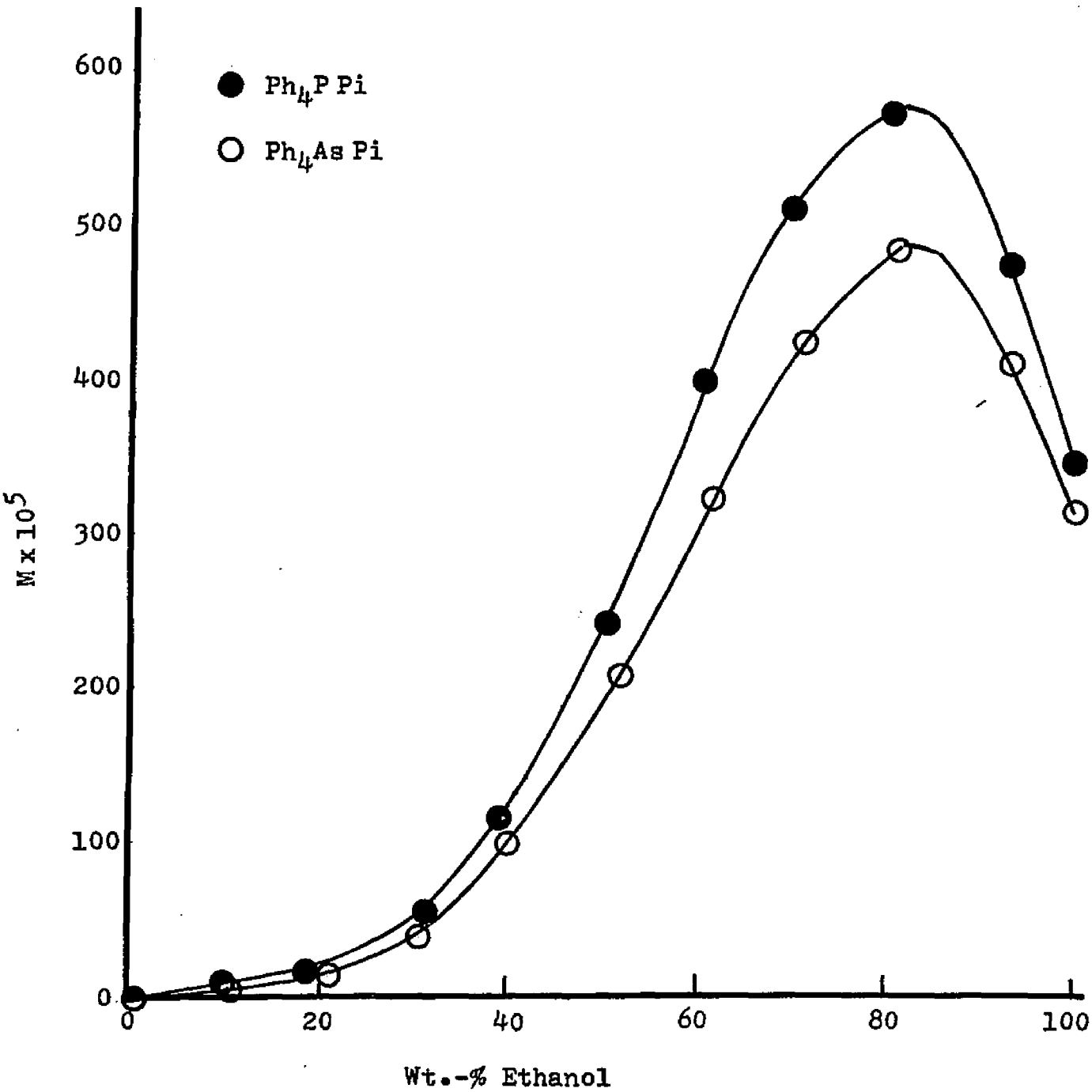
Table 20. Solubilities of Ph_4As Pi in Ethanol--Water Solvents. 25°C, Molar Scale.

wt.-% ethanol	Solubility M x 10^5
0.0	3.49
10.2	5.90
20.4	13.8
30.3	39.8
39.7	98.5
50.9	208.
60.9	321.
70.7	423.
80.7	484.
93.3	410.
100.0	315.

Table 21. Solubilities of TlCl in Ethanol--Water Solvents. 25°C, Molar Scale.

wt.-% ethanol	Solubility M x 10^5
0.0	1602.
10.1	1123.
20.7	769.
30.3	546.
39.2	388.
51.2	231.
71.0	73.1
80.5	36.0
90.6	11.6
100.0	3.45

Figure 2. Solubilities of Ph_4P Pi and Ph_4As Pi in Ethanol--Water Solvents. 25°C, Molar Scale.



Methanol.

Solubilities of Ph_4P Pi and Ph_4As Pi in methanol have been determined to be $1.41_6 \times 10^{-2}$ M and $1.34_1 \times 10^{-2}$ M, respectively, and are reported here for the first time. Solubilities of $KBPh_4$ and TAB Pi in methanol, which were used in calculating medium effects for the reference electrolytes were available from the data of Popovych and Friedman (19). Pavloupoulos and Strehlow (144) have given a complete listing of the solubility of alkali halides in methanol and Kolthoff and Chantooni (31) have compiled lists of solubility products of many compounds in methanol, water, acetonitrile, N,N-dimethylformamide and dimethylsulfoxide.

Acetonitrile.

The solubilities of Ph_4P Pi, Ph_4As Pi, KPi, $KBPh_4$, $RbBPh_4$ and $CsBPh_4$ were determined in acetonitrile and are reported in Table 22. Solubilities of various other compounds in acetonitrile were available from the data of Pavloupoulos and Strehlow (144) and from a compilation by Kolthoff and Chantooni (31). The solubility of TAB BPh_4 in acetonitrile was determined to be 0.5707 molal at 25°C. Unfortunately, its application as a reference electrolyte in that solvent is impractical because calculated activity coefficients would be unreliable at that concentration.

Table 22. Solubilities of Electrolytes in Acetonitrile. 25°C, Molar Scale.

Electrolyte	Solubility $M \times 10^2$
$Ph_4As\ Pi$	7.99
$Ph_4P\ Pi$	8.38
KPi	1.05
$KBPh_4$	5.33
$RbBPh_4$	1.70
$CsBPh_4$	1.68

Solubility of neutral compounds.

Solubilities of Ph_4C, Ph_4Si, and Ph_4Ge were determined in ethanol--water mixtures at intervals of 10 wt.-% ethanol from 60 % to 100 %, in methanol, and in acetonitrile. These solubilities are reported for the first time in Tables 23 - 25. Each reported solubility is the average of eight determinations. The molar solubility, M, molal solubility, m, and percent average deviation are reported in Tables 23 - 25. The solubilities of all three compounds in ethanol--water solvents decrease as the percent ethanol decreases. All three are slightly less soluble in pure methanol than in pure ethanol. The solubilities are greater in acetonitrile than in any of the other solvents studied.

Solubilities of ferrocene have been determined throughout the entire range of ethanol--water solvents at intervals of ~ 10 wt.-% ethanol. Molar solubilities of ferrocene and the percent average deviation of these solubilities are reported in Table 26. The reported solubilities are the average of four replicate determinations. The solubility of ferrocene decreases continually from pure ethanol to pure water. The reported solubility of ferrocent in water is 5.38×10^{-5}M. Other investigators have reported 1.7×10^{-5}M (97), 2×10^{-5}M (67), and 4.58×10^{-5}M (90).

Table 23. Solubilities of Ph_4C in Ethanol--Water Solvents, Methanol, and Acetonitrile. 25°C.

wt.-% ethanol	M x 10^4	m x 10^4	% average deviation
100.0	2.46	3.14	11.4
93.3	1.61	2.00	6.2
80.5	0.580	0.692	5.2
70.0	0.283	0.328	6.0
60.4	0.112	0.126	7.3
CH_3OH	1.73	2.20	9.0
CH_3CN	6.17	7.94	4.5

Table 24. Solubilities of Ph_4Si in Ethanol--Water Solvents, Methanol, and Acetonitrile. 25°C.

wt.-% ethanol	$M \times 10^4$	$m \times 10^4$	% average deviation
100.0	6.27	7.99	1.8
92.6	3.83	4.75	3.5
80.4	1.40	1.67	4.6
70.5	0.748	0.868	7.2
62.0	0.399	0.452	6.3
CH_3OH	5.51	7.01	3.9
CH_3CN	12.6	16.2	1.30

Table 25. Solubilities of Ph_4Ge in Ethanol--Water Solvents, Methanol, and Acetonitrile. 25°C.

wt.-% ethanol	M x 10^4	m x 10^4	% average deviation
100.0	5.47	6.95	3.0
92.8	3.08	3.83	4.3
80.4	1.31	1.55	3.2
70.0	0.793	0.919	9.1
60.4	0.263	0.297	7.7
CH_3OH	4.36	5.54	7.0
CH_3CN	10.4	13.4	0.99

Table 26. Solubilities of Ferrocene in Ethanol--Water Solvents. 25°C. Molar Scale.

wt.-% ethanol	M x 10^4	% average deviation
100.0	1024.	0.45
92.6	507.	0.31
80.4	377.	0.41
70.5	218.	0.88
60.7	118.	0.07
51.2	57.0	0.00
38.9	17.6	3.7
30.4	5.51	0.44
20.4	1.75	1.2
10.1	0.904	0.96
0.0	0.538	8.0

Electrolytic conductance studies.

The evaluation of ion-activity products of incompletely dissociated electrolytes requires knowledge of their degree of dissociation, α. Degrees of dissociation vary with concentration of salt, thus necessitating the evaluation of the association constants, K_A, in each solvent where association is appreciable. In this study, conductance measurements were made for the purpose of evaluating these association constants. Values of limiting equivalent conductance, Λ_o, and association constants were determined at 25°C for Ph_4P Pi, Ph_4As Pi, and TlCl over the range of ethanol--water solvents where dissociation was incomplete.

Conductance data was analyzed using the Shedlovsky modification of the Ostwald dilution law (135, 136). An IBM 360 computer and FORTRAN programs were used for calculations. Although some experts (137) use the symbol γ for the degree of dissociation, the symbol α will be used here.

Traditionally, the degree of dissociation, α, for a given concentration of pure electrolyte is defined as the ratio of the equivalent conductance of the solution, Λ, divided by the limiting equivalent conductance, Λ_o (137):

$$\alpha = \frac{\Lambda}{\Lambda_o} \qquad (146)$$

This definition implies that the contribution to the conductance of the solution from an ion is constant regardless of the total concentration and that any change in α is due to a change in the degree of dissociation. Equation 146 does not take into account non-ideal behavior of ions.

The mobility of an ion in an electric field is affected by the presence of other ions, and so, the equivalent conductance of a solution does not necessarily reflect the concentration of ions. Since the original formulation of α by Arrhenius, there have been many models proposed which seek to modify experimental values of the equivalent conductance so that the ratio (Λ/Λ_0) more correctly represents the degree of dissociation of the electrolyte (137). In this work, the Shedlovsky function (136), S(z) is used to correct values of Λ for non-ideal behavior of electrolytes. According to Shedlovsky, α assumes the form

$$\alpha = \frac{\Lambda}{\Lambda_0} S(z) \qquad (147)$$

where

$$S(z) = \left(\frac{z}{2} + \left[1 + \left(\frac{z}{2} \right)^2 \right]^{\frac{1}{2}} \right)^2 \qquad (148)$$

and z is defined by

$$z = S\Lambda_o^{-3/2}(C\Lambda)^{\frac{1}{2}} \qquad (149)$$

where S is the Onsager coefficient equal to $(a\Lambda_o + b)$ where a and b are functions of dielectric constant, D, temperature, T, and viscosity, η, and defined by :

$$a = \frac{0.8204 \times 10^6}{(DT)^{3/2}} \qquad b = \frac{82.501}{\eta (DT)^{\frac{1}{2}}} \qquad (150)$$

For this research, it was necessary to evaluate the association constant, K_A, for Ph_4P Pi, Ph_4As Pi, and TlCl in various ethanol--water solvents so that values of α at various concentrations could be computed. For a solution of an electrolyte, AB, dissociating into A^+ and B^- ions, the equilibrium concentrations of all species in the solution are given by :

$$[A^+] = [B^-] = C f_{\pm} \alpha \qquad (151)$$

$$[AB] = C f_{\pm}^2 (1 - \alpha) \qquad (152)$$

where $f_{\pm}$ is the mean ionic molar activity coefficient of the electrolyte. The mass action constant, K_D, for the dissociation of AB can be written as a function of α, C and $f_{\pm}$:

$$K_D = \frac{\alpha^2 C f_{\pm}^2}{1 - \alpha} \tag{153}$$

Using the Shedlovsky function S(z), and substituting $(\Lambda S(z)/\Lambda_o)$ for α in the above equation, we get :

$$K_D = \frac{([\Lambda S(z)]^2/\Lambda_o^2)\, C f_{\pm}^2}{1 - (\Lambda S(z)/\Lambda_o)} \tag{154}$$

Substituting $1/K_A$ for K_D and rearranging, we obtain the most useful form of Equation 154 for evaluating K_A and Λ_o from conductance data :

$$\frac{1}{\Lambda S(z)} = \frac{K_A \Lambda S(z)\, C f_{\pm}^2}{\Lambda_o^2} + \frac{1}{\Lambda_o} \tag{155}$$

This equation is called the Shedlovsky equation (137).

The Shedlovsky equation is linear. A plot of $1/\Lambda S(z)$ versus $(f_{\pm}^2 \Lambda S(z))$ will be linear with a slope of K_A/Λ_o^2 and an intercept of $1/\Lambda_o$. In this work, a FORTRAN computer program (see appendix B-1) and an IBM 360 computer were used to carry out the calculations involved in determining values of K_A and Λ_o for each electrolyte. A typical calculation is performed in this manner :

1) A graph of $(1/\Lambda)$ versus $C\Lambda$ is made by hand using experimental values of concentration and equivalent conductance.

2) The intercept of this graph, $(1/\Lambda_o)$, is obtained and Λ_o is calculated.

3) FORTRAN data cards are punched which include:
   a) experimental values of concentration and conductance
   b) the number of solutions
   c) values of temperature, dielectric constant (see appendix A-2), viscosity (appendix A-3), graphical estimates of Λ_o, the number of iterations to be performed in the calculation of Λ_o, and the tolerance which is the acceptable agreement between two successive determinations of Λ_o (0.0001).

4) The computer calculates activity coefficients for the electrolyte using the Debye-Huckel limiting law (20):

$$\log f_{\pm} = - \frac{1.8246 \times 10^6}{(DT)^{3/2}} \sqrt{I} \qquad (156)$$

   Initial values of concentration are used to evaluate the ionic strength.

5) The Shedlovsky function, S(z), is solved using the graphical estimate of Λ_o and experimental values of concentrations.

6) The Shedlovsky equation is solved, Λ_o and K_A are evaluated by a least-square computation and values of α are calculated for each solution.

7) Using values of αC for ionic strength, new values of $\log f_{\pm}$ are calculated and these new values are used to solve for Λ_o and K_A until successive determinations of Λ_o agree to within 0.0001.

8) Final values of Λ_o, standard deviation of Λ_o, K_A, standard deviation of K_A, K_D, and the Walden product are printed out along with individual values of concentration, , $(1/\Lambda S(z))$, $Cf_{\pm}^2 S(z)$, $f_{\pm}^2$, and α. Values

of $\Delta\Lambda$, the difference between the experimental equivalent conductance and the calculated equivalent conductance are also printed out.

Values of association constants, K_A, limiting equivalent conductances, Λ_o, standard deviations of these, and densities of ethanol--water solvents studied are reported in Tables 27 - 29 for Ph_4P Pi, Ph_4As Pi, and TlCl, respectively. The Shedlovsky equation (Eq. 155) was used for calculating K_A's and Λ_o's. Values of K_A in solvents of varying ethanol composition were interpolated from large-scale plots of $\log K_A$ versus 1/D where D is the dielectric constant of the solvent. For Ph_4P Pi and Ph_4As Pi, these plots are almost coincidental illustrating the similarity in behavior of these compounds. Below 70 wt.-% ethanol, Ph_4P Pi and Ph_4As Pi have no appreciable association and a plot of Λ versus $C^{\frac{1}{2}}$ will be linear indicating complete dissociation (145).

Once the association constant and activity coefficient were known for a particular electrolyte in a given solvent, it was possible to determine the degree of dissociation of solutions of that electrolyte via the equation

$$\alpha = \frac{-1 + (1 + 4K_A C f_{\pm}^2)^{\frac{1}{2}}}{2K_A C f_{\pm}^2} \qquad (157)$$

Table 27. Conductance Results for Ph_4P Pi. 25°C.

wt.-% ethanol	K_A	Λ_o	d_o
100.0	114.5 ± 1.0	46.95 ± 0.03	0.7851
93.4	76.4 ± 0.2	40.03 ± 0.01	0.8044
82.5	44.9 ± 0.7	33.32 ± 0.01	0.8324
72.3	27.6 ± 1.7	28.93 ± 0.03	0.8578

Table 28. Conductance Results for $Ph_4As\,Pi$. 25°C.

wt.-% ethanol	K_A	Λ_o	d_o
100.0	100.4 ± 1.2	44.38 ± 0.02	0.7851
93.0	70.7 ± 1.9	39.46 ± 0.03	0.8047
80.9	41.7 ± 0.5	32.33 ± 0.01	0.8367
68.8	11.6 ± 1.4	27.93 ± 0.03	0.8658

Table 29. Conductance Results for TlCl. 25°C.

wt.-% ethanol	K_A	Λ_o	d_o
100.0	1320 ± 147	53.27 ± 0.10	0.7851
92.0	819 ± 38	53.96 ± 0.08	0.8082
80.5	235 ± 70	48.84 ± 0.09	0.8377
70.2	116 ± 4	50.00 ± 0.08	0.8627
61.2	67.2 ± 2.6	52.28 ± 0.06	0.8855
51.2	32 ± 7	55.64 ± 0.09	0.9069
39.2	18.6 ± 0.8	62.34 ± 0.04	0.9328
30.2	18.6 ± 0.7	71.33 ± 0.06	0.9502
20.7	13 ± 1	86.56 ± 0.11	0.9652
9.9	15 ± 2	116.9 ± 0.2	0.9806
0.0	18.0 ± 0.6	158.7 ± 0.2	0.9971

Limiting ionic equivalent conductances, λ_o, of Ph_4P^+ and Ph_4As^+ are of great interest since these values can be used to calculate Stokes' radii for these ions. Values of λ_o for TAB^+ and Pi^- ions in ethanol and ethanol--water solvents are available from the data of Dill and Popovych (16). These values were calculated using the Copland and Fuoss assumption (146) that $\lambda_o TAB = \lambda_o BPh_4$. Once values of $\lambda_o TAB$ were known in the solvent, $\lambda_o Pi$ can be calculated:

$$\lambda_o Pi = \Lambda_o TAB\,Pi - \lambda_o TAB \qquad (158)$$

Values of $\Lambda_o TAB\ Pi$, $\lambda_o TAB$ and $\lambda_o Pi$ were reported in Reference 16 at even wt.-% ethanol and are given in Table 30 along with interpolated values of $\Lambda_o Ph_4P\,Pi$ and $\Lambda_o Ph_4As\ Pi$ in the same solvents from this study. $\lambda_o Ph_4P$ and $\lambda_o Ph_4As$ which are also given in Table 30 were calculated using these relationships:

$$\lambda_o Ph_4P = \Lambda_o Ph_4P\,Pi - \lambda_o Pi \qquad (159\text{-a})$$

$$\lambda Ph_4As = \Lambda_o Ph_4As\,Pi - \lambda_o Pi \qquad (159\text{-b})$$

The values of $\lambda_o Ph_4P$ and $\lambda_o Ph_4As$ are based on the Coplan-Fuoss assumption. The values for limiting ionic

Table 30. Equivalent Conductances of Electrolytes and Single Ions. 25°C.

wt.-% ethanol	Λ_oTAB Pi (16)	λ_oTAB$^+$ (16)	λ_oPi$^-$ (16)	Λ_oPh$_4$As Pi	Λ_oPh$_4$P Pi	λ_oPh$_4$As$^+$	λ_oPh$_4$P$^+$
100.0	45.70	19.79	25.91	44.38	46.95	18.47	21.04
90.0	37.3	16.0	21.3	37.5	37.7	16.2	16.4
80.0	31.8	13.7	18.1	31.9	32.1	13.8	14.0
70.0	28.1	11.6	16.5	28.2	28.2	11.7	11.7

equivalent conductance can be used to calculate Stokes' radii for the ions.

According to Stokes'law (147), a spherical ion of radius r moving through a homogeneous medium of viscosity η under the influence of force F, will maintain a velocity v given by

$$v = \frac{F}{6\pi\eta r} \qquad (160)$$

If the definition of limiting equivalent ionic conductance, λ_o, is introduced, the following equation is obtained, where z is the ionic charge :

$$\lambda_o n = \frac{8.20\text{x}10^{-9}|z|}{r} \qquad (161)$$

Ionic conductances should therefore be inversely proportional to the ionic radius. This however, is true only for large bulky ions because, Stokes'law was derived for ions or particles large in size compared with the solvent molecules. Rearranging Equation 161, we get an expression for calculating the Stokes radius of an ion from its limiting equivalent ionic conductance and the viscosity of the medium :

$$r = \frac{8.20\text{x}10^{-9}|z|}{\lambda_o n} \qquad (162)$$

Stokes' radii for $TAB^+ = BPh_4^-$, Ph_4P^+, and Ph_4As^+ ions in ethanol and ethanol--water solvents calculated via Equation 162 are given in Table 31. The fact that all these reference ions have identical or nearly identical Stokes radii is gratifying evidence for the equality of their crystal radii, and negligible specific interaction with the solvents--which are requirements for the counterions of a reference electrolyte.

Conductance measurements were performed on solutions of Ph_4P Cl in 100 % ethanol. A plot of Λ versus $C^{\frac{1}{2}}$ was linear indicating complete dissociation (145). On this basis, Ph_4P Cl and Ph_4As Cl were assumed to be completely dissociated in all ethanol--water solvents.

All electrolytes studied were assumed to be completely dissociated in acetonitrile on the basis of reported complete dissociation of alkali metal tetraphenylborates and perchlorates (148) and several tetraalkylammonium tetraphenylborates and perchlorates (122) in that solvent.

In methanol, a value of 0.94 was adopted for the degree of dissociation of Ph_4P Pi and Ph_4As Pi assuming the same association constant ($\sim$ 10) as for tetraalkylammonium picrates (129, 149, 150) and using a value for activity coefficient calculated from the Debye-Huckel equation with ion-size parameters.

Table 31. Stokes Radii of the Reference Ions in Ethanol--Water Solvents. 25°C in Å.

wt.-% ethanol	$TAB^+ = BPh_4^-$	Ph_4As^+	Ph_4P^+
100.0	3.8	4.03	3.5
90.0	3.6	3.6	3.5
80.0	3.4	3.4	3.4
70.0	3.5	3.5	3.5

Activity coefficient studies.

Once the solubility and association constant are known for a solute in a given solvent, the activity coefficient of the solute must be determined so that ion-activity products can be calculated. In this research, activity coefficients were determined by the method of Bronsted and LaMer (123) which is based on the variation of solubility of an electrolyte with ionic strength.

Activity coefficients were determined for Ph_4P Pi and Ph_4As Pi throughout the entire ethanol--water solvent system at intervals of approximately 10 wt.-% ethanol. Solubilities, C, and association constants, K_A, which are required in the calculation of activity coefficients were not always available in the exact percentage composition of ethanol that activity coefficient determinations were made in. In such cases, values of C and K_A for the exact solvent required were interpolated from large scale plots of C versus wt.-% ethanol or $\log K_A$ versus 1/Dsolvent. Activity coefficients for KPi, $KBPh_4$, and TAB Pi throughout the range of ethanol--water solvents were recalculated from the data of Dill and Popovych (139) with the inclusion of some new data for KPi in water and 10.2 wt.-% ethanol and $KBPh_4$ in 90.6 wt.-% ethanol from this study. The activity coefficients of $RbBPh_4$ and $CsBPh_4$ in 100 % ethanol were

also determined.

The mean ionic activity, $a_{\pm}$, of a saturated solution of an electrolyte is defined by

$$a_{\pm} = C\alpha f_{\pm} \qquad (163)$$

where α is the degree of dissociation, C is the molar solubility, and $f_{\pm}$ is the mean ionic activity coefficient. The value of the activity coefficient is directly dependent on the ionic strength, I, of the solution as is shown by the Debye-Huckel limiting law:

$$\log f_{\pm} = -A I^{\frac{1}{2}} \qquad (164)$$

In Equation 164, A is a parameter dependent on temperature and dielectric constant of the solvent, and I is the ionic strength of the solution. As the ionic strength increases, the numerical value of the activity coefficient decreases.

The activity of two saturated solutions of an electrolyte, one in pure solvent and the other in a solution of inert solvent salt is identical provided the solid phases in contact with both solutions are chemically the same. In pure solvent, the activity, $a_{\pm,o}$, can be written as:

$$a_{\pm,o} = \alpha_o C_o f_{\pm,o} \qquad (165)$$

where the subscript "o" refers to pure solvent. In the same solvent containing added inert solvent salt, the activity, $a_{\pm,I}$, can be written as:

$$a_{\pm,I} = \alpha_I C_I f_{\pm,I} \qquad (166)$$

where the subscript "I" refers to the added inert solvent salt. Although $f_{\pm,I}$ will be numerically smaller than $f_{\pm,o}$, C_I will be larger than C_o to preserve the equality of $a_{\pm,o}$ and $a_{\pm,I}$. Equations 165 and 166 can be equated and rearranged to give

$$\log \frac{\alpha_I C_I}{\alpha_o C_o} = \log f_{\pm,o} - \log f_{\pm,I} \qquad (167)$$

Substituting for $\log f_{\pm,I}$ from Equation 164, an equation is arrived at that is operationally useful for determining activity coefficients experimentally:

$$\log \frac{\alpha_I C_I}{\alpha_o C_o} = \log f_{\pm,o} + A I^{\frac{1}{2}} \qquad (168)$$

This is a linear equation. The parameters α_o, α_I, C_o, C_I, and I are experimentally accessible. A can be

calculated from available data. A plot of log ($\alpha_I C_I / \alpha_o C_o$) versus $I^{\frac{1}{2}}$ should be a straight line with a slope equal to the Debye-Huckel A and an intercept equal to $\log f_{\pm,o}$.

In practice, it is observed that a plot of Equation 168 is often not linear especially in regions of high ionic strength. This non-linearity represents deviations from the Debye-Huckel limiting law. Because of these deviations, it is more suitable to use an extended form of the Debye-Huckel equation when substituting for $\log f_{\pm,I}$ in Eauation 167. In the extended Debye-Huckel equations, the activity coefficient can be expressed as a power series in $I^{\frac{1}{2}}$:

$$-\log f_{\pm,I} = A_1 I^{\frac{1}{2}} + A_2 I + A_3 I^{3/2} + \ldots . \qquad (169)$$

The first term on the right hand side of Equation 169 represents the Debye-Huckel limiting law. By combining Equations 167 and 169, we arrive at

$$\log \frac{\alpha_I C_I}{\alpha_o C_o} = \log f_{\pm,o} + A_1 I^{\frac{1}{2}} + A_2 I + A_3 I^{3/2} + \ldots \qquad (170)$$

Equation 170 is used in this research for evaluation of activity coefficients. It has previously been used for the formulation of activity coefficients in the

analysis of e.m.f. (72, 140) and solubility (139) data.

By applying Equation 170, $\log(\alpha_I C_I/\alpha_o C_o)$ and ionic strengths, I, must be evaluated from experimental values of K_A, C_o, and the concentration of added solvent salt. Lithium chloride was used as the inert solvent salt. A computer program (appendix B-2) was used to calculate numberical values of $\log(\alpha_I C_I/\alpha_o C_o)$ and I. the program will account for association between the ions of the electrolyte and the solvent salt when evaluating ionic strengths. For example, in the determination of the activity coefficients of Ph_4P Pi, the following four equilibria must be taken into account:

$$Ph_4P^+ + Pi^- = Ph_4P^+Pi^- \qquad (171\text{-a})$$

$$Ph_4P^+ + Cl^- = Ph_4P^+Cl^- \qquad (171\text{-b})$$

$$Li^+ + Pi^- = Li^+Pi^- \qquad (171\text{-c})$$

$$Li^+ + Cl^- = Li^+Cl^- \qquad (171\text{-d})$$

Association constants of LiCl are known throughout the range of ethanol--water solvents (16). Lithium picrate is completely dissociated in ethanol--water solvents (139) and in the present study, it was shown that Ph_4P Cl and Ph_4As Cl are also completely dissociated

in ethanol--water solvents. Where necessary, values of K_A for $KBPh_4$, KCl and KPi were also available (16) in ethanol--water solvents.

Once values for $\log (\alpha_I C_I/\alpha_o C_o)$ and I are known, the A-coefficients in Equation 170 can be evaluated with a standard polynomial curve fitting program (appendix B-3). Values for $\log f_{\pm,o}$ and the precision of $f_{\pm,o}$ are also obtained from the program. A-coefficients are evaluated for first order through fourth order polynomials. The polynomial that best represents Equation 170 is choosen on the basis of agreement between the coefficient A_1 computed from experimental data and the theoretical Debye-Huckel limiting law slope, A_{DH}. In the absence of experimental error, A_1 would be identical to A_{DH}. The range of precision in the above computation of $f_{\pm,o}$, was 0.3 - 4 %, a typical relative error being agout 1 %. For precise results, the concentration of LiCl has to be varied from $\sim$ 2 to 200 times C_o. Smaller variations in the concentration of LiCl result in small differences between C_o and C_I which drastically decreases the precision of the method. In cases where C_o is large, this method cannot be applied because the concentration of LiCl cannot be varied over a large enough range.

In cases where the solubility of the electrolyte in pure solvent is not available, an alternate method

for analysis can be used which gives the activity of the electrolyte in the pure solvent. Equation 170 can be rearranged to the form:

$$\log (\alpha_I C_I) = \log (\alpha_o C_o f_{\pm,o}) + A_1 I^{\frac{1}{2}} + A_2 I + A_3 I^{3/2} + \ldots \quad (172)$$

To apply Equation 172, values of α_I, C_I, and I are experimentally determined, the A-coefficients for the best fit polynomial are evaluated, and the intercept, $\log (\alpha_o C_o f_{\pm,o})$ is computed.

The activity coefficients of Ph_4P Pi, Ph_4As Pi, $KBPh_4$, TAB Pi, KPi, $RbBPh_4$, and $CsBPh_4$ are presented in this section. Activity coefficients of the above compounds were determined experimentally by the method of Bronsted and LaMer (123), in which solubilities are studied at varying ionic strengths. The data is fit to a polynomial equation mathematically identical to an extended form of the Debye-Huckel equation and the best least-square-fit parameters are selected.

Tables 32 - 37 show the results of activity coefficient calculations. The degree of the polynomial employed in a given curve fitting, which is identical with the number of A-coefficients listed, was chosen on the basis of agreement between the coefficient A_i computed from experimental data and the theoretical Debye-Huckel slope, A_{DH}. The solubilities, C_o, solubility products,

and activity coefficients, $f_{\pm,o}$, reported are on the molarity scale. Tables 34 - 36 represent data of Dill and Popovych (139) that have been recalculated with the inclusion of some extra data from this study. In instances where activity coefficients have not been reported, Equation 172 was used to evaluate activity directly.

In almost every instance, solubilities and association constants were not available in the exact solvent composition in which activity coefficient data was obtained. In these cases, values of C_o and K_A were interpolated for the proper solvent composition.

Activity coefficients of thallium chloride in ethanol--water solvents were calculated using an extended form of the Debye-Huckel equation with ion-size parameters (12):

$$-\log f_{\pm}^{2} = \frac{(3.6491\times10^{6})z_i(C\alpha)^{\frac{1}{2}}}{(DT)^{3/2}\ 1+50.2904(DT)^{-\frac{1}{2}}\mathring{a}\,(C\alpha)^{\frac{1}{2}}} \qquad (173)$$

where $\mathring{a}$ is the ion-size parameter, D, T, z_i, C, and α are dielectric constant, temperature, charge, molarity, and degree of dissociation, respectively. Kielland's value (151) of 5.5 $\mathring{A}$ for the ion-size parameter of TlCl was used. The degree of dissociation, α, was at first assigned a value of unity. After calculation

Table 32. Activity Coefficients, Degree of Dissociation, and Solubility Products of Ph_4P Pi in Ethanol--Water Solvents at 25°C.

wt.-% ethanol	C_o	α_o	$f_{\pm}'_o$	A_{DH}	LSF Coefficients A_1	A_2	A_3	A_4	K_{sp} $(C_o \alpha_o f_{\pm}'_o)$
100.0	3.44×10^{-3}	0.861	0.715	2.96	2.96	-4.90	0.540	5.54	4.47×10^{-6}
93.2	4.70×10^{-3}	0.875	0.722	2.56	2.52	-5.09	5.02	-1.73	8.79×10^{-6}
80.8	5.72×10^{-3}	0.899	0.762	1.93	1.91	-3.70	3.45	-1.22	1.53×10^{-5}
70.6	5.11×10^{-3}	0.931	0.832	1.53	1.32	-1.98	1.18	----	1.56×10^{-5}
61.0	3.99×10^{-3}	0.965	0.858	1.26	1.16	-1.97	1.34	----	1.09×10^{-5}
50.7	2.42×10^{-3}	1.000	0.922	1.04	1.02	-1.91	1.48	----	4.96×10^{-6}
39.3	1.18×10^{-3}	1.000	0.945	0.859	0.764	-1.21	0.863	----	1.25×10^{-6}
31.2	5.45×10^{-4}	1.000	0.963	0.756	0.748	-1.57	1.96	-0.977	2.76×10^{-7}
19.9	1.60×10^{-4}	1.000	0.978	0.646	0.553	-0.705	----	----	2.45×10^{-8}
10.0	7.62×10^{-5}	1.000	0.986	0.571	0.566	-1.14	0.937	----	5.65×10^{-9}
0.0	4.51×10^{-5}	1.000	0.992*	0.509	----	----	----	----	2.00×10^{-9}

* Calculated using the Debye-Huckel limiting law.

Table 33. Activity Coefficients, Degree of Dissociation, and Solubility Products of Ph_4As Pi in Ethanol--Water Solvents at 25°C.

wt.-% ethanol	C_o	α_o	$f_{\pm,o}$	A_{DH}	LSF Coefficients A_1	A_2	A_3	A_4	K_{sp} $(C_o \alpha_o f_{\pm,o})$
100.0	3.15×10^{-3}	0.880	0.716	2.96	3.10	-6.30	5.25	----	3.94×10^{-6}
93.3	4.10×10^{-3}	0.887	0.738	2.57	2.50	-4.80	3.65	----	7.20×10^{-6}
80.7	4.84×10^{-3}	0.908	0.774	1.92	1.90	-3.80	3.17	----	1.16×10^{-5}
70.7	4.23×10^{-3}	0.959	0.818	1.53	1.55	-3.31	3.07	----	1.10×10^{-5}
60.9	3.21×10^{-3}	0.994	0.849	1.26	1.49	-2.43	----	----	7.33×10^{-6}
50.9	2.08×10^{-3}	1.000	0.899	1.05	1.09	-2.67	2.92	----	3.49×10^{-6}
39.7	9.85×10^{-4}	1.000	0.949	0.864	0.782	-1.54	1.40	----	8.74×10^{-7}
30.3	3.98×10^{-4}	1.000	0.964	0.746	0.759	-1.03	-4.88	17.2	1.47×10^{-7}
20.4	1.38×10^{-4}	1.000	0.981	0.650	0.615	-1.35	1.58	----	1.82×10^{-8}
10.2	5.90×10^{-5}	1.000	0.989	0.584	0.570	-1.26	1.22	----	3.41×10^{-9}
0.0	3.49×10^{-5}	1.000	0.993*	0.509	----	----	----	----	1.20×10^{-9}

* Calculated using the Debye-Huckel limiting law.

Table 34. Activity Coefficients, Degree of Dissociation, and Solubility Products of TAB Pi in Ethanol--Water Solvents at 25°C.

wt.-% ethanol	C_o	α_o	$f_{\pm,o}$	A_{DH}	LSF Coefficients A_1	A_2	A_3	K_{sp} $(C_o \alpha_o f_{\pm,o})$
100.0	6.27×10^{-2}	0.810	0.329	2.96	2.79	-3.16	1.29	2.78×10^{-4}
86.4	----------	0.848	-----	2.20	2.15	-2.53	1.06	2.62×10^{-4}
67.3	1.60×10^{-2}	0.854	0.743	1.43	1.24	-1.34	0.523	1.03×10^{-4}
53.6	7.10×10^{-3}	0.923	0.876	1.10	0.702	-0.478	-----	3.29×10^{-5}
38.4	2.02×10^{-3}	0.976	0.945	0.848	0.539	-0.351	-----	3.47×10^{-6}

Table 35. Activity Coefficients, Degree of Dissociation, and Solubility Products of $KBPh_4$ in Ethanol--Water Solvents at 25°C.

wt.-% ethanol	C_o	α_o	$f_{\pm,o}$	A_{DH}	LSF Coefficients A_1	A_2	A_3	K_{sp} $(C_o \alpha_o f_{\pm,o})$
100.0	5.04×10^{-4}	0.949	0.849	2.96	3.90	-7.54	----	1.65×10^{-7}
90.6	----------	1.000	-----	2.43	2.40	-4.96	4.28	7.52×10^{-7}
78.1	2.35×10^{-3}	0.986	0.819	1.81	2.25	-3.47	----	3.60×10^{-6}
60.6	----------	0.998	-----	1.25	1.30	-3.11	2.52	7.71×10^{-6}
38.4	----------	1.000	-----	0.846	0.749	-8.20	----	1.57×10^{-6}

Table 36. Activity Coefficients, Degree of Dissociation, and Solubility Products of KPi in Ethanol--Water Solvents at 25°C.

wt.-% ethanol	C_o	α_o	$f_{\pm,o}$	A_{DH}	LSF Coefficients A_1	A_2	A_3	K_{sp} $(C_o \alpha_o f_{\pm,o})$
100.0	1.04×10^{-3}	0.857	0.806	2.96	3.06	0.872	-----	5.18×10^{-7}
92.3	2.51×10^{-3}	0.888	0.766	2.51	2.54	-2.50	-----	2.91×10^{-6}
84.8	----------	0.970	-----	2.11	1.11	-1.67	-----	1.24×10^{-5}
68.3	1.52×10^{-2}	0.985	0.776	1.46	1.06	-0.811	-----	1.35×10^{-4}
58.8	1.95×10^{-2}	1.000	0.723	1.21	1.25	-1.69	-----	1.99×10^{-4}
51.0	2.20×10^{-2}	1.000	0.807	1.05	0.681	-0.410	-----	3.15×10^{-4}
37.3	1.98×10^{-2}	1.000	0.813	0.832	0.753	-0.871	0.404	2.59×10^{-4}
20.6	1.59×10^{-2}	1.000	0.887	0.652	0.437	-0.167	-----	1.99×10^{-4}
10.2	1.78×10^{-2}	1.000	0.866	0.572	0.550	-0.509	-----	2.37×10^{-4}
0.0	2.33×10^{-2}	1.000	0.844	0.510	0.654	-1.26	0.930	3.87×10^{-4}

Table 37. Activity Coefficients, Degree of Dissociation, and Solubility Products of $RbBPh_4$ and $CsBPh_4$ in 100 % Ethanol at 25°C.

Electrolyte	α_o	$(C_o \alpha_o f_{\pm,o})$	A_{DH}	LSF Coefficients A_1	A_2	A_3	K_{sp}
$RbBPh_4$	1.000	1.25×10^{-4}	2.96	3.12	-8.44	12.3	1.56×10^{-8}
$CsBPh_4$	1.000	1.17×10^{-4}	2.96	3.00	-5.32	3.56	1.37×10^{-8}

of $f_{\pm}^2$, α was calculated using Equation 157. When a value for α was calculated, a new value of $f_{\pm}^2$ was determined using Equation 173, this was in turn used to calculate a new value for α. The whole process was repeated (usually 3 times) until successive values of $f_{\pm}^2$ and α agreed to within 0.1 %. The calculations were performed on a programmable electronic calculator (Wang Laboratories, Inc.).

In acetonitrile, activity coefficients were determined via the Debye-Huckel equation with ion-size parameters. For individual ions, the equation takes the form (76)

$$-\log f = \frac{1.64\, C^{\frac{1}{2}}}{1 + 0.485\, a\, C^{\frac{1}{2}}} \qquad (174)$$

where the ion-size parameters, a, were approximated by Stokes radii. Values of $a = 5$ Å were adopted for the tetraphenyl ions, $a = 3$ Å, for the alkali-metal and picrate ions, and $a = 2.5$ Å, for the halide ions (46, 122). Fortunately, $\log f$ is not a very sensitive function of a, changing by only a few hundredths per 1 Å for the solutions studied here. As noted before, complete dissociation was assumed for all electrolytes in acetonitrile.

In methanol, activity coefficients were calculated using the Debye-Huckel equation :

$$-\log f_{\pm}^{2} = \frac{3.803\,(C\alpha)^{\frac{1}{2}}}{1 + 0.5099\,a\,(C\alpha)^{\frac{1}{2}}} \qquad (175)$$

where a value of $a = 6.5$ was used (19) for PH_4P^+, Ph_4As^+, and Pi^- ions. A value of $\alpha = 0.94$ was adopted for Ph_4P Pi, and Ph_4As Pi (76), as discussed in section VII-C. For both compounds in methanol, $f_{\pm} = 0.48$. Listings of activity coefficients not reported in this section can be found in section VII-F.

Differential thermal analysis.

Various authors (26, 60) have raised objections to the solubility method for determining medium effects based on the possible formation of crystal solvates. As has been pointed out in section II-B-3, if crystal solvates are formed, the free energy of the saturated aqueous and nonaqueous solutions will not be equal. In such a case, various corrections could be employed (Equations 38, 39). However, it is most desirable to avoid the complications of crystal solvate formation by choosing to work with compounds that do not form solvates.

In this research, thermograms were taken of all compounds studied here whose medium effects were determined by the solubility method. A thermogram is a plot of ΔT versus T where ΔT is the difference in temperature between the compound being studied and an inert reference compound with a constant heat capacity over the range of temperatures studied. The sample and reference compound are heated at a predetermined constant rate. Thermocouples measure the difference in temperature between the two compounds as they are heated. Variations in temperature can indicate phase changes, water or solvent elimination, chemical reactions, polymerization, and a host of other things (141, 142).

The differential thermograms were recorded over

the temperature range 20 - 240°C for samples of $KBPh_4$, $RbBPh_4$, $CsBPh_4$, TAB BPh_4, Ph_4P Pi, Ph_4As Pi, KPi, TlCl, Ph_4C, Ph_4Si, and Ph_4Ge wetted with water (except for Ph_4C, Ph_4Si, Ph_4Ge), acetonitrile, methanol, ethanol, and 50 wt.-% ethanol in water. In all cases, the thermograms were horizontal straight lines indicating an absence of solvates in all these solvent-solute combinations.

On the basis of DTA data, Duval (142) has reported that $KBPh_4$, $RbBPh_4$, $CsBPh_4$, and KPi are stable to 265, 240, 210, and 220°C, respectively, and that these compounds do not form hydrates. Recently, Kolthoff and Chantooni (31) reported no solvate formation for $KBPh_4$, TlCl, Ph_4As Pi, TAB Pi, $RbBPh_4$, and $CsBPh_4$ in water, methanol, acetonitrile, dimethylformamide, and dimethylsulfoxide.

Thermodynamic medium effects of electrolytes and neutral compounds.

From this study.

Calculations.

Once solubilities, activity coefficients, and degrees of dissociation are known for an electrolyte in water and in various nonaqueous solvents, medium effects for that compound can be calculated using Equation 176:

$$\log {}_m\gamma_i = \log \frac{(a_i)_{sat}}{(a_i^*)_{sat}} = \frac{{}^wK_{sp}}{{}^sK_{sp}} \qquad (176)$$

where $(a_i)_{sat}$ and $(a_i^*)_{sat}$ are the thermodynamic ion-activity products in water and the nonaqueous solvent, respectively. Rearranging Equation 176 and substituting ion-activity products (K_{sp}) for activities, we get:

$$\log {}_m\gamma_i = pK_{sp}(i,s) - pK_{sp}(i,H_2O) \qquad (177)$$

If solvents other than water are used as the reference solvent, Equation 177 becomes:

$$\log {}_m\gamma_i = pK_{sp}(i,s) - pK_{sp}(i,\text{reference solvent}) \qquad (178)$$

For non-electrolytes of low solubility, the medium effect is very well approximated by the ratio of the aqueous and nonaqueous solubilities (25) :

$$\log {}_m\gamma_{\text{non-elec}} = \log \frac{(C)_{sat}}{(C^*)_{sat}} \qquad (179)$$

Medium effects of electrolytes and neutral molecules are usually reported in their logarithmic form (4), a convention which will be adhered to in this paper.

When the standard potential of an electrode reversible to a univalent positive ion, $E^o(M)$, is known in water and in the nonaqueous solvent, Equation 49 can be used to calculate $(\log {}_m\gamma_M - \log {}_m\gamma_H)$:

$${}_sE^o(M,s) - {}_wE^o(M,H_2O) = 2.303\frac{RT}{F}\log {}_m\gamma_M - 2.303\frac{RT}{F}\log {}_m\gamma_H \qquad (49)$$

Similarly, standard potentials for electrodes reversible to divalent positive ions, $E^o(Z)$, and univalent negative ions $E^o(X)$ can be used to calculate other combinations of medium effects for single ions via Equations 51 and 55 :

$${}_sE^o(Z,s) - {}_wE^o(Z,H_2O) = 2.303\frac{RT}{2F}\log {}_m\gamma_Z - 2.303\frac{RT}{F}\log {}_m\gamma_H \qquad (51)$$

$$ {}_wE^{\circ}(X,H_2O) - {}_sE^{\circ}(X,s) = 2.303\frac{RT}{F}\log {}_m\gamma_X + \quad (55) $$

$$ + 2.303\frac{RT}{F}\log {}_m\gamma_H $$

Solubility data is often given on the molar scale but medium effects are usually reported on the molal scale. For dilute solutions, it is a relatively simple matter to convert molarities, M, to malalities, m :

$$ m = \frac{M}{d_o} \quad (180) $$

where d_o is the density of the pure solvent. Molar solubility products, K_{sp}molar, can be converted to molal solubility products, K_{sp}molal, via Equation 181 :

$$ pK_{sp}\text{molal} = pK_{sp}\text{molar} - 2\log d_o \quad (181) $$

Consequently, the medium effects can be converted from the molar to the molal scale with the aid of Equation 182 :

$$ \log {}_m\gamma_i\text{molal} = \log {}_m\gamma_i\text{molar} + 2\log d_{\text{solvent}} - \quad (182) $$

$$ - 2\log d_{\text{reference solvent}} $$

It is possible to calculate medium effects for

electrolytes using combinations of experimentally available medium effects. For example, $Ph_4P\ BPh_4$ has a very low solubility in water and thus, it is difficult to determine its medium effect in other solvents. However, the medium effects of $Ph_4P\ Pi$, $KBPh_4$ and KPi are available and they can be used to calculate the medium effect of $Ph_4P\ BPh_4$:

$$\log {}_m\gamma_{Ph_4P\ BPh_4} = \log {}_m\gamma_{Ph_4P\ Pi} + \log {}_m\gamma_{KBPh_4} - \log {}_m\gamma_{KPi} \quad (183)$$

Solubilities of slightly soluble compounds in water, ${}_wpK$, can be calculated from their medium effects in a given solvent and their solubility product in that solvent, ${}_spK_{sp}$:

$${}_wpK_{sp} = {}_spK_{sp} - \log {}_m\gamma_i \quad (184)$$

Equation 184 can also be used to calculate $pK_{sp}(i,s)$ if $\log {}_m\gamma_i$ and $pK_{sp}(i,H_2O)$ are known.

Medium effects in ethanol--water solvents.

Tables 38 - 43 give results of solubility, conductance, and activity coefficient studies of Ph_4P Pi, Ph_4As Pi, TAB Pi, $KBPh_4$, KPi, and TlCl in ethanol--water solvents. In these tables, values of K_{sp} and pK_{sp} are given on the molar and molal scale. In places where there are no reported values for solubility, C_o, activity coefficient, $f_{\pm,o}$, or degree of dissociation of the saturated solutions, α_o, values of mean ionic activity, $a_{\pm,o}$ ($C_o \alpha_o f_{\pm,o}$), were interpolated directly from large-scale plots of $a_{\pm,o}$ versus wt.-% ethanol. In other cases, where a value is given for α_o but no values are reported for C_o or $f_{\pm,o}$, mean ionic activity was evaluated directly via Equation 172.

Medium effects of electrolytes in ethanol--water solvents calculated via Equation 178 are given in Tables 44 - 47. Tables 44 and 45 give values of $\log {}_m\gamma_i$ on the molal and molar scale, respectively, based on water as the reference solvent. Tables 46 and 47 give values of $\log {}_m\gamma_i$ on the molal and molar scales, respectively, based on ethanol as the reference solvent. Medium effects of HCl and KCl in ethanol--water solvents were taken from the data of Kill, Itzkowitz, and Popovych (72). Due to the low solubility of Ph_4P BPh_4, Ph_4As BPh_4, and TAB BPh_4 in water, medium effects for these compounds were obtained by the usual indirect

Table 38. Solubility Products of Ph_4P Pi in Ethanol--Water Solvents at 25°C.

wt.-% ethanol	C_o	$f_{\pm,o}$	α_o	$a_{\pm,o} \times 10^5$	K_{sp} molar	pK_{sp} molar	K_{sp} molal	pK_{sp} molal
0.0	4.51×10^{-5}	0.992	1.000	4.47	2.00×10^{-9}	8.699	2.01×10^{-9}	8.693
10.0	7.62×10^{-5}	0.986	1.000	7.52	5.65×10^{-9}	8.248	5.88×10^{-9}	8.231
19.9	1.60×10^{-4}	0.978	1.000	15.6	2.45×10^{-8}	7.611	2.62×10^{-8}	7.582
20.0	----------	-----	-----	16.0	2.56×10^{-8}	7.592	2.74×10^{-8}	7.562
30.0	----------	-----	-----	48.0	2.30×10^{-7}	6.638	2.55×10^{-7}	6.594
31.2	5.45×10^{-4}	0.963	1.000	52.5	2.76×10^{-7}	6.560	3.06×10^{-7}	6.514
39.3	1.18×10^{-3}	0.945	1.000	112.	1.25×10^{-6}	5.904	1.44×10^{-6}	5.843
40.0	----------	-----	-----	120.	1.44×10^{-6}	5.842	1.66×10^{-6}	5.780
50.0	----------	-----	-----	218.	4.75×10^{-6}	5.323	5.74×10^{-6}	5.241
50.7	2.42×10^{-3}	0.922	1.000	223.	4.96×10^{-6}	5.305	6.01×10^{-6}	5.221
60.0	----------	-----	-----	325.	1.06×10^{-5}	4.976	1.34×10^{-5}	4.872
61.0	3.99×10^{-3}	0.858	0.965	330.	1.09×10^{-5}	4.962	1.39×10^{-5}	4.856
70.0	----------	-----	-----	394.	1.55×10^{-5}	4.809	2.08×10^{-5}	4.681

Table 38. (Continued).

wt.-% ethanol	C_o	$f_{\pm,o}$	α_o	$a_{\pm,o} \times 10^5$	K_{sp} molar	pK_{sp} molar	K_{sp} molal	pK_{sp} molal
70.6	5.11×10^{-3}	0.832	0.931	396.	1.56×10^{-5}	4.806	2.10×10^{-5}	4.677
80.0	----------	-----	-----	394.	1.55×10^{-5}	4.809	2.21×10^{-5}	4.657
80.8	5.72×10^{-3}	0.762	0.899	392.	1.53×10^{-5}	4.814	2.19×10^{-5}	4.660
90.0	----------	-----	-----	339.	1.15×10^{-5}	4.940	1.74×10^{-5}	4.760
93.2	4.70×10^{-3}	0.722	0.875	296.	8.79×10^{-6}	5.056	1.36×10^{-5}	4.867
100.0	3.44×10^{-3}	0.714	0.861	211.	4.47×10^{-6}	5.350	7.25×10^{-6}	5.140

Table 39. Solubility Products of Ph_4As Pi in Ethanol--Water Solvents at 25°C.

wt.-% ethanol	C_o	$f_{\pm,o}$	α_o	$a_{\pm,o} \times 10^5$	K_{sp} molar	pK_{sp} molar	K_{sp} molal	pK_{sp} molal
0.0	3.49×10^{-5}	0.993	1.000	3.47	1.20×10^{-9}	8.919	1.21×10^{-9}	8.917
10.0	----------	-----	-----	5.80	3.36×10^{-9}	8.473	3.50×10^{-9}	8.456
10.2	5.90×10^{-5}	0.989	1.000	5.84	3.41×10^{-9}	8.467	3.55×10^{-9}	8.450
20.0	----------	-----	-----	13.0	1.69×10^{-8}	7.772	1.81×10^{-8}	7.742
20.4	1.38×10^{-4}	0.981	1.000	13.5	1.82×10^{-8}	7.739	1.96×10^{-8}	7.709
30.0	----------	-----	-----	37.5	1.41×10^{-7}	6.852	1.56×10^{-7}	6.808
30.3	3.98×10^{-4}	0.964	1.000	38.4	1.47×10^{-7}	6.832	1.63×10^{-7}	6.787
39.7	9.85×10^{-4}	0.949	1.000	93.5	8.74×10^{-7}	6.059	1.01×10^{-6}	5.997
40.0	----------	-----	-----	100.	1.00×10^{-6}	6.000	1.15×10^{-6}	5.938
50.0	----------	-----	-----	174.	3.03×10^{-6}	5.519	3.66×10^{-6}	5.437
50.9	2.08×10^{-3}	0.899	1.000	187.	3.49×10^{-6}	5.457	4.24×10^{-6}	5.373
60.0	----------	-----	-----	265.	7.02×10^{-6}	5.154	8.93×10^{-6}	5.049
60.9	3.21×10^{-3}	0.849	0.994	271.	7.33×10^{-6}	5.135	9.35×10^{-6}	5.029

Table 39. (Continued).

wt.-% ethanol	C_o	$f_{\pm,o}$	α_o	$a_{\pm,o} \times 10^5$	K_{sp} molar	pK_{sp} molar	K_{sp} molal	pK_{sp} molal
70.0	----------	-----	-----	329.	1.08×10^{-5}	4.966	1.45×10^{-5}	4.838
70.7	4.23×10^{-3}	0.818	0.959	331.	1.10×10^{-5}	4.959	1.48×10^{-5}	4.830
80.0	----------	-----	------	341.	1.16×10^{-5}	4.935	1.65×10^{-5}	4.782
80.7	4.84×10^{-3}	0.774	0.908	340.	1.16×10^{-5}	4.937	1.65×10^{-5}	4.782
90.0	----------	-----	-----	300.	9.00×10^{-6}	5.046	1.36×10^{-5}	4.867
93.3	4.10×10^{-3}	0.738	0.887	268.	7.20×10^{-6}	5.142	1.11×10^{-5}	4.954
100.0	3.15×10^{-3}	0.716	0.880	199.	3.94×10^{-6}	5.404	6.39×10^{-6}	5.194

Table 40. Solubility Products of TAB Pi in Ethanol--Water Solvents at 25°C.

wt.-% ethanol	C_o	$f_{\pm,o}$	α_o	$a_{\pm,o} \times 10^4$	K_{sp} molar	pK_{sp} molar	K_{sp} molal	pK_{sp} molal
0.0	2.26×10^{-4}	0.983	1.000	2.22	4.94×10^{-8}	7.307	4.96×10^{-8}	7.304
10.0	2.82×10^{-4}	0.978	0.997	2.75	7.56×10^{-8}	7.121	7.87×10^{-8}	7.104
20.0	4.06×10^{-4}	0.970	0.996	3.92	1.54×10^{-7}	6.813	1.65×10^{-7}	6.783
30.0	9.03×10^{-4}	0.950	0.989	8.48	7.20×10^{-7}	6.143	7.96×10^{-7}	6.099
38.4	2.02×10^{-3}	0.945	0.976	18.6	3.47×10^{-6}	5.459	3.98×10^{-6}	5.400
40.0	----------	-----	-----	21.3	4.54×10^{-6}	5.343	5.23×10^{-6}	5.282
50.0	----------	-----	-----	46.7	2.18×10^{-5}	4.661	2.63×10^{-5}	4.579
53.6	7.10×10^{-3}	0.876	0.923	57.4	3.29×10^{-5}	4.483	4.04×10^{-5}	4.394
60.0	----------	-----	-----	78.0	6.08×10^{-5}	4.216	7.73×10^{-5}	4.112
67.3	1.60×10^{-2}	0.743	0.854	102.	1.03×10^{-4}	3.987	1.36×10^{-4}	3.866
70.0	----------	-----	-----	111.	1.23×10^{-4}	3.912	1.64×10^{-4}	3.784
80.0	----------	-----	-----	142.	2.02×10^{-4}	3.695	2.86×10^{-4}	3.543

Table 40. (Continued).

wt.-% ethanol	C_o	$f_{\pm,o}$	α_o	$a_{\pm,o} \times 10^4$	K_{sp} molar	pK_{sp} molar	K_{sp} molal	pK_{sp} molal
86.4	----------	-----	0.848	162.	2.62×10^{-4}	3.582	3.87×10^{-4}	3.412
90.0	----------	-----	-----	166.	2.76×10^{-4}	3.560	4.16×10^{-4}	3.381
100.0	6.27×10^{-2}	0.329	0.810	167.	2.78×10^{-4}	3.556	4.52×10^{-4}	3.345

Table 41. Solubility Products of $KBPh_4$ in Ethanol--Water Solvents at 25°C.

wt.-% ethanol	C_o	$f_{\pm,o}$	α_o	$a_{\pm,o} \times 10^4$	K_{sp} molar	pK_{sp} molar	K_{sp} molal	pK_{sp} molal
0.0	1.74×10^{-4}	0.985	1.000	1.71	2.94×10^{-8}	7.532	2.95×10^{-8}	7.530
10.0	2.20×10^{-4}	0.981	1.000	2.16	4.66×10^{-8}	7.332	4.85×10^{-8}	7.315
20.0	3.40×10^{-4}	0.972	1.000	3.30	1.09×10^{-7}	6.962	1.17×10^{-7}	6.932
30.0	6.70×10^{-4}	0.958	1.000	6.42	4.12×10^{-7}	6.385	4.56×10^{-7}	6.341
38.4	----------	-----	1.000	12.5	1.57×10^{-6}	5.803	1.80×10^{-6}	5.745
40.0	----------	-----	-----	13.7	1.88×10^{-6}	5.727	2.16×10^{-6}	5.665
50.0	----------	-----	-----	20.9	4.37×10^{-6}	5.360	5.28×10^{-6}	5.278
60.0	----------	-----	-----	27.5	7.56×10^{-6}	5.121	9.61×10^{-6}	5.017
60.6	----------	-----	0.998	27.8	7.71×10^{-6}	5.113	9.82×10^{-6}	5.008
70.0	----------	-----	-----	25.0	6.25×10^{-6}	5.204	8.38×10^{-6}	5.077
78.1	2.35×10^{-3}	0.819	0.986	19.0	3.60×10^{-6}	5.444	5.05×10^{-6}	5.297

Table 41. (Continued).

wt.-% ethanol	C_o	$f_{\pm,o}$	α_o	$a_{\pm,o} \times 10^4$	K_{sp} molar	pK_{sp} molar	K_{sp} molal	pK_{sp} molal
80.0	----------	-----	-----	17.4	3.03×10^{-6}	5.519	4.30×10^{-6}	5.367
90.0	----------	-----	-----	9.00	8.10×10^{-7}	6.092	1.22×10^{-6}	5.912
90.6	----------	-----	1.000	8.67	7.52×10^{-7}	6.124	1.14×10^{-6}	5.943
100.0	5.04×10^{-4}	0.848	0.949	4.06	1.65×10^{-7}	6.783	2.67×10^{-7}	6.573

Table 42. Solubility Products of KPi in Ethanol--Water Solvents at 25°C.

wt.-% ethanol	C_o	$f_{\pm,o}$	α_o	$a_{\pm,o} \times 10^4$	K_{sp} molar	pK_{sp} molar	K_{sp} molal	pK_{sp} molal
0.0	2.33×10^{-2}	0.844	1.000	197.	3.87×10^{-4}	3.413	3.89×10^{-4}	3.410
10.0	----------	-----	-----	155.	2.39×10^{-4}	3.622	2.48×10^{-4}	3.605
10.2	1.78×10^{-2}	0.866	1.000	154.	2.37×10^{-4}	3.625	2.47×10^{-4}	3.607
20.0	----------	-----	-----	141.	1.97×10^{-4}	3.705	2.11×10^{-4}	3.675
20.6	1.59×10^{-2}	0.887	1.000	141.	1.99×10^{-4}	3.701	2.14×10^{-4}	3.671
30.0	----------	-----	-----	153.	2.33×10^{-4}	3.634	2.57×10^{-4}	3.590
37.3	1.98×10^{-2}	0.813	1.000	161.	2.59×10^{-4}	3.586	2.95×10^{-4}	3.530
40.0	----------	-----	-----	164.	2.70×10^{-4}	3.569	3.11×10^{-4}	3.507
50.0	----------	-----	-----	176.	3.11×10^{-4}	3.508	3.75×10^{-4}	3.426
51.0	2.20×10^{-2}	0.807	1.000	177.	3.15×10^{-4}	3.502	3.83×10^{-4}	3.417
58.8	1.95×10^{-2}	0.723	1.000	141.	1.99×10^{-4}	3.701	2.52×10^{-4}	3.599
60.0	----------	-----	-----	136.	1.84×10^{-4}	3.734	2.34×10^{-4}	3.630

Table 42. (Continued).

wt.-% ethanol	C_o	$f_{\pm,o}$	α_o	$a_{\pm,o} \times 10^4$	K_{sp} molar	pK_{sp} molar	K_{sp} molal	pK_{sp} molal
68.3	1.52×10^{-2}	0.776	0.985	116.	1.35×10^{-4}	3.869	1.75×10^{-4}	3.758
70.0	----------	-----	-----	113.	1.27×10^{-4}	3.896	1.70×10^{-4}	3.769
80.0	----------	-----	-----	62.5	3.91×10^{-5}	4.408	5.55×10^{-5}	4.256
84.8	----------	-----	0.970	35.2	1.24×10^{-5}	4.906	1.82×10^{-5}	4.741
90.0	----------	-----	-----	21.9	4.80×10^{-6}	5.319	7.25×10^{-6}	5.140
92.3	2.51×10^{-3}	0.766	0.888	17.1	2.91×10^{-6}	5.537	4.46×10^{-6}	5.351
100.0	1.04×10^{-3}	0.806	0.857	7.20	5.18×10^{-7}	6.286	8.41×10^{-7}	6.076

Table 43. Solubility Products of TlCl in Ethanol--Water Solvents at 25°C.

wt.-% ethanol	C_o	$f_{\pm,o}$	α_o	$a_{\pm,o} \times 10^5$	K_{sp} molar	pK_{sp} molar	K_{sp} molal	pK_{sp} molal
0.0	1.60×10^{-2}	0.978	0.898	140_7.	1.98×10^{-4}	3.704	1.99×10^{-4}	3.701
10.0	----------	-----	-----	100_8.	1.02×10^{-4}	3.993	1.06×10^{-4}	3.976
10.1	1.12×10^{-2}	0.979	0.911	100_1.	1.00×10^{-4}	3.999	1.04×10^{-4}	3.981
20.0	----------	-----	-----	710.	5.04×10^{-5}	4.298	5.40×10^{-5}	4.268
20.7	7.69×10^{-3}	0.980	0.921	692.	4.79×10^{-5}	4.319	5.14×10^{-5}	4.289
30.0	----------	-----	-----	500.	2.50×10^{-5}	4.602	2.77×10^{-5}	4.558
30.3	5.46×10^{-3}	0.980	0.927	496.	2.46×10^{-5}	4.609	2.73×10^{-5}	4.564
39.2	3.88×10^{-3}	0.980	0.928	353.	1.25×10^{-5}	4.904	1.43×10^{-5}	4.844
40.0	----------	-----	-----	344.	1.18×10^{-5}	4.927	1.36×10^{-5}	4.865
50.0	----------	-----	-----	227.	5.15×10^{-6}	5.288	6.22×10^{-6}	5.206
51.2	2.31×10^{-3}	0.981	0.932	211.	4.46×10^{-6}	5.351	5.42×10^{-6}	5.266
60.0	----------	-----	-----	132.	1.74×10^{-6}	5.759	2.21×10^{-6}	5.655
70.0	----------	-----	-----	70.5	4.97×10^{-7}	6.304	8.17×10^{-7}	6.088

Table 43. (Continued).

wt.-% ethanol	C_o	$f_{\pm,o}$	α_o	$a_{\pm,o} \times 10^5$	K_{sp} molar	pK_{sp} molar	K_{sp} molal	pK_{sp} molal
71.0	7.31×10^{-4}	0.984	0.931	67.0	4.48×10^{-7}	6.348	6.05×10^{-7}	6.218
80.0	----------	-----	-----	34.2	1.17×10^{-7}	6.932	1.66×10^{-7}	6.780
80.5	3.60×10^{-4}	0.986	0.929	33.0	1.09×10^{-7}	6.964	1.55×10^{-7}	6.810
90.0	----------	-----	-----	11.6	1.35×10^{-8}	7.871	2.03×10^{-8}	7.692
90.6	1.16×10^{-4}	0.989	0.936	10.7	1.15×10^{-8}	7.938	1.75×10^{-8}	7.757
100.0	3.45×10^{-5}	0.993	0.959	3.28	1.08×10^{-9}	8.967	1.75×10^{-9}	8.757

Table 44. Medium Effects, $\log_m \gamma$, of Electrolytes in Ethanol--Water Solvents. Water is the Reference Solvent. 25°C, Molal Scale.

wt.-% ethanol	Ph_4P Pi	Ph_4As Pi	TAB Pi	$KBPh_4$	KPi	KCl	HCl	Ph_4P--BPh_4	Ph_4As--BPh_4	TAB-BPh_4
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
10.0	-0.466 ±0.006	-0.461 ±0.006	-0.200 ±0.005	-0.215 ±0.009	0.19 ±0.02	0.27	0.13 ±0.01	-0.88 ±0.02	-0.87 ±0.02	-0.61 ±0.02
20.0	-1.134 ±0.008	-1.174 ±0.008	-0.521 ±0.005	-0.598 ±0.009	0.26 ±0.03	0.60	0.25	-2.00 ±0.03	-2.04 ±0.03	-1.38 ±0.03
30.0	-2.103 ±0.006	-2.11 ±0.01	-1.205 ±0.005	-1.188 ±0.009	0.18 ±0.02	0.98	0.37	-3.47 ±0.02	-3.48 ±0.02	-2.57 ±0.02
40.0	-2.916 ±0.007	-2.978 ±0.007	-2.022 ±0.006	-1.86 ±0.02	0.10 ±0.02	1.39	0.47	-4.88 ±0.03	-4.95 ±0.03	-3.98 ±0.03
50.0	-3.46 ±0.02	-3.48 ±0.01	-2.725 ±0.009	-2.25 ±0.02	0.02 ±0.02	1.85	0.62	-5.72 ±0.03	-5.75 ±0.03	-4.99 ±0.03
60.0	-3.82 ±0.01	-3.87 ±0.01	-3.19 ±0.01	-2.51 ±0.01	0.22 ±0.03	2.37	0.79 ±0.01	-6.56 ±0.03	-6.60 ±0.03	-5.92 ±0.03
70.0	-4.015 ±0.009	-4.08 ±0.01	-3.52 ±0.03	-2.45 ±0.02	0.36 ±0.02	2.95	1.12	-6.83 ±0.03	-6.89 ±0.03	-6.33 ±0.04

Table 44. (Continued).

wt.-% ethanol	Ph_4P Pi	Ph_4As Pi	TAB Pi	$KBPh_4$	KPi	KCl	HCl	Ph_4P-BPh_4	Ph_4As-BPh_4	TAB-BPh_4
80.0	-4.040 ±0.009	-4.13 ±0.01	-3.76 ±0.04	-2.16 ±0.02	0.85 ±0.02	3.62	1.57	-7.05 ±0.03	-7.14 ±0.03	-6.77 ±0.05
90.0	-3.936 ±0.006	-4.05 ±0.01	-3.92 ±0.04	-1.62 ±0.07	1.73 ±0.02	4.72	2.21	-7.28 ±0.07	-7.40 ±0.07	-7.27 ±0.08
100.0	-3.56 ±0.02	-3.723 ±0.009	-3.96 ±0.03	-0.96 ±0.02	2.66 ±0.02	6.12	5.13	-7.18 ±0.03	-7.34 ±0.03	-7.58 ±0.04

Table 45. Medium Effects, $\log_m \gamma$, of Electrolytes in Ethanol--Water Solvents. Water is the Reference Solvent. 25°C, Molar Scale.

wt.-% ethanol	Ph_4P Pi	Ph_4As Pi	TAB Pi	$KBPh_4$	KPi	KCl	HCl	Ph_4P--BPh_4	Ph_4As--BPh_4	TAB--BPh_4
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
10.0	-0.451	-0.446	-0.185	-0.200	0.210	0.285	0.144	-0.861	-0.856	-0.595
20.0	-1.107	-1.147	-0.494	-0.570	0.292	0.627	0.277	-1.969	-2.010	-1.356
30.0	-2.061	-2.068	-1.164	-1.147	0.221	1.021	0.413	-3.429	-3.435	-2.532
40.0	-2.857	-2.919	-1.964	-1.805	0.156	1.449	0.529	-4.819	-4.881	-3.925
50.0	-3.376	-3.401	-2.645	-2.172	0.095	1.930	0.696	-5.643	-5.668	-4.913
60.0	-3.723	-3.766	-3.091	-2.411	0.322	2.472	0.902	-6.455	-6.498	-5.823
70.0	-3.890	-3.954	-3.395	-2.328	0.484	3.075	1.241	-6.701	-6.765	-6.207
80.0	-3.890	-3.985	-3.611	-2.013	0.996	3.770	1.728	-6.899	-6.994	-6.620
90.0	-3.759	-3.874	-3.747	-1.441	1.907	4.897	2.386	-7.106	-7.221	-7.094
100.0	-3.349	-3.515	-3.751	-0.749	2.873	6.328	5.342	-6.971	-7.137	-7.373

Table 46. Medium Effects, $\log_m \gamma$, of Electrolytes in Ethanol--Water Solvents. Ethanol is the Reference Solvent. 25°C, Molal Scale.

wt.-% ethanol	Ph_4P Pi	Ph_4As Pi	TAB Pi	$KBPh_4$	KPi	KCl	HCl	Ph_4P--BPh_4	Ph_4As--BPh_4	TAB--BPh_4
0.0	3.557	3.723	3.959	0.957	-2.665	-6.12	-5.134	7.179	7.345	7.581
10.0	3.091	3.262	3.759	0.742	-2.471	-5.90	-5.004	6.304	6.474	6.971
20.0	2.423	2.548	3.438	0.359	-2.401	-5.57	-4.884	5.182	5.308	6.198
30.0	1.454	1.614	2.754	-0.232	-2.486	-5.18	-4.762	3.709	3.868	5.008
40.0	0.641	0.744	1.936	-0.908	-2.568	-4.73	-4.664	2.301	2.405	3.597
50.0	0.102	0.243	1.234	-1.295	-2.650	-4.27	-4.518	1.456	1.597	2.588
60.0	-0.267	-0.145	0.766	-1.556	-2.446	-3.75	-4.334	0.623	0.745	1.656
70.0	-0.458	-0.356	0.439	-1.496	-2.307	-3.20	-4.018	0.353	0.454	1.249
80.0	-0.483	-0.412	0.198	-1.206	-1.820	-2.52	-3.556	0.130	0.201	0.811
90.0	-0.379	-0.328	0.035	-0.660	-0.936	-1.26	-2.925	-0.104	-0.053	0.310
100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Table 47. Medium Effects, $\log_m \gamma$, of Electrolytes in Ethanol--Water Solvents. Ethanol is the Reference Solvent. 25°C, Molar Scale.

wt.-% ethanol	Ph_4P Pi	Ph_4As Pi	TAB Pi	$KBPh_4$	KPi	KCl	HCl	Ph_4P--BPh_4	Ph_4As--BPh_4	TAB--BPh_4
0.0	3.349	3.515	3.751	0.749	-2.873	-6.328	-5.342	6.971	7.137	7.373
10.0	2.898	3.069	3.566	0.549	-2.664	-6.093	-5.197	6.111	6.281	6.778
20.0	2.242	2.368	3.257	0.179	-2.581	-5.751	-5.065	5.002	5.128	6.017
30.0	1.288	1.448	2.587	-0.398	-2.652	-5.346	-4.928	3.542	3.702	4.842
40.0	0.492	0.596	1.788	-1.056	-2.717	-4.879	-4.813	2.153	2.256	3.448
50.0	-0.027	0.115	1.106	-1.423	-2.778	-4.398	-4.646	1.328	1.469	2.460
60.0	-0.374	-0.251	0.660	-1.662	-2.552	-3.856	-4.440	0.516	0.639	1.550
70.0	-0.541	-0.439	0.356	-1.579	-2.390	-3.283	-4.100	0.270	0.372	1.167
80.0	-0.541	-0.470	0.140	-1.264	-1.878	-2.578	-3.614	0.073	0.144	0.753
90.0	-0.410	-0.359	0.004	-0.692	-0.967	-1.291	-2.956	-0.135	-0.084	0.279
100.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

calculations :

$$\log {}_m\gamma_{Ph_4P\ BPh_4} = \log {}_m\gamma_{Ph_4P\ Pi} + \log {}_m\gamma_{KBPh_4} - \log {}_m\gamma_{KPi} \quad (137)$$

$$\log {}_m\gamma_{Ph_4As\ BPh_4} = \log {}_m\gamma_{Ph_4As\ Pi} + \log {}_m\gamma_{KBPh_4} - \log {}_m\gamma_{KPi} \quad (138)$$

$$\log {}_m\gamma_{TAB\ BPh_4} = \log {}_m\gamma_{TAB\ Pi} + \log {}_m\gamma_{KBPh_4} - \log {}_m\gamma_{KPi} \quad (139)$$

Molal medium effects, $\log {}_m\gamma_i$ referred to water as the reference solvent, given in Table 44, include standard deviations. A detailed discussion of error analysis of medium effects is given in section VII-F-1-e.

Medium effects of TlCl in ethanol--water solvents referred to water as the reference solvent, are given in Table 48.

Numerical values of medium effects of Ph_4P Pi and Ph_4As Pi are negative in ethanol--water solvents indicating that solvation of these compounds is favored in the nonaqueous solvent. Medium effects of these compounds decrease rapidly from 20 to 70 wt.-% ethanol,

Table 48. Medium Effects, $\log_m \gamma$, of TlCl in Ethanol--Water Solvents. Water is the Reference Solvent. 25°C, Molal Scale.

wt.-% ethanol	$\log_m \gamma_{TlCl}$
0.0	0.0
10.0	0.275
20.0	0.567
30.0	0.857
40.0	1.164
50.0	1.505
60.0	1.954
70.0	2.387
80.0	3.079
90.0	3.991
100.0	5.056

level off at around 80 wt.-% ethanol, and then increase slightly from 80 to 100 wt.-% ethanol. The numerical values of $\log {}_{m}\gamma_{Ph_4P\ Pi}$ and $\log {}_{m}\gamma_{Ph_4As\ Pi}$ are quite close, their differences varying from 0.004 log units in 10 wt.-% ethanol to 0.16 log units in 100 wt.-% ethanol. Numerical values of $\log {}_{m}\gamma_{TAB\ Pi}$ decrease rapidly from 10 to 70 wt.-% ethanol and then continue to decrease slowly from 80 to 100 wt.-% ethanol.

Numerical values of medium effects for KCl increase steadily from 10 to 100 wt.-% ethanol indicating that hydration of KCl rather than solvation is favored in ethanol--water solvents.

Numerical values of $\log {}_{m}\gamma_{HCl}$ increase gradually from 10 to 90 wt.-% ethanol where it assumes a value of 2.210 (molal scale). From 90 to 100 wt.-% ethanol, $\log {}_{m}\gamma_{HCl}$ increases quite rapidly by 2.924 log units indicating a drastic change in solvating power of the solvents in that region.

Numerical values of $\log {}_{m}\gamma_{KPi}$ increase from 10 to 20 wt.-% ethanol, decrease from 20 to 50 wt.-% ethanol, and then increase from 50 to 100 wt.-% ethanol. This complex behavior is probably due to the potassium ion since the medium effects of the other picrates studied do not vary in this manner.

Numerical values of $\log {}_{m}\gamma_{KBPh_4}$ decrease from water to 60 wt.-% ethanol and increase from 60 to 100

wt.-% ethanol where $\log {}_{m}\gamma_{KBPh_4}$ equals -0.957.

Numerical values of medium effects of the three reference electrolytes, $Ph_4P\ BPh_4$, $Ph_4As\ BPh_4$, and TAB BPh_4 decrease from 10 to 100 wt.-% ethanol. In the case of $\log {}_{m}\gamma_{Ph_4P\ BPh_4}$ and $\log {}_{m}\gamma_{Ph_4As\ BPh_4}$, there is a slight increase of 0.11 and 0.05 log units, respectively, from 90 to 100 wt.-% ethanol. Medium effects for the reference electrolytes are negative throughout the ethanol--water solvent system indicating that they are preferentially solvated (they are in a lower energy state) in the nonaqueous solvents.

Medium effects, $\log {}_{m}\gamma$, of $RbBPh_4$ and $CsBPh_4$ in 100 % ethanol were determined to be -0.94 and -1.15, respectively. It should be noted that medium effects for RbPi, CsPi, HPi, RbCl, CsCl, and other compounds and electroneutral combinations of ions are accessible from the available medium effect data in ethanol--water solvents. For example, to calculate $\log {}_{m}\gamma_{RbPi}$ and $(\log {}_{m}\gamma_{K} - \log {}_{m}\gamma_{Rb})$ we could use the relationships:

$$\log {}_{m}\gamma_{RbPi} = \log {}_{m}\gamma_{RbBPh_4} + \log {}_{m}\gamma_{KPi} - \log {}_{m}\gamma_{KBPh_4} \qquad (185)$$

$$\log {}_{m}\gamma_{K} - \log {}_{m}\gamma_{Rb} = \log {}_{m}\gamma_{KPi} - \log {}_{m}\gamma_{RbPi} \qquad (186)$$

In a similar manner, many other combinations of medium

effects can be calculated using the data in Tables 44 - 48.

Medium effects, $\log {}_{m}\gamma$, for the neutral compounds Ph_4C, Ph_4Si, and Ph_4Ge in ethanol--water solvents are given in Table 49. These compounds are very insoluble ($m\,Ph_4C = 1x10^{-5}m$ in 60 wt.-% ethanol) in water-rich solvents, a fact that necessitates the choice of 100 % ethanol as the reference solvent when reporting their medium effects. Medium effects of all three of these compounds decrease steadily from pure ethanol to 60.0 wt.-% ethanol. The average value of the medium effects of all three tetraphenyl compounds is also given in Table 49. The precision in the solubility determinations of these compounds, and the closeness of their medium effects allows us to use their average as the representative value when discussing medium effects for tetraphenyl molecules in a given solvent.

Table 50 contains a listing of medium effects of ferrocene, $\log {}_{m}\gamma_{Foc}$, in ethanol--water solvents. These are given on both the molar and molal scale. Numerical values of $\log {}_{m}\gamma_{Foc}$ decrease steadily from 10 to 100 wt.-% ethanol indicating that ferrocene is solvated better in the ethanolic solvents. Assuming that $\log {}_{m}\gamma_{Foc}$ is equal to the neutral component of $\log {}_{m}\gamma_{Fic}$, and assuming that the electrostatic component can be accurately estimated via the Born equation, we

Table 49. Medium Effects, $\log_m \gamma$, of Ph_4C, Ph_4Si, and Ph_4Ge in Ethanol--Water Solvents. Ethanol is the Reference Solvent. 25°C, Molal Scale.

wt.-% ethanol	Ph_4C	Ph_4Si	Ph_4Ge	Average
100.0	0.0	0.0	0.0	0.0
93.3	0.20	----	----	----
92.8	----	----	0.26	----
92.6	----	0.23	----	----
90.0*	0.34	0.33	0.36	0.34
80.5	0.66	----	----	----
80.4	----	0.68	0.65	----
80.0*	0.67	0.69	0.66	0.67
70.5	----	0.96	----	----
70.0	0.98	0.98*	0.88	0.95
62.0	----	1.25	----	----
60.4	1.40	----	1.37	----
60.0*	1.42	1.27	1.41	1.37

* Interpolated graphically.

Table 50. Medium Effects, $\log {}_m\gamma$, of Ferrocene and Ferricinium Ion in Ethanol--Water Solvents at 25°C.

wt.-% ethanol	$\log {}_m\gamma_{Foc}$ molar	$\log {}_m\gamma_{Foc}$ molal	$\log {}_m\gamma_{Born}$ r = 3.8 Å	$\log {}_m\gamma_{Fic}$ (calc.)
0.0	0.0	0.0	0.0	0.0
10.0	-0.22*	-0.23	0.03	-0.20
10.1	-0.225	-0.232	----	-----
20.0	-0.50*	-0.51	0.07	-0.44
20.4	-0.511	-0.525	----	-----
30.0	-1.00*	-1.02	0.12	-0.90
30.4	-1.010	-1.031	----	-----
38.9	-1.515	-1.544	----	-----
40.0	-1.57*	-1.60	0.17	-1.43
50.0	-1.98*	-2.02	0.25	-1.77
51.2	-2.024	-2.065	----	-----
60.0	-2.32*	-2.37	0.33	-2.04
60.7	-2.340	-2.392	----	-----
70.0	-2.59*	-2.65	0.43	-2.22
70.5	-2.607	-2.670	----	-----
80.0	-2.84*	-2.91	0.57	-2.34
80.4	-2.845	-2.921	----	-----
90.0	-2.925*	-3.013	0.731	-2.282
92.6	-2.974	-3.066	----	-----
100.0	-3.279	-3.383	0.909	-2.474

* Interpolated Graphically.

can calculate $\log_{m}\gamma_{Fic}$ using the relationship:

$$\log_{m}\gamma_{Fic} = \log_{m}\gamma_{Foc} + \log_{m}\gamma_{(Born)} \qquad (187)$$

Table 50 contains a listing of $\log_{m}\gamma_{Fic}$ calculated using Equation 187. The Born charging term was calculated using a value of 3.8 Å (8) for the radius of ferricinium. It is interesting to note that numerical values of $\log_{m}\gamma_{(Born)}$ become more positive from 10 to 100 wt.-% ethanol with a value of +0.909 log units in 100 % ethanol (see Table 50). Numerical values of $\log_{m}\gamma_{Foc}$ are negative throughout the ethanol--water solvent system. This is excellent experimental verification for the existence of a large neutral contribution to the medium effect of large ions. The neutral component of the medium effect of ferricinium ion is not only larger in magnitude than the electrostatic component but it is opposite in sign as well.

Medium effects in methanol.

Table 51 contains a listing of ion-activity products and medium effects of electrolytes and electroneutral combinations of ions in methanol. Where solubility products for the particular electrolyte or combination of ions are not given, medium effects were calculated from standard potentials using Equations 49, 51, or 55. Table 56 contains a listing of standard potentials for various electrodes in water and methanol.

Medium effects for the reference electrolytes Ph_4P BPh_4, Ph_4As BPh_4, and TAB BPh_4 are negative in methanol as they are in ethanol, having values of -8.19, -8.36, and -9.01, respectively. Medium effects for these compounds were calculated in the usual manner using Equations 137 - 139. Two values of $\log {}_m\gamma_{TAB\ BPh_4}$ are reported in Table 51. The value of -8.60 is preferred since it is more recent.

The large positive values of $\log {}_m\gamma$ for alkali-metal halides and hydrochloric acid in methanol reflect the relative hydrogen bonding powers of methanol and water. Due to hydrogen bonding, halides and the proton are more strongly solvated in water than in methanol. Large ions such as picrate and tetraphenylborate are more strongly solvated in the organic solvent (50).

Many intercomparisons can be made amongst data in Table 51. Sums and differences of medium effects

Table 51. Solubility Products and Medium Effects of Electrolytes in Methanol. 25°C, Molal Scale.

Electrolyte	pK(CH_3OH)	pK(H_2O)	$\log_m \gamma$
Ph_4As Pi	3.91	8.92	-5.01
Ph_4P Pi	3.86	8.70	-4.84
TAB Pi	1.70	7.31	-5.61
Ph_4P BPh_4	----	----	-8.19 (calc)
Ph_4As BPh_4	----	----	-8.36 (calc)
TAB BPh_4 (19)	4.92	13.93 (calc)	-9.01
TAB BPh_4 (17)	----	----	-8.60 (calc)
Bu_4N Pi (19)	1.22	5.87	-4.65
KPi (19)	4.25	3.36	+0.89
$KBPh_4$ (19)	5.02	7.53	-2.51
KCl (19)	3.15	-0.904	+4.05
KBr (31)	2.75	1.14	+1.61
$KClO_4$	4.9 (154)	1.94 (153)	+2.96
HCl (18)	----	----	+3.93
$RbBPh_4$	6.07 (18)	8.54	-2.47
RbBr	2.9 (31)	-1.13 (26)	+4.03
RbPi (31)	5.0	3.7	+1.3
$RbClO_4$	5.6 (154)	2.54 (153)	+3.06
$CsBPh_4$	6.4 (29)	8.80	-2.40
CsCl	3.0 (144)	-0.8 (31)	+3.8
CsPi (31)	5.4	4.24	+1.16
$CsClO_4$	5.2 (154)	2.4 (153)	+2.8

Table 51. (Continued).

Electrolyte	pK(CH_3OH)	pK(H_2O)	$\log_m Y$
TlCl	6.7 (31)	3.76 (144)	+2.94
TlBr	8.4 (31)	5.47 (144)	+2.93
$TlNO_3$	4.4 (31)	1.32 (144)	+3.08
$TlClO_4$	3.1 (31)	1.12 (144)	+1.98
TlPi (31)	4.3	4.1	+0.2
$AgBPh_4$	14.6 (31)	17.2 (153)	-2.6
AgCl (155)	13.4	9.74	+3.66
AgBr (155)	15.7	12.2	+3.5
AgI (155)	18.6	16.0	+2.6
AgBz (31)	6.5	3.7	+2.8
AgAc (31)	6.8	2.7	+4.1
Na - H (155, 156)	---	---	-0.24
Li - H (156, 157)	---	---	-0.85
Cu - H (155, 156)	---	---	-0.52
Zn - 2H (155, 156)	---	---	+0.78
Cd - 2H (155, 156)	---	---	-0.91

for electroneutral combinations of ions calculated using data from Table 51 should be internally consistent. For example, $(\log {}_{m}\gamma_{K} - \log {}_{m}\gamma_{Ag})$ calculated via the following three paths should be constant if all the data used is accurate:

$$\log {}_{m}\gamma_{K} - \log {}_{m}\gamma_{Ag} = \log {}_{m}\gamma_{KBPh_4} - \log {}_{m}\gamma_{AgBPh_4} = 0.1 \quad (188)$$

$$\log {}_{m}\gamma_{K} - \log {}_{m}\gamma_{Ag} = \log {}_{m}\gamma_{KCl} - \log {}_{m}\gamma_{AgCl} = 0.39 \quad (189)$$

$$\log {}_{m}\gamma_{K} - \log {}_{m}\gamma_{Ag} = \log {}_{m}\gamma_{KBr} - \log {}_{m}\gamma_{AgBr} = -1.9 \quad (190)$$

The above calculations are not the only ones that can be used to illustrate the lack of internal consistency in the data. Values for $(\log {}_{m}\gamma_{Br} - \log {}_{m}\gamma_{BPh_4})$, which should be constant, can be calculated in these three ways from the dats in Table 51:

$$\log {}_{m}\gamma_{Br} - \log {}_{m}\gamma_{BPh_4} = \log {}_{m}\gamma_{KBr} - \log {}_{m}\gamma_{KBPh_4} = 4.12 \quad (191)$$

$$\log {}_{m}\gamma_{Br} - \log {}_{m}\gamma_{BPh_4} = \log {}_{m}\gamma_{RbBr} - \log {}_{m}\gamma_{CsBPh_4} = 6.50 \quad (192)$$

$$\log {}_{m}\gamma_{Br} - \log {}_{m}\gamma_{BPh_4} = \log {}_{m}\gamma_{AgBr} - \log {}_{m}\gamma_{AgBPh_4} = 6.1 \quad (193)$$

In general, many of the medium effects from the literature cannot be trusted. There is a lack of general agreement among many combinations of medium effects available as illustrated by the two previous sets of calculations. Statistical analyses have rarely been given for medium effects. There is a need for more precise ion-activity product data in general.

Discrepancies arising in the calculation of medium effects for the reference electrolytes do not invalidate a given reference-electrolyte assumption, just as perfect agreement among the results calculated by different paths would not prove its validity.

Medium effects for the neutral tetraphenyl compounds in methanol at 25°C (molal scale) referred to ethanol as the reference solvent, are as follows:

$$\log {}_m\gamma_{Ph_4C} = 0.15$$

$$\log {}_m\gamma_{Ph_4Si} = 0.06$$

$$\log {}_m\gamma_{Ph_4Ge} = 0.10$$

$$\log {}_m\gamma_{average} = 0.10$$

An average value is given since differences among the medium effects of the three compounds do not amount to

more than experimental error. Medium effects for these neutral tetraphenyl compounds in methanol are quite small indicating that large neutral molecules have about the same solvation energies in ethanol and methanol.

The solubility of ferrocene in methanol can be calculated using Parker's value (27) of +3.6 for $\log {}_{m}\gamma_{Foc}$ (molar scale, 25°C) referred to methanol as a reference solvent, and, the aqueous solubility of ferrocene determined in this study of 5.38×10^{-5} M:

$$pK(Foc,CH_3OH) = pK(Foc,H_2O) - \log {}_{m}\gamma_{Foc} \qquad (194)$$

This is a practical application of Equation 184. Because ferrocene is a neutral molecule, pK(Foc) is equal to $-\log C(Foc)$. The molar solubility of ferrocene in methanol at 25°C is 0.214 M.

Medium effects in acetonitrile.

Table 52 is a listing of molal ion-activity products in water and acetonitrile and medium effects of electrolytes and other electroneutral combinations of ions in that solvent. Where available, molar solubilities and activity coefficients are included in the table. In places where values of $\log_m \gamma$ are given without values of pK, medium effects were calculated from standard potentials using Equaitons 49, 51, or 55 (see Table 56). Medium effects for TAB BPh_4 are not reported due to the high solubility of this compound in acetonitrile (0.5707m, 25°C), thus making calculated activity coefficients unreliable.

Medium effects for Ph_4P BPh_4 and Ph_4As BPh_4 were calculated using Equations 137 and 138, respectively. Medium effects $\log_m \gamma$, for both compounds are large negative numbers having values of -11.45 ± 0.08 and -11.63 ± 0.08 for $\log_m \gamma Ph_4P$ BPh_4 and $\log_m \gamma Ph_4As$ BPh_4, respectively.

The large positive values of $\log_m \gamma$ for alkali-metal halides reflect the poor ability of dipolar aprotic acetonitrile to solvate small anions (50) whose solvation energy depends on strong H-bonding which is available in water but not in acetonitrile. In general, numerical values of $\log_m \gamma$ for metallic halides decrease from the chloride to the iodide indicating

Table 52. Solubility Products and Medium Effects of Electrolytes in Acetonitrile. 25°C, Molal Scale.

Electrolyte	C, M x 10^2	$f_{\pm}^2$	pK(CH_3CN) molal	pK(H_2O) molal	$\log_m \gamma$
Ph_4As Pi	7.99	0.249	2.58	8.92	-6.34 ±0.04
Ph_4P Pi	8.38	0.244	2.55	8,70	-6.15 ±0.04
KPi	1.05	0.510	4.03	3.41 (139)	-0.62 ±0.04
$KBPh_4$	5.33	0.298	2.85	7.53 (139)	-4.68 ±0.04
KCl	0.025 (144)	0.889	7.04	-0.90 (18)	+7.94
KBr	----	----	5.9 (31)	-1.14 (31)	+7.04
$KClO_4$	----	----	4.4 (160)	1.94 (153)	+2.46
$RbBPh_4$	1.70	0.455	3.66	8.54	-4.88 ±0.04
RbCl	0.023 (144)	0.893	7.11	-1.31 (26)	+8.42
RbI	6.2 (144)	0.242	2.83	-1.21 (26)	+4.04
RbBr	0.22 (144)	0.717	5.24	-1.13 (26)	+6.37
RbPi (31)	----	----	4.8	3.7	+1.1
$RbClO_4$	----	----	4.8 (31)	2.54 (153)	+2.26
$CsBPh_4$	1.68	0.456	3.67	8.80	-5.13 ±0.05
CsCl	----	----	5.4 (31)	-0.8 (31)	+6.2
CsPi (31)	----	----	4.94	4.24	+0.70
$CsClO_4$	----	----	4.26 (31)	2.4 (153)	+1.86
TlCl (26)	0.00319*	1.00	12.99	3.76	+9.23

* Molalities.

Table 52. (Continued).

Electrolyte	C, M x 10^2	$f_{\pm}^2$	pK(CH_3CN) molal	pK(H_2O) molal	$\log_m \gamma$
TlBr (26)	0.00425*	1.00	12.74	5.47	+7.27
TlI (26)	0.00807*	1.00	12.19	7.19	+5.00
TlSCN (26)	0.904*	0.94	8.11	3.77	+4.34
$TlNO_3$ (26)	5.03	0.86	6.66	1.32	+5.34
$TlClO_4$ (26)	331.	0.42	3.33	1.12	+2.21
TlPi (31)	----	----	5.7	4.1	+1.6
$AgBPh_4$	----	----	7.8 (31)	17.2 (153)	-9.4
AgCl	----	----	13.4 (26)	9.74 (155)	+3.66
AgBr	----	----	13.4 (26)	12.2 (155)	+1.2
AgI	----	----	14.7 (26)	16.0 (155)	-1.3
AgBz (31)	----	----	7.2	3.7	+3.5
AgAc (31)	----	----	8.9	2.7	+6.2
$Ph_4P\ BPh_4$	----	----	5.68	-17.13(calc)	-11.45 ± 0.08 (calc)
$Ph_4As\ BPh_4$	----	----	----	----	-11.63 ± 0.08 (calc)
Li - H (161, 156)	----	----	----	----	-3.13
Na - H (161, 156)	----	----	----	----	-2.64
Cu - H (161, 156)	----	----	----	----	-15.23
Ca - 2H (161, 156)	----	----	----	----	+4.06

* Molalities.

Table 52. (Continued).

Electrolyte	C, M x 10^2	$f_{\pm}^2$	pK(CH_3CN) molal	pK(H_2O) molal	$\log_m \gamma$
Zn - 2H (161, 156)	----	----	----	----	+0.78
Cd - 2H (161, 156)	----	----	----	----	-2.27
Pb - 2H (161, 156)	----	----	----	----	+0.20
Cu - 2H (161, 156)	----	----	----	----	-20.86

that additional forces such as mutual polarizability of ion and solvent molecule become appreciable for large ions. Picrates and perchlorates seem to be strongly solvated in acetonitrile (46) and the same can be said for tetraphenylborates. Values of $\log_m \gamma$ for the series $AgBPh_4$, AgI, AgBr, and AgCl continually increase. The same is true for the corresponding rubidium, potassium and thallium (I) series. This indicates the preference of acetonitrile for large anions as opposed to small ones.

The well-known affinity of Ag^+ ions for acetonitrile (158, 159) manifests itself in the numerically small values of $\log_m \gamma$ for silver halides and the large negative value of -9.4 for $\log_m \gamma_{AgBPh_4}$.

Two outstanding values on Table 52 are -15.23 and -20.86 for $(\log_m \gamma_{Cu} - \log_m \gamma_H)$ and $(\log_m \gamma_{Cu} - 2\log_m \gamma_H)$, respectively. These very large negative medium effects reflect the preference of Cu^+ and Cu^{+2} ions for acetonitrile (159), as compared to water.

Many intercomparisons can be made among the data in Table 52 to check internal consistency of medium effects for the electrolytes. Calculating $(\log_m \gamma_K - \log_m \gamma_{Ag})$ three ways

$$\log_m \gamma_K - \log_m \gamma_{Ag} = \log_m \gamma_{KBPh_4} - \log_m \gamma_{AgBPh_4} = +4.7 \qquad (195)$$

$$\log {}_{m}\gamma_{K} - \log {}_{m}\gamma_{Ag} = \log {}_{m}\gamma_{KCl} - \log {}_{m}\gamma_{AgCl} = +4.3 \qquad (196)$$

$$\log {}_{m}\gamma_{K} - \log {}_{m}\gamma_{Ag} = \log {}_{m}\gamma_{KBr} - \log {}_{m}\gamma_{AgBr} = +5.8 \qquad (197)$$

we obtain three different values ranging from +4.3 to +5.8. This indicates a lack of internal consistency in the data. Values of ($\log {}_{m}\gamma_{Cl} - \log {}_{m}\gamma_{Pi}$) calculated in a similar manner range from +5.5 to +7.63 and values of ($\log {}_{m}\gamma_{Cl} - \log {}_{m}\gamma_{Br}$) range from 0.90 to +2.46. There is a definite need for more precise determinations of ion-activity products in water, acetonitrile and methanol. Very rarely are error analyses performed as was done in this study. All data in Table 52 determined in this study have been completely analyzed as to their precision (see section VII-F-2). The standard deviation in most values of $\log {}_{m}\gamma$ given in Table 52 is $\pm$0.04 log units.

Medium effects for the neutral compounds Ph_4C, Ph_4Si, and Ph_4Ge were also determined in acetonitrile relative to 100 % ethanol :

$$\log {}_{m}\gamma_{Ph_4C} = -0.40$$

$$\log {}_{m}\gamma_{Ph_4Si} = -0.31$$

$$\log {}_{m}\gamma_{Ph_4Ge} = -0.28$$

$$\log {}_{m}\gamma_{average} = -0.33$$

The average value of $\log {}_{m}\gamma$ for the three uncharged compounds is given because all three medium effects are essentially equal, within experimental error. Thus, ethanol--water solvents, methanol, and acetonitrile do not differentiate between the three compounds even though all three have different central atoms. This is an extremely interesting and important point suggesting strongly that in the tetraphenyl compounds and ions, the central atom plays a small role in determining the value of the medium effect. Based on the above evidence, it is reasonable to assume that ions like Ph_4P^+, Ph_4As^+, and BPh_4^- will not have different medium effects because of their differing central atoms.

Although the solubility of ferrocene in acetonitrile was not evaluated in this study, it can be calculated with the aid of Parker's value of -0.3 for $\log {}_{m}\gamma_{Foc}$ (27) referred to methanol as a reference solvent:

$$-0.3 = \log \frac{M(CH_3OH)}{M(CH_3CN)}$$

Using $M(CH_3OH) = +0.214$ molar (calculated using Parker's data (27) and the value $M(H_2O) = 5.38 \times 10^{-5}$ molar), $M(CH_3CN)$ is calculated to be +0.427 molar.

Error analysis.

A complete error analysis was performed on all the medium effects reported in this thesis. To do this, errors in solubility, C, activity coefficient, f, and degree of dissociation, α, had to be determined.

The relative error in the solubility determination of picrates and tetraphenylborates, (dC/C), was assigned a value of 0.006 and 0.01, respectively, based on analysis of known solutions of KPi and $KBPh_4$. The relative error in activity coefficients, $(df_{\pm,o}/f_{\pm,o})$, was reported in the computer print out sheets of the least square analysis program used to fit experimental data to Equation 170.

$df_{\pm,o}$ is the standard deviation of the activity coefficient. The relative error of the degree of dissociation, $(d\alpha/\alpha)$ was calculated by the method of propogation of errors:

$$\frac{d\alpha}{\alpha} = \left[\frac{dK_A}{K_A} + \frac{dC}{C} + \frac{df_{\pm}}{f_{\pm}}\right]\left[\frac{1}{(1 + 4K_A C f_{\pm})^{\frac{1}{2}}} - 1\right] \qquad (198)$$

Once the relative errors in C, $f_{\pm,o}$, and α are known, relative errors in ion-activity products $(dK_{sp}/(C\alpha f_{\pm,o})^2)$ are calculated using the equation:

$$\frac{dK_{sp}}{(C\alpha f_{\pm,o})^2} = \frac{dK_{sp}}{K_{sp}} = \left[2\left(\frac{d\alpha}{\alpha}\right)^2 + 2\left(\frac{dC}{C}\right)^2 + 2\left(\frac{df_{\pm,o}}{f_{\pm,o}}\right)^2 \right]^{\frac{1}{2}} \quad (199)$$

The relative error of the medium effect for a particular compound, $(d_m\gamma/_m\gamma)$, was determined by taking the square-root of the sum of the squares of the relative errors of the two solubility products involved:

$$\frac{d_m\gamma}{m\gamma} = \left[\left(\frac{dK_{sp}(H_2O)}{K_{sp}(H_2O)}\right)^2 + \left(\frac{dK_{sp}(s)}{K_{sp}(s)}\right)^2 \right]^{\frac{1}{2}} \quad (200)$$

The absolute error in $\log_m\gamma$, $d\log_m\gamma$, was evaluated using the equation

$$d\log_m\gamma = 0.43\,\frac{d_m\gamma}{m\gamma} \quad (201)$$

In the case of HCl where medium effects were evaluated from standard potentials of the Ag/AgCl electrode, errors in $\log_m\gamma_{HCl}$ were determined from the equation

$$d\log_m\gamma_{HCl} = \left[\left(\frac{dE^o(AgCl,H_2O)}{E^o(AgCl,H_2O)}\right)^2 + \left(\frac{dE^o(AgCl,s)}{E^o(AgCl,s)}\right)^2 \right]^{\frac{1}{2}} \quad (202)$$

where dE^{o} represents the standard deviation of the standard potential of the electrode. A similar equation was used to evaluate $d \log {}_{m}\gamma_{KCl}$.

Table 53 lists the results of the error analysis for $KBPh_4$, KPi, TAB Pi, Ph_4P Pi, Ph_4As Pi, $RbBPh_4$, and $CsBPh_4$ in ethanol--water solvents. Table 54 lists the results of the error analysis of $KBPh_4$, $RbBPh_4$, $CsBPh_4$, Ph_4P Pi, Ph_4As Pi, and KPi in acetonitrile. Table 55 lists results of the error analysis of HCl and KCl in ethanol--water solvents.

The absolute error in $\log {}_{m}\gamma$ for the reference electrolytes was was calculated by the method of propogation of errors. For example:

$$d \log {}_{m}\gamma_{Ph_4P\ BPh_4} = \left[(d \log {}_{m}\gamma_{Ph_4P\ Pi})^2 + (d \log {}_{m}\gamma_{KBPh_4})^2 + \right. \qquad (203)$$
$$\left. + (d \log {}_{m}\gamma_{KPi})^2 \right]^{\frac{1}{2}}$$

It must be pointed out that rarely, if ever, are error analyses reported in the literature for the experimental data from which medium effects are calculated. This is probably the first time that a rigorous error analysis has been performed both on the solubility products and on a series of medium effects.

Table 53. Error Analysis for Electrolytes in Ethanol--Water Solvents. 25°C, Molal Scale.

$KBPh_4$

wt.-% ethanol	$\frac{dC}{C}$	$\frac{d\alpha}{\alpha}$	$\frac{df_{\pm}{}'_o}{f_{\pm}{}'_o}$	$\frac{dK_{sp}}{K_{sp}}$	$\frac{d_m\gamma}{m\gamma}$	$d \log_m \gamma$
100.0	0.01	0.002	0.0038	0.055	0.057	0.025
90.6	0.01	-----	------	0.17	0.17	0.073
78.1	0.01	-----	0.0033	0.048	0.050	0.022
60.6	0.01	-----	------	0.026	0.030	0.013
38.4	0.01	-----	------	0.043	0.045	0.019
30.0	0.01	-----	------	0.014	0.020	0.009
20.0	0.01	-----	------	0.014	0.020	0.009
10.0	0.01	-----	------	0.014	0.020	0.009
0.0	0.01	-----	------	0.014	-----	-----

KPi

100.0	0.006	0.004	0.013	0.021	0.044	0.019
92.3	0.006	0.006	0.016	0.026	0.047	0.020
84.8	0.006	-----	-----	0.038	0.054	0.023
68.3	0.006	-----	0.033	0.047	0.061	0.023
58.8	0.006	-----	0.196	0.277	0.280	0.120
51.0	0.006	-----	0.006	0.012	0.040	0.017
37.3	0.006	-----	0.013	0.020	0.043	0.019
20.6	0.006	-----	0.039	0.056	0.068	0.029

Table 53. (Continued).

wt.-% ethanol	$\frac{dC}{C}$	$\frac{d\alpha}{\alpha}$	$\frac{df_{\pm,o}}{f_{\pm,o}}$	$\frac{dK_{sp}}{K_{sp}}$	$\frac{d_m\gamma}{m\gamma}$	$d \log_m \gamma$
			KPi (continued)			
10.2	0.006	-----	0.018	0.027	0.047	0.020
0.0	0.006	-----	0.027	0.039	-----	-----
			TAB Pi			
100.0	0.006	0.028	0.035	0.064	0.065	0.028
86.4	0.006	-----	-----	0.091	0.091	0.039
67.3	0.006	0.006	0.020	0.030	0.031	0.013
53.6	0.006	0.006	0.010	0.019	0.021	0.009
38.4	0.006	-----	0.005	0.011	0.014	0.006
30.0	0.006	-----	-----	0.009	0.012	0.005
20.0	0.006	-----	-----	0.009	0.012	0.005
10.0	0.006	-----	-----	0.009	0.012	0.005
0.0	0.006	-----	-----	0.009	0.012	0.005
			Ph_4P Pi			
100.0	0.006	0.008	0.030	0.045	0.046	0.020
93.2	0.006	0.005	0.004	0.012	0.015	0.006
80.8	0.006	0.002	0.011	0.018	0.020	0.009
70.6	0.006	0.009	0.009	0.020	0.022	0.009
61.0	0.006	-----	0.014	0.021	0.023	0.010
50.7	0.006	-----	0.039	0.055	0.056	0.024
39.3	0.006	-----	0.009	0.015	0.017	0.007
31.2	0.006	-----	0.003	0.010	0.013	0.006

Table 53. (Continued).

wt.-% ethanol	$\frac{dC}{C}$	$\frac{d\alpha}{\alpha}$	$\frac{df_{\pm,o}}{f_{\pm,o}}$	$\frac{dK_{sp}}{K_{sp}}$	$\frac{d_m\gamma}{m\gamma}$	$d \log_m \gamma$
			Ph_4P Pi (continued)			
19.9	0.006	-----	0.010	0.016	0.018	0.008
10.0	0.006	-----	0.005	0.011	0.014	0.006
0.0	0.006	-----	-----	0.009	-----	-----
			Ph_4As Pi			
100.0	0.006	0.005	0.012	0.020	0.022	0.009
93.3	0.006	0.008	0.013	0.023	0.024	0.011
80.7	0.006	0.004	0.014	0.022	0.024	0.010
70.7	0.006	0.005	0.017	0.026	0.028	0.012
60.9	0.006	-----	0.020	0.029	0.030	0.013
50.9	0.006	-----	0.019	0.028	0.029	0.013
39.7	0.006	-----	0.009	0.015	0.017	0.007
30.3	0.006	-----	0.015	0.022	0.024	0.010
20.4	0.006	-----	0.010	0.016	0.018	0.008
10.2	0.006	-----	0.004	0.010	0.013	0.006
0.0	0.006	-----	-----	0.009	-----	-----
			$RbBPh_4$			
100.0	0.01	-----	-----	0.092	0.097	0.042
0.0	0.01	-----	-----	0.028	-----	-----
			$CsBPh_4$			
100.0	0.01	-----	-----	0.119	0.131	0.057
0.0	0.01	-----	-----	0.057	-----	-----

Table 54. Error Analysis for Electrolytes in Acetonitrile. 25°C, Molal Scale.

Electrolyte	$\frac{dC}{C}$	$\frac{df_{\pm}'^{o}}{f_{\pm}'^{o}}$	$\frac{dK_{sp}}{K_{sp}}$	$\frac{d_m\gamma}{m\gamma}$	$d \log_m \gamma$
$KBPh_4$	0.01	0.069	0.099	0.100	0.043
$RbBPh_4$	0.01	0.069	0.099	0.103	0.044
$CsBPh_4$	0.01	0.069	0.099	0.114	0.049
Ph_4P Pi	0.006	0.069	0.098	0.099	0.042
Ph_4As Pi	0.006	0.069	0.098	0.099	0.042
KPi	0.006	0.069	0.098	0.106	0.045

Table 55. Error Analysis of HCl and KCl in Ethanol--Water Solvents. 25°C, Molal Scale.

wt.-% ethanol	$E^{o}(i,s)$	$\frac{dE^{o}(i,s)}{E^{o}(i,s)}$	$d \log_{m}\gamma$
		HCl	
100.0	-0.08138 (162) ±0.00005	0.0006	0.0006
98.0	0.0215 (163) ±0.0005	0.0233	0.0233
90.0	0.09166 (72) ±0.00005	0.0006	0.0006
80.0	0.129 (166) ±0.002	0.0155	0.0155
70.0	0.1563 (72) ±0.0005	0.0032	0.0032
60.0	0.175 (166) ±0.002	0.0114	0.0114
50.0	0.18588 (165) ±0.00005	0.0003	0.0003
40.0	0.19454 (165) ±0.00005	0.0003	0.0003
30.0	0.20033 (165) ±0.00005	0.0003	0.0003
20.0	0.20757 (164) ±0.00005	0.0002	0.0003
10.0	0.21467 (164) ±0.00005	0.0002	0.0003
0.0	0.22234 (167) ±0.00005	0.0002	------

Table 55. (Continued).

wt.-% ethanol	$E^{\circ}(i,s)$	$\frac{dE^{\circ}(i,s)}{E^{\circ}(i,s)}$	$d \log_m \gamma$
		KCl (72)	
100.0	1.8187 ±0.0005	0.00003	0.0000
92.3	1.8721 ±0.0005	0.00003	0.0000
80.3	1.9696 ±0.0005	0.00003	0.0000
60.2	2.0464 ±0.0005	0.00002	0.0000
40.0	2.1075 ±0.0005	0.00002	0.0000
20.3	2.1558 ±0.0005	0.00002	0.0000
15.0	2.1714 ±0.0005	0.00002	0.0000
0.0	2.1931 ±0.0005	0.00002	0.0000

From the literature.

Standard potentials of various electrodes in ethanol, methanol, and acetonitrile taken from the literature are given in Table 56. Values of ${}_sE^o(Ag/AgCl,s)$ and ${}_sE^o(K,s)$ in ethanol--water solvents are given in Table 57. These standard potentials were used in conjunction with Equations 49, 51, and 55 to calculate medium effects for electroneutral combinations of ions.

Table 56. Standard Potentials, ${}_sE^\circ(i,s)$, in Water, Ethanol, Methanol, and Acetonitrile (in Volts). 25°C, Molal Scale.

Electrode	${}_wE^\circ(i,H_2O)$(156)	${}_sE^\circ(i,C_2H_5OH)$	${}_sE^\circ(i,CH_3OH)$	${}_sE^\circ(i,CH_3CN)$(161)
Na/Na^+	-2.714	-2.657 (169)	-2.728 (155)	-2.87
Li/Li^+	-3.045	-3.042 (169)	-3.095 (157)	-3.23
Ca/Ca^{+2}	+2.87	-----	-----	+2.75
Zn/Zn^{+2}	-0.763	-----	-0.74 (155)	-0.74
Cd/Cd^{+2}	-0.403	-----	-0.43 (155)	-0.47
Pb/Pb^{+2}	-0.126	-----	-----	-0.12
Cu/Cu^{+2}	+0.337	-----	-----	+0.28
Cu/Cu^+	+0.521	-----	+0.490 (155)	-0.38
Ag/AgBr	-0.095	-0.182 (168)	-----	----

Table 57. Standard Potentials, ${}_sE^\circ(i,s)$, in Ethanol--Water Solvents (in Volts). 25°C, Molal Scale.

wt.-% ethanol	${}_sE^\circ(K,s)$ (72)	${}_sE^\circ(Ag,AgCl,s)$
100.0	-2.865	-0.08138 (162)
98.0	-----	0.0215 (163)
94.3	-----	0.066 (166)
92.3	-2.757	-----
88.5	-----	0.1053 (163)
80.3	-2.799	-----
80.0	-----	0.129 (166)
71.9	-----	0.1554 (163)
60.2	-2.830	-----
60.0	-----	0.175 (166)
50.0	-----	0.18588 (165)
46.0	-----	0.1928 (163)
40.0	-2.8687	0.19454 (165)
30.0	-----	0.20033 (165)
20.3	-2.9021	-----
20.0	-----	0.20757 (164)
15.0	-2.9136	-----
10.0	-----	0.21467 (164)
0.0	-2.9230	0.22234 (167)

Estimation of medium effects for single ions by the reference-electrolyte method.

Ethanol--water solvents.

Calculations by the tetraphenyl-ion assumption.

Thermodynamic medium effects for the three reference electrolytes, Ph_4P BPh_4, Ph_4As BPh_4, and TAB BPh_4 are now available in ethanol--water solvents, methanol, and acetonitrile. Medium effects for various other electrolytes are also available in these solvents. Thus, we are ready now to apply the reference-electrolyte assumption to yield medium effects first for the reference ions, which can then be used to obtain medium effects for other single ions.

The reference-electrolyte assumption states that for an electrolyte composed of large symmetrical ions as similar as available in size, structure, surface charge density, polarizability, and undergoing no specific interactions with solvent, the medium effect can be apportioned equally between the anion and cation. Applying the reference-electrolyte assumption to the three reference electrolytes studied, we obtain values of medium effects for single ions as follows:

$$\log {}_{m}\gamma_{Ph_4P} = \log {}_{m}\gamma_{BPh_4} = \tfrac{1}{2}\log {}_{m}\gamma_{Ph_4P\,BPh_4} \qquad (140)$$

$$\log {}_{m}\gamma_{Ph_4As} = \log {}_{m}\gamma_{BPh_4} = \tfrac{1}{2}\log {}_{m}\gamma_{Ph_4As\,BPh_4} \qquad (141)$$

$$\log {}_{m}\gamma_{TAB} = \log {}_{m}\gamma_{BPh_4} = \tfrac{1}{2}\log {}_{m}\gamma_{TAB\,BPh_4} \qquad (142)$$

Numerical values of $\log {}_{m}\gamma$ for the reference ions in ethanol--water solvents on the molar and molal scales with either water or ethanol as reference solvent are listed in Tables 58 - 61.

Medium effects for potassium ion have been calculated from the known values of ${}_{m}\gamma_{KBPh_4}$ and $\log {}_{m}\gamma_{BPh_4}$:

$$\log {}_{m}\gamma_{K} = \log {}_{m}\gamma_{KBPh_4} - \log {}_{m}\gamma_{BPh_4} \qquad (204)$$

Similarly, medium effects for picrate, chloride, and hydrogen ions have been calculated via the relationships:

$$\log {}_{m}\gamma_{Pi} = \log {}_{m}\gamma_{KPi} - \log {}_{m}\gamma_{K} \qquad (205)$$

$$\log {}_{m}\gamma_{Cl} = \log {}_{m}\gamma_{KCl} - \log {}_{m}\gamma_{K} \qquad (206)$$

$$\log {}_{m}\gamma_{H} = \log {}_{m}\gamma_{HCl} - \log {}_{m}\gamma_{Cl} \qquad (207)$$

Table 58. Medium Effects, $\log_m \gamma$, for Reference Ions in Ethanol--Water Solvents. Water is the Reference Solvent, 25°C, Molal Scale.

wt.-% ethanol	$Ph_4P^+ = BPh_4^-$	$Ph_4As^+ = BPh_4^-$	$TAB^+ = BPh_4^-$
0.0	0.0	0.0	0.0
10.0	-0.438 ±0.01	-0.435 ±0.01	-0.305 ±0.01
20.0	-0.998 ±0.02	-1.018 ±0.02	-0.692 ±0.02
30.0	-1.735 ±0.01	-1.738 ±0.01	-1.287 ±0.01
40.0	-2.439 ±0.01	-2.470 ±0.01	-1.992 ±0.01
50.0	-2.862 ±0.02	-2.874 ±0.02	-2.496 ±0.01
60.0	-3.278 ±0.02	-3.300 ±0.02	-2.962 ±0.02
70.0	-3.413 ±0.01	-3.445 ±0.02	-3.166 ±0.02
80.0	-3.524 ±0.01	-3.572 ±0.02	-3.385 ±0.02
90.0	-3.642 ±0.04	-3.699 ±0.04	-3.635 ±0.04
100.0	-3.590 ±0.02	-3.672 ±0.01	-3.791 ±0.02

Table 59. Medium Effects, $\log {}_m\gamma$, for Reference Ions in Ethanol--Water Solvents. Water is the Reference Solvent. 25°C, Molar Scale.

wt.-% ethanol	Ph_4P^+ = = BPh_4^-	Ph_4As^+ = = BPh_4^-	TAB^+ = = BPh_4^-
0.0	0.0	0.0	0.0
10.0	-0.430	-0.428	-0.298
20.0	-0.985	-1.005	-0.678
30.0	-1.715	-1.718	-1.266
40.0	-2.409	-2.441	-1.963
50.0	-2.822	-2.834	-2.457
60.0	-3.228	-3.249	-2.912
70.0	-3.351	-3.383	-3.103
80.0	-3.449	-3.497	-3.310
90.0	-3.553	-3.610	-3.547
100.0	-3.486	-3.569	-3.687

Table 60. Medium Effects, $\log_m \gamma$, for Reference Ions in Ethanol--Water Solvents. Ethanol is the Reference Solvent. 25°C, Molal Scale.

wt.-% ethanol	Ph_4P^+ = = BPh_4^-	Ph_4As^+ = = BPh_4^-	TAB^+ = = BPh_4^-
0.0	3.590	3.672	3.791
10.0	3.152	3.237	3.486
20.0	2.591	2.654	3.099
30.0	1.854	1.934	2.504
40.0	1.151	1.202	1.798
50.0	0.728	0.799	1.294
60.0	0.311	0.373	0.828
70.0	0.176	0.227	0.625
80.0	0.065	0.101	0.406
90.0	-0.052	-0.026	0.155
100.0	0.0	0.0	0.0

Table 61. Medium Effects, $\log_m \gamma$, for Reference Ions in Ethanol--Water Solvents. Ethanol is the Reference Solvent. 25°C, Molar Scale.

wt.-% ethanol	$Ph_4P^+ = BPh_4^-$	$Ph_4As^+ = BPh_4^-$	$TAB^+ = BPh_4^-$
0.0	3.486	3.569	3.687
10.0	3.055	3.141	3.389
20.0	2.501	2.564	3.009
30.0	1.771	1.851	2.421
40.0	1.076	1.128	1.724
50.0	0.664	0.735	1.230
60.0	0.258	0.320	0.775
70.0	0.135	0.186	0.583
80.0	0.036	0.072	0.377
90.0	-0.068	-0.042	0.140
100.0	0.0	0.0	0.0

A listing of medium effects, $\log {}_m\gamma$, for K^+, Pi^-, Cl^-, and H^+ ions in ethanol--water solvents, on the molar and molal scales, using both water and ethanol as reference solvents, is given in Tables 62 - 65. In these tables, medium effects for single ions are listed according to the reference electrolyte used to obtain the value of $\log {}_m\gamma_{BPh_4}$.

The differences between values of $\log {}_m\gamma_{BPh_4}$ obtained using Ph_4P BPh_4 and Ph_4As BPh_4 are usually quite small and within experimental error (see Table 66). Because of this, medium effects for the reference ions obtained from both tetraphenyl electrolytes can be averaged to obtain the "tetraphenyl" (Ph_4^+) medium effects. Table 67 lists average values of $\log {}_m\gamma_{BPh_4}$ based on the Ph_4P BPh_4 and Ph_4As BPh_4 reference electrolytes. This average value, termed $\log {}_m\gamma_{Ph_4}$, can be formulated with the equation

$$\log {}_m\gamma_{Ph_4} = \tfrac{1}{2} \log {}_m\gamma_{Ph_4P\ BPh_4} + \tfrac{1}{2} \log {}_m\gamma_{Ph_4As\ BPh_4} \qquad (208)$$

Medium effects for K^+, Pi^-, Cl^-, and H^+ based on $\log {}_m\gamma_{Ph_4}$ are reported in Table 68 along with their standard deviations.

Medium effects for single ions in ethanol--water solvents obtained via the Ph_4^+ or the TAB^+ assumptions

Table 62. Medium Effects, $\log_m \gamma$, for Single Ions in Ethanol--Water Solvents. Water is the Reference Solvent. 25°C, Molal Scale.

wt.-% ethanol	K^+ Ph_4P^+	K^+ Ph_4As^+	K^+ TAB^+	Pi^- Ph_4P^+	Pi^- Ph_4As^+	Pi^- TAB^+
0.0	0.0	0.0	0.0	0.0	0.0	0.0
10.0	0.223	0.221	0.090	-0.028	-0.026	0.105
20.0	0.401	0.421	0.094	-0.136	-0.156	0.171
30.0	0.547	0.550	0.098	-0.368	-0.371	0.081
40.0	0.574	0.606	0.128	-0.477	-0.509	-0.031
50.0	0.610	0.622	0.244	-0.594	-0.606	-0.229
60.0	0.766	0.788	0.450	-0.546	-0.568	-0.230
70.0	0.960	0.992	0.713	-0.602	-0.634	-0.354
80.0	1.361	1.409	1.222	-0.516	-0.563	-0.376
90.0	2.024	2.082	2.018	-0.295	-0.352	-0.288
100.0	2.633	2.716	2.834	+0.033	-0.050	-0.168

wt.-% ethanol	Cl^- Ph_4P^+	Cl^- Ph_4As^+	Cl^- TAB^+	H^+ Ph_4P^+	H^+ Ph_4As^+	H^+ TAB^+
0.0	0.0	0.0	0.0	0.0	0.0	0.0
10.0	0.047	0.050	0.180	0.083	0.080	-0.051
20.0	0.199	0.179	0.506	0.051	0.071	-0.256
30.0	0.433	0.430	0.882	-0.061	-0.058	-0.510
40.0	0.816	0.785	1.263	-0.346	-0.315	-0.793
50.0	1.240	1.228	1.606	-0.624	-0.612	-0.989
60.0	1.604	1.583	1.920	-0.804	-0.782	-1.120
70.0	1.990	1.958	2.237	-0.874	-0.842	-1.121
80.0	2.259	2.211	2.398	-0.681	-0.633	-0.820
90.0	2.696	2.639	2.702	-0.487	-0.430	-0.493
100.0	3.487	3.404	3.286	+1.647	+1.730	+1.848

Table 63. Medium Effects, $\log_m \gamma$, for Single Ions in Ethanol--Water Solvents. Water is the Reference Solvent. 25°C, Molar Scale.

wt.-% ethanol	K^+ Ph_4P^+	K^+ Ph_4As^+	K^+ TAB^+	Pi^- Ph_4P^+	Pi^- Ph_4As^+	Pi^- TAB^+
0.0	0.0	0.0	0.0	0.0	0.0	0.0
10.0	0.230	0.228	0.097	-0.021	-0.018	0.112
20.0	0.414	0.435	0.108	-0.122	-0.143	0.184
30.0	0.568	0.571	0.119	-0.347	-0.350	0.102
40.0	0.604	0.635	0.157	-0.448	-0.479	-0.001
50.0	0.649	0.662	0.284	-0.554	-0.566	-0.189
60.0	0.817	0.838	0.501	-0.495	-0.517	-0.179
70.0	1.023	1.055	0.775	-0.539	-0.571	-0.292
80.0	1.436	1.484	1.297	-0.441	-0.488	-0.301
90.0	2.113	2.170	2.107	-0.206	-0.263	-0.200
100.0	2.737	2.820	2.938	+0.137	+0.054	-0.065

wt.-% ethanol	Cl^- Ph_4P^+	Cl^- Ph_4As^+	Cl^- TAB^+	H^+ Ph_4P^+	H^+ Ph_4As^+	H^+ TAB^+
0.0	0.0	0.0	0.0	0.0	0.0	0.0
10.0	-0.086	-0.084	0.047	0.230	0.228	0.097
20.0	0.213	0.193	0.519	0.064	0.084	-0.242
30.0	0.453	0.450	0.902	-0.040	-0.037	-0.489
40.0	0.845	0.814	1.292	-0.316	-0.285	-0.763
50.0	1.281	1.268	1.646	-0.585	-0.572	-0.950
60.0	1.655	1.634	1.971	-0.754	-0.732	-1.069
70.0	2.052	2.020	2.300	-0.811	-0.779	-1.058
80.0	2.334	2.286	2.473	-0.606	-0.559	-0.745
90.0	2.784	2.727	2.791	-0.399	-0.342	-0.405
100.0	3.591	3.509	3.390	+1.750	+1.833	+1.951

Table 64. Medium Effects, $\log_m \gamma$, for Single Ions in Ethanol--Water Solvents. Ethanol is the Reference Solvent. 25°C, Molal Scale.

wt.-% ethanol	K^+ Ph_4P^+	K^+ Ph_4As^+	K^+ TAB^+	Pi^- Ph_4P^+	Pi^- Ph_4As^+	Pi^- TAB^+
0.0	-2.633	-2.716	-2.834	-0.033	0.050	0.168
10.0	-2.410	-2.495	-2.744	-0.061	0.025	0.273
20.0	-2.232	-2.295	-2.740	-0.169	-0.106	0.339
30.0	-2.086	-2.166	-2.736	-0.400	-0.320	0.250
40.0	-2.058	-2.110	-2.706	-0.510	-0.458	0.138
50.0	-2.023	-2.094	-2.589	-0.627	-0.556	-0.060
60.0	-1.867	-1.928	-2.384	-0.579	-0.517	-0.062
70.0	-1.673	-1.724	-2.121	-0.634	-0.583	-0.186
80.0	-1.272	-1.307	-1.612	-0.548	-0.513	-0.208
90.0	-0.608	-0.634	-0.816	-0.327	-0.301	-0.120
100.0	0.0	0.0	0.0	0.0	0.0	0.0

wt.-% ethanol	Cl^- Ph_4P^+	Cl^- Ph_4As^+	Cl^- TAB^+	H^+ Ph_4P^+	H^+ Ph_4As^+	H^+ TAB^+
0.0	-3.487	-3.404	-3.286	-1.647	-1.730	-1.848
10.0	-3.490	-3.405	-3.156	-1.514	-1.599	-1.848
20.0	-3.338	-3.275	-2.830	-1.546	-1.609	-2.054
30.0	-3.094	-3.014	-2.444	-1.668	-1.748	-2.317
40.0	-2.672	-2.620	-2.024	-1.992	-2.044	-2.640
50.0	-2.247	-2.176	-1.681	-2.271	-2.341	-2.837
60.0	-1.883	-1.822	-1.366	-2.451	-2.512	-2.967
70.0	-1.528	-1.477	-1.079	-2.490	-2.541	-2.939
80.0	-1.249	-1.213	-0.908	-2.308	-2.343	-2.648
90.0	-0.652	-0.626	-0.444	-2.273	-2.299	-2.481
100.0	0.0	0.0	0.0	0.0	0.0	0.0

Table 65. Medium Effects, $\log_m \gamma$, for Single Ions in Ethanol--Water Solvents. Ethanol is the Reference Solvent. 25°C, Molar Scale.

wt.-% ethanol	K^+ Ph_4P^+	K^+ Ph_4As^+	K^+ TAB^+	Pi^- Ph_4P^+	Pi^- Ph_4As^+	Pi^- TAB^+
0.0	-2.737	-2.820	-2.938	-0.137	-0.054	0.065
10.0	-2.507	-2.592	-2.840	-0.157	-0.072	0.177
20.0	-2.322	-2.385	-2.830	-0.259	-0.196	0.249
30.0	-2.169	-2.249	-2.819	-0.483	-0.403	0.167
40.0	-2.133	-2.185	-2.781	-0.584	-0.533	0.064
50.0	-2.087	-2.158	-2.654	-0.691	-0.620	-0.124
60.0	-1.920	-1.981	-2.437	-0.632	-0.570	-0.115
70.0	-1.714	-1.765	-2.162	-0.676	-0.625	-0.227
80.0	-1.301	-1.336	-1.641	-0.577	-0.542	-0.237
90.0	-0.624	-0.650	-0.831	-0.343	-0.317	-0.135
100.0	0.0	0.0	0.0	0.0	0.0	0.0

wt.-% ethanol	Cl^- Ph_4P^+	Cl^- Ph_4As^+	Cl^- TAB^+	H^+ Ph_4P^+	H^+ Ph_4As^+	H^+ TAB^+
0.0	-3.591	-3.509	-3.390	-1.750	-1.833	-1.951
10.0	-3.587	-3.501	-3.253	-1.611	-1.696	-1.945
20.0	-3.429	-3.366	-2.921	-1.636	-1.699	-2.144
30.0	-3.177	-3.097	-2.527	-1.751	-1.831	-2.401
40.0	-2.746	-2.695	-2.099	-2.066	-2.118	-2.714
50.0	-2.311	-2.240	-1.745	-2.335	-2.406	-2.901
60.0	-1.936	-1.875	-1.419	-2.504	-2.565	-3.021
70.0	-1.569	-1.518	-1.121	-2.531	-2.582	-2.980
80.0	-1.278	-1.242	-0.937	-2.336	-2.372	-2.677
90.0	-0.667	-0.641	-0.460	-2.289	-2.315	-2.496
100.0	0.0	0.0	0.0	0.0	0.0	0.0

Table 66. Difference Between the Estimates of $\log {}_m\gamma_{BPh_4}$ From the $Ph_4P\,BPh_4$ and $Ph_4As\,BPh_4$ Reference Electrolytes in Ethanol--Water Solvents. Water is the Reference Solvent. 25°C, Molal Scale.

wt.-% ethanol	$(\log {}_m\gamma_{Ph_4P} - \log {}_m\gamma_{Ph_4As})$
0.0	0.0
10.0	-0.002
20.0	+0.020
30.0	+0.003
40.0	+0.031
50.0	+0.012
60.0	+0.022
70.0	+0.032
80.0	+0.048
90.0	+0.057
100.0	+0.083

Table 67. Average Value of $\log {}_{m}\gamma_{BPh_4}$ Based on the $Ph_4P\,BPh_4$ and $Ph_4As\,BPh_4$ Reference Electrolytes, $\log {}_{m}\gamma_{Ph_4}$, in Ethanol--Water Solvents. Water is the Reference Solvent. 25°C, Molal Scale.

wt.-% ethanol	$\log {}_{m}\gamma_{Ph_4}$
0.0	0.0
10.0	-0.437
20.0	-1.008
30.0	-1.737
40.0	-2.455
50.0	-2.868
60.0	-3.289
70.0	-3.429
80.0	-3.548
90.0	-3.671
100.0	-3.631

Table 68. Medium Effects, $\log_m \gamma$, for Single Ions in Ethanol--Water Solvents Based on the TAB BPh_4 and the Ph_4^+ Assumptions. Water is the Reference Solvent. 25°C, Molal Scale.

wt.-% ethanol	K^+		Pi^-		Cl^-		H^+	
	Ph_4^+	TAB^+	Ph_4^+	TAB^+	Ph_4^+	TAB^+	Ph_4^+	TAB^+
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
10.0	0.22 ±0.02	0.08 ±0.01	-0.02 ±0.02	0.10 ±0.01	0.05 ±0.02	0.19 ±0.01	0.08 ±0.02	-0.06 ±0.02
20.0	0.41 ±0.03	0.09 ±0.02	-0.14 ±0.03	0.17 ±0.02	0.19 ±0.03	0.51 ±0.02	0.06 ±0.03	-0.26 ±0.02
30.0	0.55 ±0.02	0.10 ±0.01	-0.36 ±0.02	0.09 ±0.01	0.43 ±0.02	0.88 ±0.01	-0.06 ±0.02	-0.51 ±0.01
40.0	0.60 ±0.04	0.13 ±0.02	-0.49 ±0.02	-0.03 ±0.02	0.79 ±0.04	1.26 ±0.02	-0.32 ±0.04	-0.79 ±0.02
50.0	0.61 ±0.04	0.25 ±0.02	-0.61 ±0.03	-0.22 ±0.02	1.24 ±0.04	1.60 ±0.02	-0.62 ±0.04	-0.98 ±0.02
60.0	0.78 ±0.03	0.45 ±0.02	-0.55 ±0.03	-0.23 ±0.02	1.59 ±0.03	1.92 ±0.02	-0.80 ±0.03	-1.13 ±0.02
70.0	0.97 ±0.04	0.72 ±0.03	-0.63 ±0.02	-0.35 ±0.04	1.98 ±0.04	2.23 ±0.03	-0.86 ±0.04	-1.11 ±0.03
80.0	1.38 ±0.04	1.22 ±0.03	-0.54 ±0.02	-0.38 ±0.05	2.24 ±0.04	2.40 ±0.03	-0.67 ±0.04	-0.83 ±0.03
90.0	2.05 ±0.11	2.01 ±0.08	-0.32 ±0.05	-0.29 ±0.06	2.67 ±0.11	2.71 ±0.08	-0.46 ±0.11	-0.50 ±0.08
100.0	2.67 ±0.04	2.83 ±0.03	-0.01 ±0.03	-0.17 ±0.04	3.45 ±0.04	3.29 ±0.03	+1.68 ±0.04	+1.84 ±0.03

can differ by as much as 0.46 log units. Table 69 lists differences between medium effects for single ions in ethanol--water solvents obtained from the two assumptions.

Medium effects for thallium (I) ion in ethanol--water solvents were calculated using the equation

$$\log {}_m\gamma_{Tl} = \log {}_m\gamma_{TlCl} - \log {}_m\gamma_{Cl} \qquad (209)$$

Values for $\log {}_m\gamma_{Tl}$ based on the Ph_4P BPh_4, Ph_4As BPh_4, TAB BPh_4, and the Ph_4^+ assumptions are listed in Table 70.

Table 71 lists values of $\log {}_m\gamma$ for Na^+, Li^+, Rb^+, Cs^+, and Br^- ions calculated from e.m.f. (for Na^+, Li^+, Br^-) and solubility (for Rb^+, Cs^+) data using the TAB BPh_4 and Ph_4^+ assumptions. E.m.f. data give values of $(\log {}_m\gamma_M - \log {}_m\gamma_H)$ (where $M = Li^+$, Na^+) or $(\log {}_m\gamma_X + \log {}_m\gamma_H)$ (where $X = Br$). From these combinations, values of $\log {}_m\gamma_M$ or $\log {}_m\gamma_X$ can be calculated :

$$\log {}_m\gamma_M = (\log {}_m\gamma_M - \log {}_m\gamma_H) + \log {}_m\gamma_H \qquad (210)$$

$$\log {}_m\gamma_X = (\log {}_m\gamma_X + \log {}_m\gamma_H) - \log {}_m\gamma_H \qquad (211)$$

Values for $\log {}_m\gamma_{Rb}$ and $\log {}_m\gamma_{Cs}$ in 100 % ethanol

Table 69. Difference Between Estimates of $\log {}_m\gamma_{BPh_4}$ From the Ph_4^+ and TAB BPh_4 Assumptions in Ethanol--Water Solvents. Water is the Reference Solvent. 25°C, Molal Scale.

wt.-% ethanol	$(\log {}_m\gamma_{TAB} - \log {}_m\gamma_{Ph_4})$
0.0	0.0
10.0	0.13
20.0	0.32
30.0	0.45
40.0	0.46
50.0	0.37
60.0	0.33
70.0	0.26
80.0	0.16
90.0	0.03
100.0	-0.17

Table 70. Medium Effects of Thallium (I), $\log {}_{m}\gamma_{Tl}$, in Ethanol--Water Solvents. Water is the Reference Solvent. 25°C, Molal Scale.

wt.-% ethanol	Ph_4P^+	Ph_4As^+	TAB^+	Ph_4^+
0.0	0.0	0.0	0.0	0.0
10.0	0.228	0.225	0.095	0.226
20.0	0.368	0.388	0.061	0.378
30.0	0.424	0.427	-0.025	0.426
40.0	0.348	0.379	-0.099	0.364
50.0	0.265	0.277	-0.101	0.271
60.0	0.350	0.371	0.034	0.361
70.0	0.397	0.429	0.150	0.413
80.0	0.820	0.868	0.681	0.844
90.0	1.295	1.352	1.289	1.323
100.0	1.569	1.652	1.770	1.611

Table 71. Medium Effects, $\log {}_{m}\gamma$, for Single Ions in 100 % Ethanol. Water is the Reference Solvent. 25°C, Molal Scale.

Ion	$\log {}_{m}\gamma$ TAB^{+}	$\log {}_{m}\gamma$ Ph_4^{+}
Li^{+}	+1.89	+1.73
Na^{+}	+2.80	+2.64
Rb^{+}	+2.85 ± 0.04	+2.69 ± 0.04
Cs^{+}	+2.64 ± 0.06	+2.48 ± 0.06
Br^{-}	-0.37	-0.21

were calculated using values of -0.94 and -1.15 for $\log {}_{m}\gamma_{RbBPh_4}$ and $\log {}_{m}\gamma_{CsBPh_4}$, respectively:

$$\log {}_{m}\gamma_{Rb} = \log {}_{m}\gamma_{RbBPh_4} - \log {}_{m}\gamma_{BPh_4} \qquad (212)$$

$$\log {}_{m}\gamma_{Cs} = \log {}_{m}\gamma_{CsBPh_4} - \log {}_{m}\gamma_{BPh_4} \qquad (213)$$

Error analysis.

Standard deviations of $\log_m \gamma$ fpr the reference electrolytes were evaluated from previously determined values of $d \log_m \gamma$ (see Tables 53, 55) for the appropriate electrolytes:

$$d \log_m \gamma_{Ph_4P\ BPh_4} = \left[(d \log_m \gamma_{Ph_4P\ Pi})^2 + (d \log_m \gamma_{KBPh_4})^2 + (d \log_m \gamma_{KPi})^2 \right]^{\frac{1}{2}} \quad (214)$$

$$d \log_m \gamma_{Ph_4As\ BPh_4} = \left[(d \log_m \gamma_{Ph_4As\ Pi})^2 + (d \log_m \gamma_{KBPh_4})^2 + (d \log_m \gamma_{KPi})^2 \right]^{\frac{1}{2}} \quad (215)$$

$$d \log_m \gamma_{TAB\ BPh_4} = \left[(d \log_m \gamma_{TAB\ Pi})^2 + (d \log_m \gamma_{KBPh_4})^2 + (d \log_m \gamma_{KPi})^2 \right]^{\frac{1}{2}} \quad (216)$$

Values of $d \log_m \gamma$ for the reference electrolytes along with values of $d \log_m \gamma$ for the reference ions determined using the following equations are listed in Table 72.

$$d \log_m \gamma_{Ph_4P} = d \log_m \gamma_{BPh_4} = \tfrac{1}{2} d \log_m \gamma_{Ph_4PBPh_4} \quad (217)$$

$$d \log_m \gamma_{Ph_4As} = d \log_m \gamma_{BPh_4} = \tfrac{1}{2} d \log_m \gamma_{Ph_4As\ BPh_4} \quad (218)$$

$$d \log_{m}\gamma_{TAB} = d \log_{m}\gamma_{BPh_4} = \tfrac{1}{2} d \log_{m}\gamma_{TAB\,BPh_4} \qquad (219)$$

Standard deviations in the medium effect for potassium ions, $d \log_{m}\gamma_{K}$, in ethanol--water solvents were calculated using the equation:

$$d \log_{m}\gamma_{K} = \left[(d \log_{m}\gamma_{KBPh_4})^2 + (d \log_{m}\gamma_{\text{reference ion}})^2 \right]^{\frac{1}{2}} \qquad (220)$$

Values for $d \log_{m}\gamma_{K}$ using the three reference electrolytes and the Ph_4^+ assumption appear in Table 73 along with values of $d \log_{m}\gamma_{Pi}$, $d \log_{m}\gamma_{Cl}$, and $d \log_{m}\gamma_{H}$ calculated using the following equations:

$$d \log_{m}\gamma_{Pi} = \left[(d \log_{m}\gamma_{KPi})^2 + (d \log_{m}\gamma_{K})^2 \right]^{\frac{1}{2}} \qquad (221)$$

$$d \log_{m}\gamma_{Cl} = \left[(d \log_{m}\gamma_{KCl})^2 + (d \log_{m}\gamma_{K})^2 \right]^{\frac{1}{2}} \qquad (222)$$

$$d \log_{m}\gamma_{H} = \left[(d \log_{m}\gamma_{HCl})^2 + (d \log_{m}\gamma_{Cl})^2 \right]^{\frac{1}{2}} \qquad (223)$$

Standard deviations of $\log_{m}\gamma$ for single ions in ethanol--water solvents are about 0.02 - 0.04 log units in most cases. This corresponds to a precision of a few percent in the determination of medium effects. This is

Table 72. Standard Deviations of Medium Effects, $d \log {}_m\gamma$, of Reference Electrolytes and Reference Ions in Ethanol--Water Solvents. Water is the Reference Solvent. 25°C, Molal Scale.

wt.-% ethanol	$d \log {}_m\gamma_{Ph_4P\text{-}BPh_4}$	$\frac{d \log {}_m\gamma_{Ph_4P\text{-}BPh_4}}{d \log {}_m\gamma_{BPh_4}}$	$d \log {}_m\gamma_{Ph_4As\text{-}BPh_4}$	$\frac{d \log {}_m\gamma_{Ph_4As\text{-}BPh_4}}{d \log {}_m\gamma_{BPh_4}}$	$d \log {}_m\gamma_{TAB\text{-}BPh_4}$	$\frac{d \log {}_m\gamma_{TAB\text{-}BPh_4}}{d \log {}_m\gamma_{BPh_4}}$
0.0	0.0	0.0	0.0	0.0	0.0	0.0
10.0	0.023	0.011	0.023	0.011	0.023	0.011
20.0	0.032	0.016	0.032	0.016	0.032	0.016
30.0	0.023	0.011	0.024	0.012	0.023	0.011
40.0	0.029	0.015	0.029	0.015	0.029	0.015
50.0	0.035	0.017	0.030	0.015	0.030	0.015
60.0	0.033	0.017	0.033	0.017	0.033	0.017
70.0	0.030	0.015	0.030	0.015	0.041	0.021
80.0	0.030	0.015	0.030	0.015	0.049	0.025
90.0	0.073	0.037	0.074	0.037	0.083	0.042
100.0	0.035	0.017	0.030	0.015	0.041	0.021

Table 73. Standard Deviations of Medium Effects, $d \log_m \gamma$, for Single Ions in Ethanol--Water Solvents. Water is the Reference Solvent. 25°C, Molal Scale.

wt.-% ethanol	K^+ Ph_4P BPh_4	K^+ Ph_4As BPh_4	K^+ TAB BPh_4	K^+ Ph_4^+	Pi^- Ph_4P BPh_4	Pi^- Ph_4As BPh_4	Pi^- TAB BPh_4	Pi^- Ph_4^+
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
10.0	0.015	0.015	0.014	0.021	0.013	0.013	0.012	0.018
20.0	0.019	0.019	0.018	0.026	0.018	0.018	0.017	0.026
30.0	0.015	0.015	0.014	0.021	0.013	0.016	0.012	0.020
40.0	0.025	0.025	0.025	0.035	0.016	0.016	0.016	0.023
50.0	0.026	0.025	0.025	0.036	0.026	0.018	0.017	0.032
60.0	0.019	0.019	0.019	0.027	0.019	0.019	0.019	0.027
70.0	0.025	0.025	0.029	0.035	0.017	0.018	0.036	0.025
80.0	0.025	0.025	0.032	0.035	0.017	0.018	0.047	0.025
90.0	0.079	0.079	0.081	0.112	0.037	0.038	0.058	0.053
100.0	0.026	0.025	0.029	0.036	0.026	0.017	0.036	0.032

Table 73. (Continued).

wt.-% ethanol	Cl^- $Ph_4P\ BPh_4$	Cl^- $Ph_4As\ BPh_4$	Cl^- TAB BPh_4	Cl^- Ph_4^+	H^+ $Ph_4P\ BPh_4$	H^+ $Ph_4As\ BPh_4$	H^+ TAB BPh_4	H^+ Ph_4^+
0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
10.0	0.015	0.015	0.014	0.021	0.018	0.018	0.018	0.025
20.0	0.019	0.019	0.018	0.026	0.019	0.019	0.018	0.026
30.0	0.015	0.015	0.014	0.021	0.015	0.015	0.014	0.021
40.0	0.025	0.025	0.025	0.035	0.025	0.025	0.025	0.035
50.0	0.026	0.025	0.025	0.036	0.026	0.025	0.025	0.036
60.0	0.019	0.019	0.019	0.027	0.022	0.022	0.022	0.031
70.0	0.025	0.025	0.029	0.035	0.025	0.025	0.029	0.035
80.0	0.025	0.025	0.032	0.035	0.025	0.025	0.032	0.035
90.0	0.079	0.079	0.081	0.112	0.079	0.079	0.081	0.112
100.0	0.026	0.025	0.029	0.036	0.026	0.025	0.029	0.036

certainly excellent precision considering the many steps required to arrive at some medium effects for single ions. No other method yet proposed for estimating medium effects for single ions has yielded such precise results.

Interpretation of results.

Structure of solvent.

Medium effects are defined as differences between standard free energies of solvation and hydration and for this reason it is important to know as much as possible about the arrangement of solvent molecules in the bulk solvent so that medium effects can be interpreted properly. Water is undoubtedly the most widely studied solvent as far as solvent structure is concerned (48, 59, 82, 114, 32, 77, 170). The presently accepted model of the structure of water put forth by Bernal and Fowler (48) in 1933, pictures water as a highly-structured three-dimensional hydrogen-bonded liquid in which a large portion of the water molecules are tetrahedrally bonded to each other to form the water network. Some water molecules are not bound to this rigid structure and these are found in intermediate or interstitial positions. There is an interchange between the molecules in the more rigid structure and the interstitial or unbonded water molecules. The whole solvent structure is constantly changing due to this dynamic equilibrium. This view of liquid water has not changed much (32, 77) over the past twenty years.

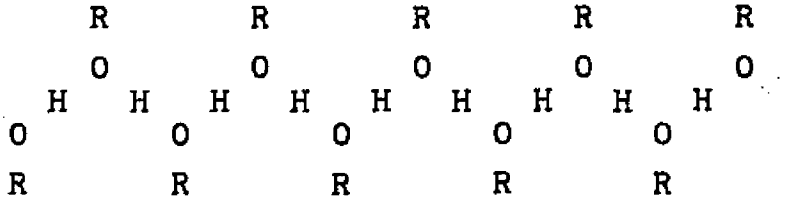
Frank and Wen's (82) famous "iceberg" model of liquid water was proposed in 1957. In this model,

water is pictured as a collection of non-bonded bulk water molecules in which highly structured water "icebergs" are floating. These icebergs, which are held together by hydrogen bonds, do not necessarily have the same structural characteristics of solid ice. The "icebergs" are more open-spaced than bulk water. They have finite lifetimes on the order of 10^{-11} seconds (82) and they are in dynamic equilibrium with bulk water. In Frank and Wen's model, bulk water is thought to be more dense and much less structured than the "icebergs". The extent of "iceberg" formation in this model and the extent of the three-dimensional, tetrahedral, hydrogen-bonded structure in the model of Bernal and Fowler is not fully understood. The one thing that is perfectly clear is that water is a highly structured liquid.

Alcohols and organic solvents in general do not exhibit the structural characteristics of water. This is perhaps due to the inability of the alcohols to form three-dimensional network structures (171). The alcohols are undoubtedly structured in some way (83, 114) but there is no evidence for large aggregate formation in them (114).

Most investigators are of the opinion that alcohols form small straight-chained polymeric groupings that are in dynamic equilibrium with unassociated bulk molecules (83, 114, 172). Evidence for the associated

structure of liquid alcohols is given by Pauling (83). From X-ray crystallographic data, we know that crystalline alcohols contain long polymeric chains of the type



If a lot of these hydrogen bonds are not broken as the crystal melts, the heat of fusion, ΔH_f, of the crystal will be small. This is exactly what is observed. ΔH_f values for alcohols are small indicating that liquid alcohols retain some degree of hydrogen-bonding that was present in the crystal. The heats of vaporization, ΔH_{vap}, and the boiling points of alcohols do show the effects of hydrogen-bond breaking. The boiling points of alcohols are high and their ΔH_{vap} values are large. Thus, the liquid state of alcohols is stable over a wide range of temperatures, for example, -117°C to +78°C for ethanol.

Thomas (171) feels that straight-chain alcohols form dimers in the pure liquid state. In doing this, the molecules can remain lengthwise with respect to each other and thus retain maximum van der Waals interactions. Thomas feels that any cyclical polymerization

of the straight-chain alcohols would require too much entropy. The non-linear alcohols such as $C(CH_3)_3OH$, do exhibit high degrees of association. These do not loose favorable van der Waals interaction positions by associating in non-linear groupings.

Franks and Ives (114) have written a comprehensive review about the structural properties of liquid alcohols and alcohol--water mixtures. They feel that each alcohol oxygen participates in only two hydrogen bonds due to the cooperative nature of the hydrogen bond which limits the alcohol to acting as one proton donor and one proton acceptor, and due to steric hindrance caused by the big organic groups which prohibits complex three-dimensional arrangements. In Franks and Ives' model of liquid alcohol, the polymeric chains do not usually exceed a length of 5 - 7 molecules. The alcohol chains are in equilibrium with unassociated molecules in the bulk liquid.

There is no doubt that alcohols are "polymerized" to some extent via hydrogen-bonding. The dielectric constants of ethanol and methanol of 24.3 (173) and 32.6 (174), respectively, are higher than would be anticipated from the moderate value of the OH- group dipole moment (1.53D) (114). This is consistent with a mode of association of these alcohols which leads to cooperative reinforcement of dipole fields.

Although much detail is lacking in our knowledge of the structure of alcohol and water, it is clear that both liquids do exhibit a high degree of internal orderliness that is due to hydrogen bonding. The nature of the water and alcohol structures are quite different and the complex structure-breaking and bond-formation that occurs when alcohol and water are mixed is little understood. One thing that is clear about alcohol--water mixtures is that they too exhibit some degree of structuring.

Let us discuss the change in solvent structure which occurs when alcohol is added to water. A small amount of alcohol added to water, will not disturb the three-dimensional polymeric structure of water very much. The water can accomodate some alcohol (especially ethanol and methanol) molecules in its interstitial cites. The water structure has a certain resistance to disruption as is evidenced by the similarity in heat capacity (C_p) versus temperature for water and alcohol--water mixtures up to $\sim$ 30 wt.-% (114). The heat that is liberated when alcohol is added to water can be attributed to formation of strong hydrogen bonds between alcohol and water molecules. These bonds are probably more extensive than in pure alcohol and stronger than water--water hydrogen bonds due to the greater capacity for alcohol to act as a hydrogen-bond acceptor because

of the inductive effects of the alkyl groups. Another contribution to the heat given off upon mixing alcohol with water comes from the increase in entropy of the water as its extensive network is destroyed.

After more than ~ 20 wt.-% alcohol is added to water, the three-dimensional water structure starts to decay due to alcohol's inability to participate in extensive hydrogen-bonded clusters. More and more water molecules become associated with the alcohol. There is a point at around 10 wt.-% alcohol (ethanol) at which the water structure is most extensive and, after which the water structure is subject to destruction. The equilibrium between associated "iceberg" water and interstitial water molecules is shifted in solvents of alcohol composition above ~ 20 wt.-% doe to the lack of unbonded interstitial water caused by alcohol molecules associating with this "free" water. As more alcohol is added, the entire nature of the "iceberg" changes. New types of structural entities are formed which incorporate alcohol molecules. At a certain point, probably about 70 wt.-% for ethanol, the formation of these new types of "icebergs" is most favorable. In this region of the alcohol--water solvent system, alcohol--water icebergs are probably in equilibrium with "interstitial" unassociated alcohol and water molecules.

Increases in the alcohol composition above a certain point ($\sim$ 70 wt.-% for ethanol--water solvents) have the effect of tying up any remaining unassociated water molecules. As the solvent approaches pure alcohol, the last remaining free water molecules become bound to the alcohol and the solvent takes on characteristics of pure alcohol. Between 98 and 100 wt.-% alcohol, the last few free water molecules are being bonded and as will be seen later, there occurs a drastic change in the basicity of the solvent.

Solvation of solutes.

The addition of particles to a liquid can have various effects depending on the size, charge, and chemistry of the particle. Generally, there are three regions around a particle in a structured liquid (32, 59, 77, 82, 114). In the region of solvent adjacent to the particle, the solvent molecules are disturbed to some extent and have a different spacial arrangement compared to bulk solvent. If the dissolved particle is charged, the solvent dipoles can be lined up in the field of the ion. For small ions, this orientation effect is strong, and, in the case of solvents of high dielectric constant, the solvent molecules will remain bound to the ion. The solvent molecules in this first solvation sphere around a small ion are overwhelmingly influenced by the charge on the ion. In this first region, solvent dipoles are not participating in the structural network of the solvent. For larger ions, with smaller surface charge densities, solvent molecules in this first region will be oriented to a lesser extent and beyond a certain radius, not at all. Solvent molecules adjacent to uncharged solute particles will be affected due to the discontinuity in the medium. For highly structuredsolvents, such as water, uncharged particles actually serve to increase the structure of the solvent. The uncharged particle cannot disrupt

"icebergs" that form in its vicinity. Also, the uncharged particle protects the "icebergs" from interaction with unbound water molecules. Thus, "icebergs" are longer-lived in the vicinity of uncharged particles. One good piece of evidence for the structure-enhancing effect of uncharged particles in water is the enormous partial molal heat capacity of the rare gases in water. As the temperature of the solution increases, the "icebergs" melt and this accounts for the large heat capacities of the solutions. Very large ions with minimal surface charge densities might also be structure-enhancers.

In the region between the first solvation sphere and the bulk of the solvent, the solvent molecules have two forces operating on them. First, there is the orienting force of the electric field of the particle, if the particle is charged, or, if the particle is uncharged, the solvent molecules are still affected by the solvent molecules in the first solvation sphere. Secondly, solvent molecules in this intermediate region are affected by the ordering forces of the solvent network in the bulk of the solvent. Because of these two forces operating in this intermediate region, solvent molecules in this region display a greater degree of randomness than do solvent molecules in the bulk of the solution.

Around small charged particles, there is possibly

a third solvation sphere beyond the second in which solvent molecules have more orientational order than bulk solvent due to the effects of the ionic field penetrating into this region. This region, which is important for small ions only, is not well defined. It is probably nonexistent around uncharged particles.

The factor of size plays an important role in the solvation of solutes (32, 59, 77, 82). Protons, having negligible volume, fit into solvent structures without disturbing the positions of solvent molecules. Any change in solvent structure around a proton will be due solely to electrostatic interactions between the proton and the solvent molecules. In aqueous solutions, other ions such as K^+ fit nicely into the interstitial regions (77). Hunt beleives that the hydrated potassium ion is tetrahedral and thus, it fits naturally into the water structure. Of course, the exact geometry of an ion and its first solvation layer is dependent on the sizes of ion and solvent molecules, the dipole moment and the dielectric constant of the solvent, and the charge on the ion.

The medium effect can be visualized in terms of the difference in energy required to produce the three solvation regions around similar particles in the two solvents under consideration. Medium effects for single ions in ethanol--water solvents obtained in this study will

now be discussed in terms of the structure of ethanol--water solvents.

Discussion.

Medium effects for single ions in ethanol--water solvents based on the three reference-electrolyte assumptions

$$\log {}_m\gamma_{Ph_4P} = \log {}_m\gamma_{BPh_4} = \tfrac{1}{2} \log {}_m\gamma_{Ph_4P\ BPh_4} \qquad (140)$$

$$\log {}_m\gamma_{Ph_4As} = \log {}_m\gamma_{BPh_4} = \tfrac{1}{2} \log {}_m\gamma_{Ph_4As\ BPh_4} \qquad (141)$$

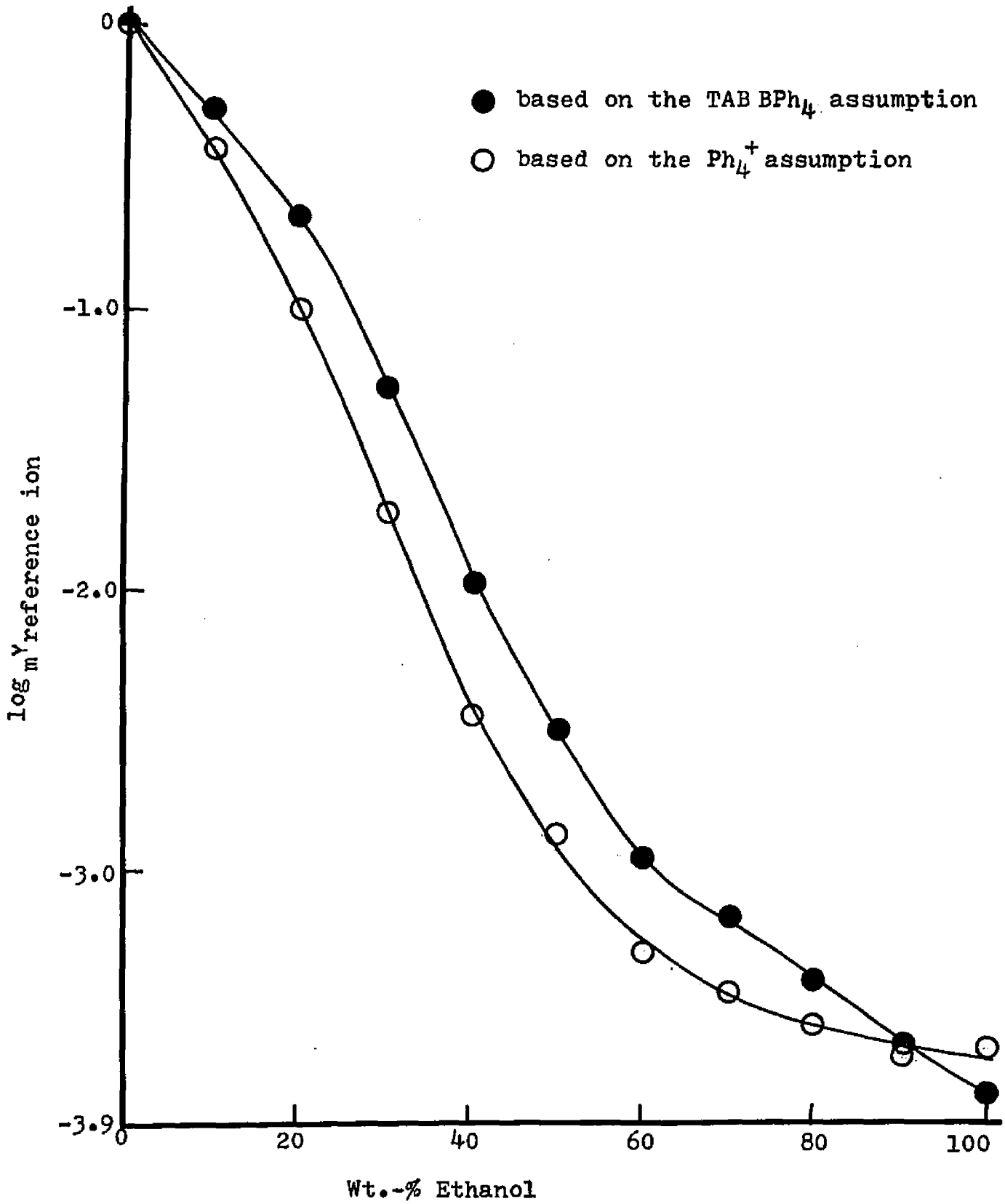
$$\log {}_m\gamma_{TAB} = \log {}_m\gamma_{BPh_4} = \tfrac{1}{2} \log {}_m\gamma_{TAB\ BPh_4} \qquad (142)$$

are reported in Tables 58 - 71 in section VIII-A-1 of this thesis. All medium effects are reported on the molal and the molar scales referred both to water and to ethanol as reference solvents.

Medium effects for the reference ions $TAB^+ = BPh_4^-$ and $Ph_4^+ = BPh_4^-$ are presented in Figure 3. Numerical values of $\log {}_m\gamma$ derived from the $Ph_4P^+ = BPh_4^-$ and $Ph_4As^+ = BPh_4^-$ assumptions are so close that their average value, $\log {}_m\gamma_{Ph_4}$ has been plotted. Using the average value of $\log {}_m\gamma_{Ph_4}$ is termed the "tetraphenyl (Ph_4^+) assumption".

Logarithms of the medium effects for the reference ions continually decrease from water to ethanol indicating preferential solvation of these ions in the

Figure 3. Medium Effects, $\log_m \gamma$, of Reference Ions in Ethanol--Water Solvents. Water is the Reference Solvent. 25°C, Molal Scale.



alcohol-rich solvents. All of the reference ions are large ($r = \sim 4 - 5$ Å) and have small surface charge densities. Because of this, they affect the solvent structure in much the same way as uncharged particles of similar size. These reference ions are preferentially solvated in ethanol-rich solvents as compared to water because the large ions fit better in these less-structured solvents. They cannot occupy interstitial positions in aqueous solution and so, they must interfere with the overall water structure in order to dissolve. In alcohol-rich solvents where the solvent structure is not as rigid, these large reference ions can enter into solution with less effort. In 100 % ethanol, $\log {}_m\gamma$ values for the reference ions are about -4.

From Figure 3 and Table 67, we see that there is a slight increase in $\log {}_m\gamma$ from 90 to 100 wt.-% ethanol for the Ph_4^+ reference ions. This slight increase might reflect a change in the rigidity of the ethanol--water mixtures in this region due to the exclusion of the last bit of water. Values for $\log {}_m\gamma_{TAB}$ continually decrease in this solvent region. The most drastic change in $\log {}_m\gamma$ for the Ph_4^+ ions occurs between 0 and 50 wt.-% ethanol where $\log {}_m\gamma$ decreases from o to -3. This reflects the sharp decrease in the rigidity of the solvent in this region. The rate of change of $\log {}_m\gamma$ for the Ph_4^+ ions decreases after $\sim$ 50 - 60 wt.-%

ethanol indicating a slowing down in the change of the rigidity of the solvent.

The variation of $\log {}_m\gamma_{\text{reference ion}}$ in ethanol--water solvents also reflects the intrinsic solvating powers of water and ethanol for large ions. In the low wt.-% ethanol regions, where a few ethanol molecules become available, values of $\log {}_m\gamma_{\text{reference ion}}$ immediately decrease indicating that ethanol participates favorably in solvation of the reference ions. As the proportion of ethanol is increased, the reference ions become bound more tightly. The change in slope in Figure 3 around 50 - 60 wt.-% ethanol is an indication that additional ethanol is not participating in primary solvation (in the first solvation sphere around the ions), but is influencing the solvation energy of the ions from the second and third solvation layers.

Values of medium effects for the reference ions are approximately the same for all three reference electrolytes studied. This is an indication that the central atom in these large ions is not of primary importance in determining the value of $\log {}_m\gamma$. In the case of the three tetraphenyl ions studied, Ph_4P^+, Ph_4As^+, and BPh_4^-, this is very good evidence for the validity of the assumption of the equality of their medium effects. Indeed, it is a thermodynamic fact that $\log {}_m\gamma_{Ph_4P} = \log {}_m\gamma_{Ph_4As}$ within experimental error.

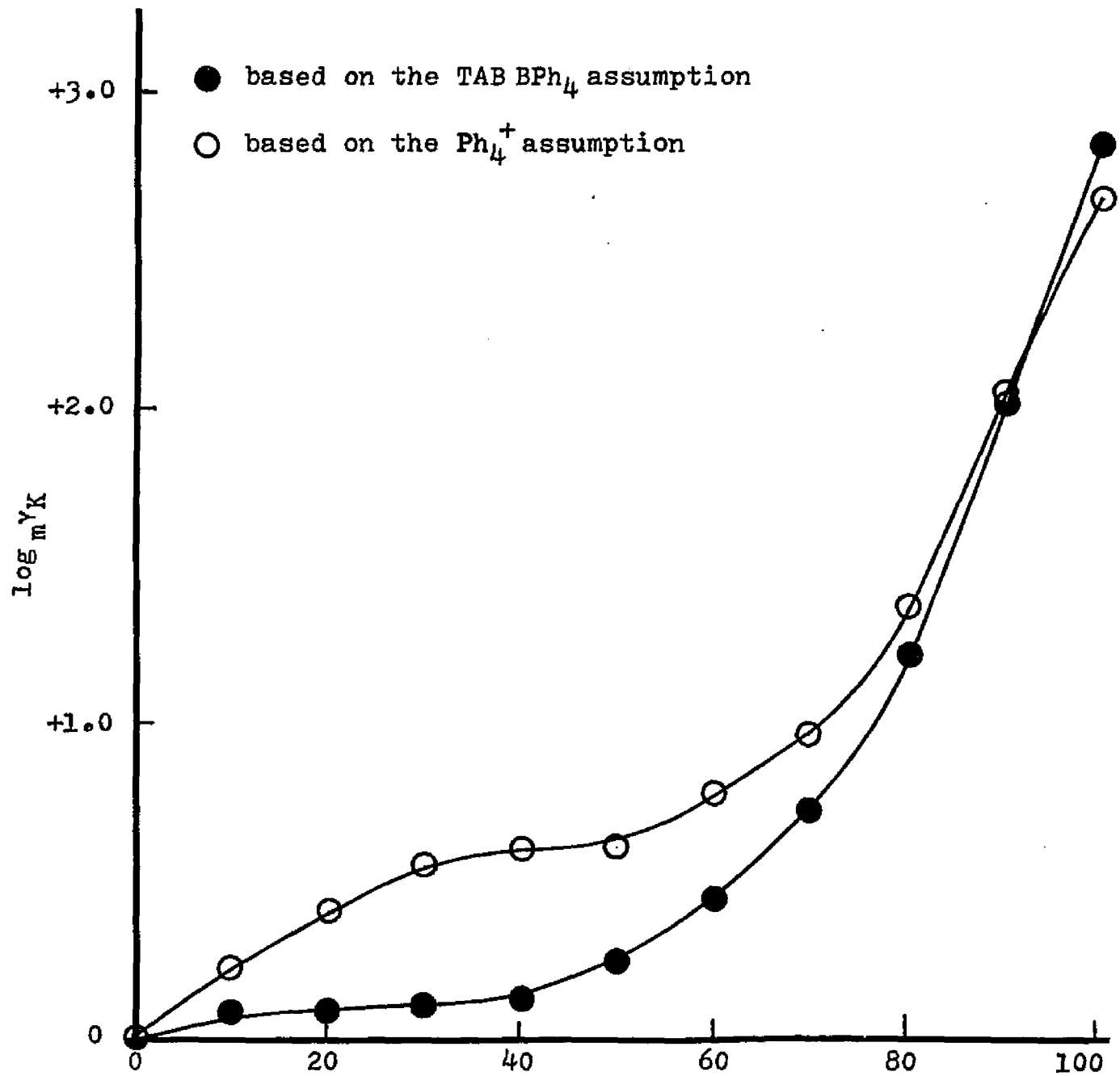
The fact that $\log_m \gamma$ for the reference ions continually <u>decreases</u> as the percentage ethanol increases is an indication of the tremendous significance of the neutral component of the medium effect for large ions. If solvation energies for large ions were predominantly electrostatic in nature, values for $\log_m \gamma_{\text{reference ion}}$ would continually <u>increase</u> from water to ethanol. However, just the opposite is the case. Medium effects for the reference ions in ethanol--water solvents vary in a manner similar to those of the uncharged molecules, Ph_4C, Ph_4Si, Ph_4Ge in the same solvents, indicating that medium effects for large ions are determined mainly by their neutral (non-electrostatic) components. Further discussion of the relationship between medium effects of the reference ions and of structurally analogous uncharged molecules will be found in section VIII-D, "additivity of electrostatic and neutral contributions to the medium effect for large ions".

Medium effects, $\log_m \gamma$, for the potassium ion in ethanol--water solvents are listed in Table 68 and presented in Figure 4. Numerical values of $\log_m \gamma_K$ are positive throughout the ethanol--water solvent system indicating that potassium exists in a lower energy state in water than in the ethanol--water solvents. In other words, potassium ions are preferentially

solvated by water rather than ethanol. Values of $\log_m \gamma_K$ are quite small up to about 60 wt.-% ethanol. According to Hunt, (77), the solvated potassium ion is tetrahedral and it fits nicely into the water structure. Thus, we would expect K^+ ions to have approximately the same solvation energy in water-rich solvents where K^+ ions are primarily solvated by water molecules. Above 60 wt.-% ethanol, the first solvation sphere is no longer occupied exclusively by water. Ethanol molecules start positioning themselves close to the K^+ ion and this is reflected in an increase in numerical values of $\log_m \gamma_K$ in solvents containing more than $\sim$ 60 wt.-% ethanol.

Additional evidence that K^+ ions are exclusively solvated by water up to about 60 wt.-% ethanol can be found in a paper by Dill, Itzkowitz, and Popovych (72). In the above study, values of $\log_m \gamma_K$ in ethanol--water solvents calculated via the Stokes modified (71) Born equation were compared with experimental values derived using the TAB BPh_4 assumption (17). Values of $\log_m \gamma_K$ obtained from both methods were essentially identical up to $\sim$ 60 wt.-% ethanol. Above this, the values diverged. The Stokes equation for estimating solvation energies of single ions assumes that only water molecules occupy the first solvation sphere. Apparantly, this requirement is met for potassium ions up to about

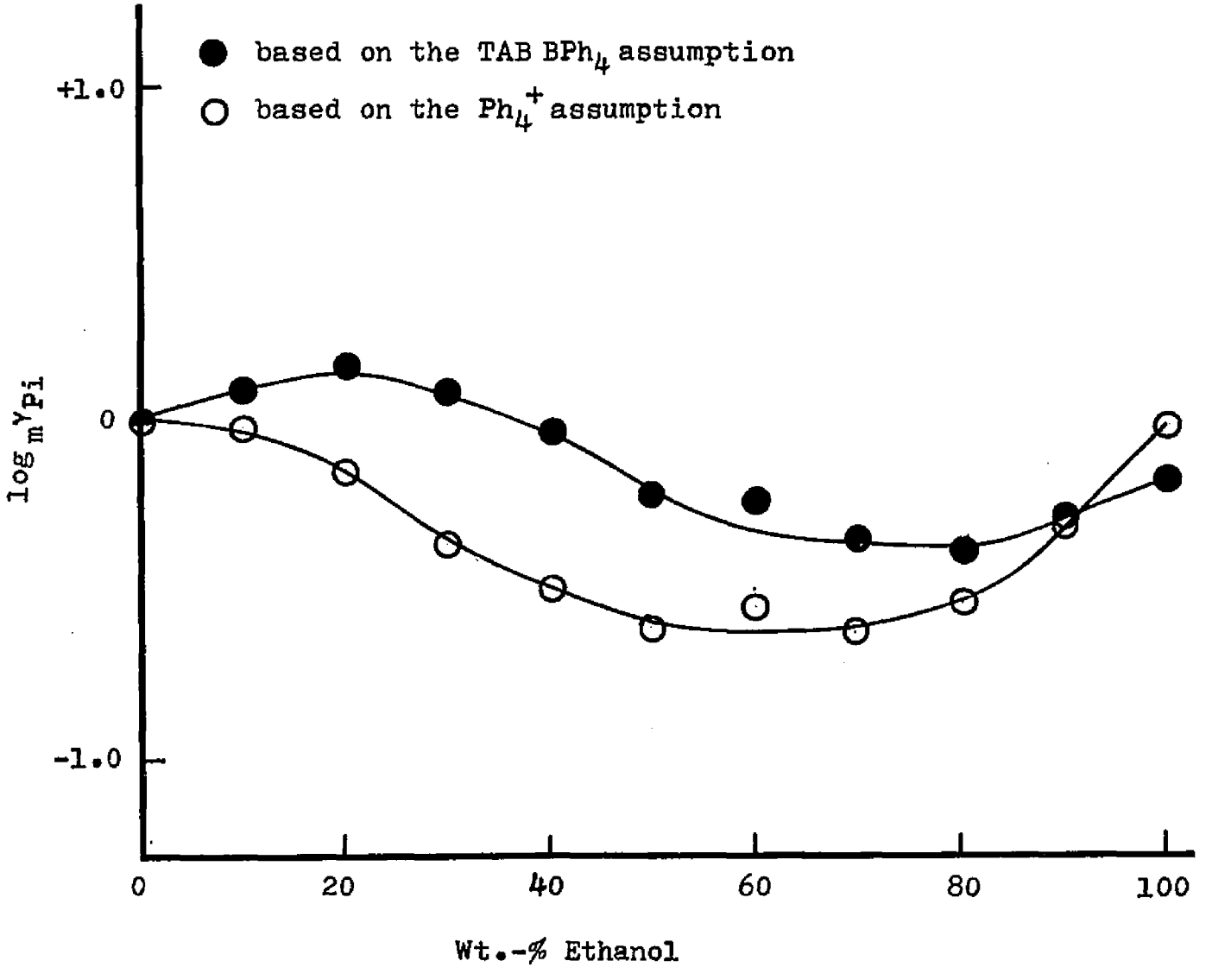
Figure 4. Medium Effects, $\log_m \gamma$, for K^+ Ion in Ethanol--Water Solvents. Water is the Reference Solvent. 25°C, Molal Scale.



60 wt.-% ethanol. In ethanol--water mixtures containing more than 60 wt.-% ethanol, the Stokes equation does not yield values of $\log_m \gamma_K$ which are in agreement with those obtained using reference-electrolyte assumptions. Between 60 and 100 wt.-% ethanol, $\log_m \gamma_K$ increases by $\sim$ 2 log units. Upon studying Figure 4, one might conclude that potassium ions are solvated better by water molecules than by ethanol molecules. This is not necessarily true. Individual ethanol molecules may be better electron pair donors than individual water molecules (114) thus solvating K^+ ions better. However, the solvation energy of an ion is determined by its interaction with liquid solvent, thus being the total effect of all the ion-solvent interactions both electrostatic and neutral. Sincethe medium effects for K^+ ions are positive in ethanol, we can conclude that potassium ions are solvated more favorably by liquid water than by liquid ethanol.

Figure 5 illustrates the variation of $\log_m \gamma$ for the picrate ion in ethanol--water solvents. Medium effects for picrate are not very large in the absolute sense. Numerical values of $\log_m \gamma_{Pi}$ are listed in Table 68. The largest absolute value is -0.63 for $\log_m \gamma_{Pi}$ in 70 wt.-% ethanol based on the Ph_4^+ assumption. In 100 % ethanol, $\log_m \gamma_{Pi}$ is -0.01 and -0.17 based on the Ph_4^+ and TAB BPh_4 assumptions, respectively.

Figure 5. Medium Effects, $\log_m \gamma$, for Pi^- Ion in Ethanol--Water Solvents. Water is the Reference Solvent. 25°C, Molal Scale.

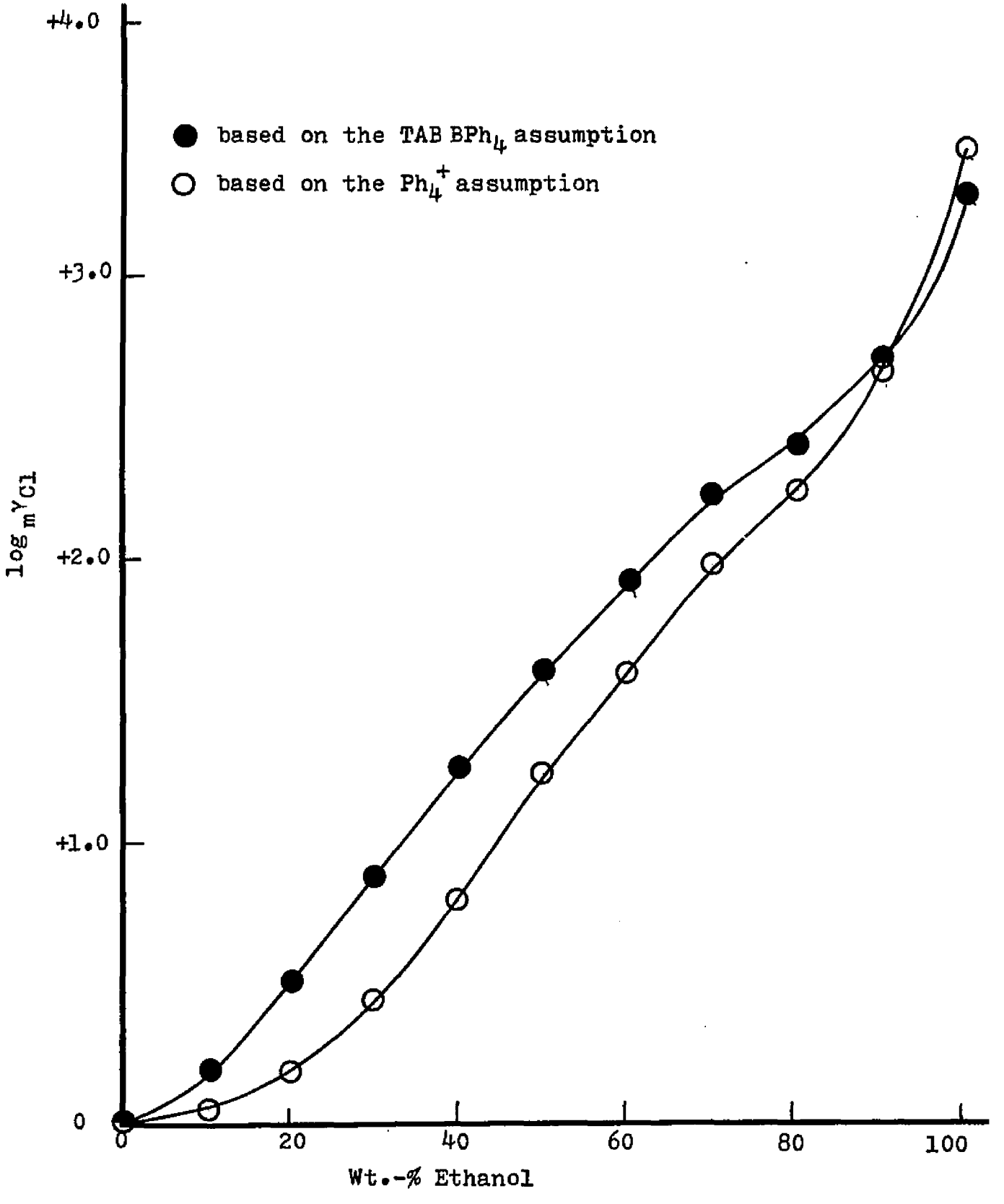


This indicates that Pi^- ions are solvated only a bit more strongly in ethanol than in water.

Picrate ions seem to be most favorably solvated in ethanol--water solvents around 60 wt.-% ethanol. In this region of solvent composition, there are probably a maximum number of unbound water and alcohol molecules which are available for solvating ions. The water and alcohol dipoles tend to stabilize the Pi^- ions and the alcohol molecules further stabilize them through mutual polarization.

Medium effects for the chloride ion, $\log {}_m\gamma_{Cl}$, are listed in Table 68 and are graphically presented in Figure 6. Numerical values for $\log {}_m\gamma_{Cl}$ continually increase from water to 100 % ethanol. The variation is approximately linear with no sharp changes in the slope of the plot in Figure 6. Small negative ions such as chloride are solvated more strongly by water than by alcohols. This is due to the greater availability of protons in water for hydrogen-bond stabilization of the negative ions. As the percentage of water is decreased, the solvation energy is increased and the medium effect increases. The expected sharp change in $\log {}_m\gamma_{Cl}$ at about 60 wt.-% ethanol appears in the curves as a slight change in slope in the region between 60 and 80 wt.-% ethanol. It is more pronounced in the curve based on the TAB BPh_4 assumption.

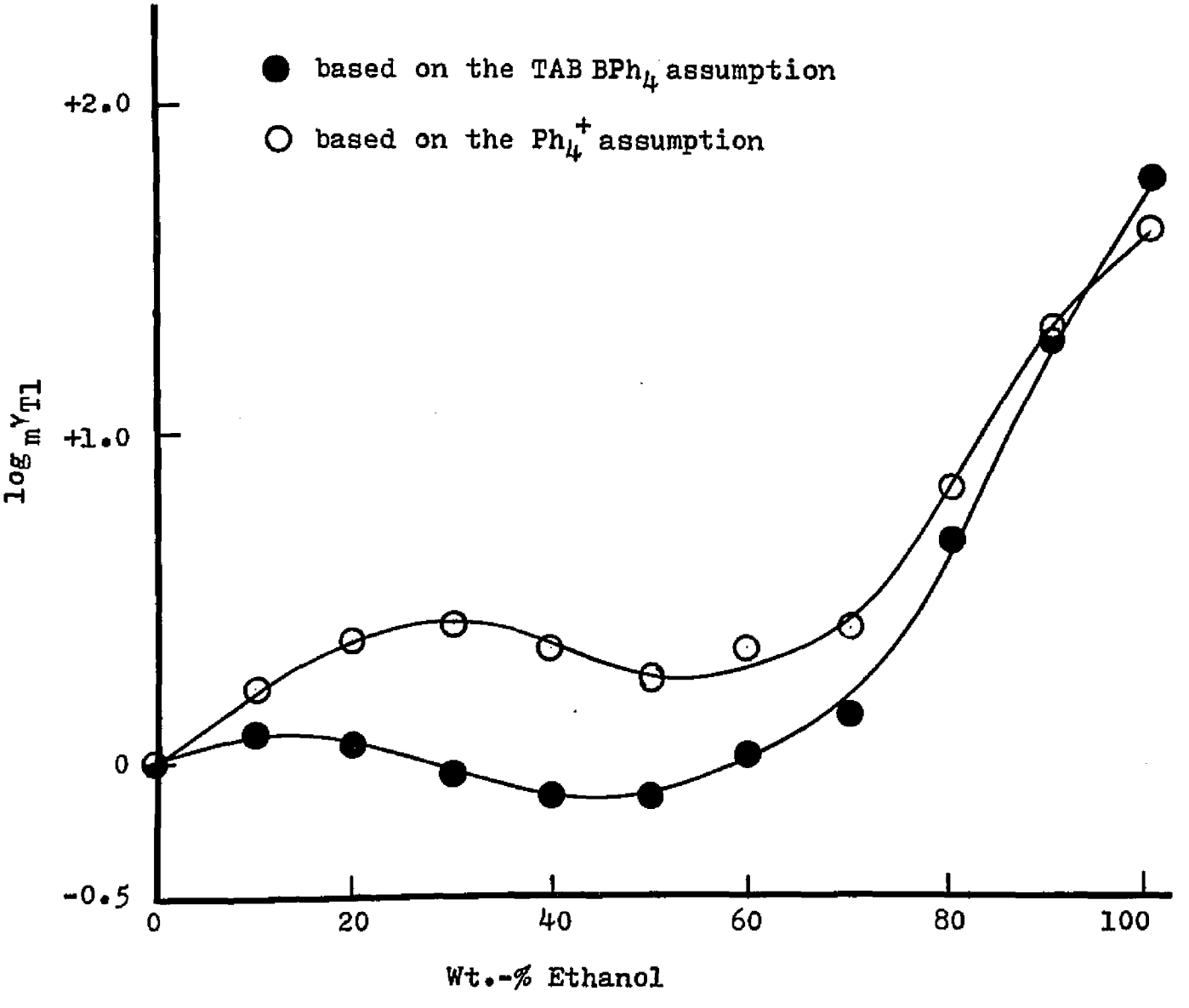
Figure 6. Medium Effects, $\log_m \gamma$, for Cl^- Ion in Ethanol--Water Solvents. Water is the Reference Solvent. 25°C, Molal Scale.



Values of $\log {}_m\gamma_{Tl}$ in ethanol--water solvents are listed in Table 70. Figure 7 illustrates the variation of $\log {}_m\gamma_{Tl}$ in ethanol--water solvents. This variation is visually similar to the variation of $\log {}_m\gamma_K$ in ethanol--water solvents (see Figure 4). Two major differences between the variations in $\log {}_m\gamma_{Tl}$ and $\log {}_m\gamma_K$ are the definite dip in the $\log {}_m\gamma_{Tl}$ curve around 50 wt.-% ethanol and the generally larger values of $\log {}_m\gamma_K$. Apparantly, thallous ion is more strongly solvated by water than by ethanol. The greatest change in $\log {}_m\gamma_{Tl}$ occurs in the region between 70 and 100 wt.-% ethanol indicating that as unbound water becomes scarce, the solvation energy of Tl^+ increases. The small dip in the curve of $\log {}_m\gamma_{Tl}$ versus wt.-% ethanol at $\sim$ 50 wt.-% ethanol might represent a region of maximum unbound water. Predictions of $\log {}_m\gamma_K$ and $\log {}_m\gamma_{Tl}$ in ethanol--water solvents based on the unmodified Born equations qualitatively agree with the experimental slopes in Figures 4 and 7 except for the hint of a dip appearing in the experimental curves. This is perhaps due to the variation in basicity of ethanol--water mixtures.

To summarize, small ions, such as Tl^+, and Cl^-, seem to be solvated more strongly by water than ethanol so that the medium effects, $\log {}_m\gamma$ for small ions in 100 % ethanol are positive. The solvating power of ethanol--water solvents does not vary linearly with

Figure 7. Medium Effects, $\log {}_m\gamma$, for Tl^+ Ion in Ethanol--Water Solvents. Water is the Reference Solvent. 25°C, Molal Scale.

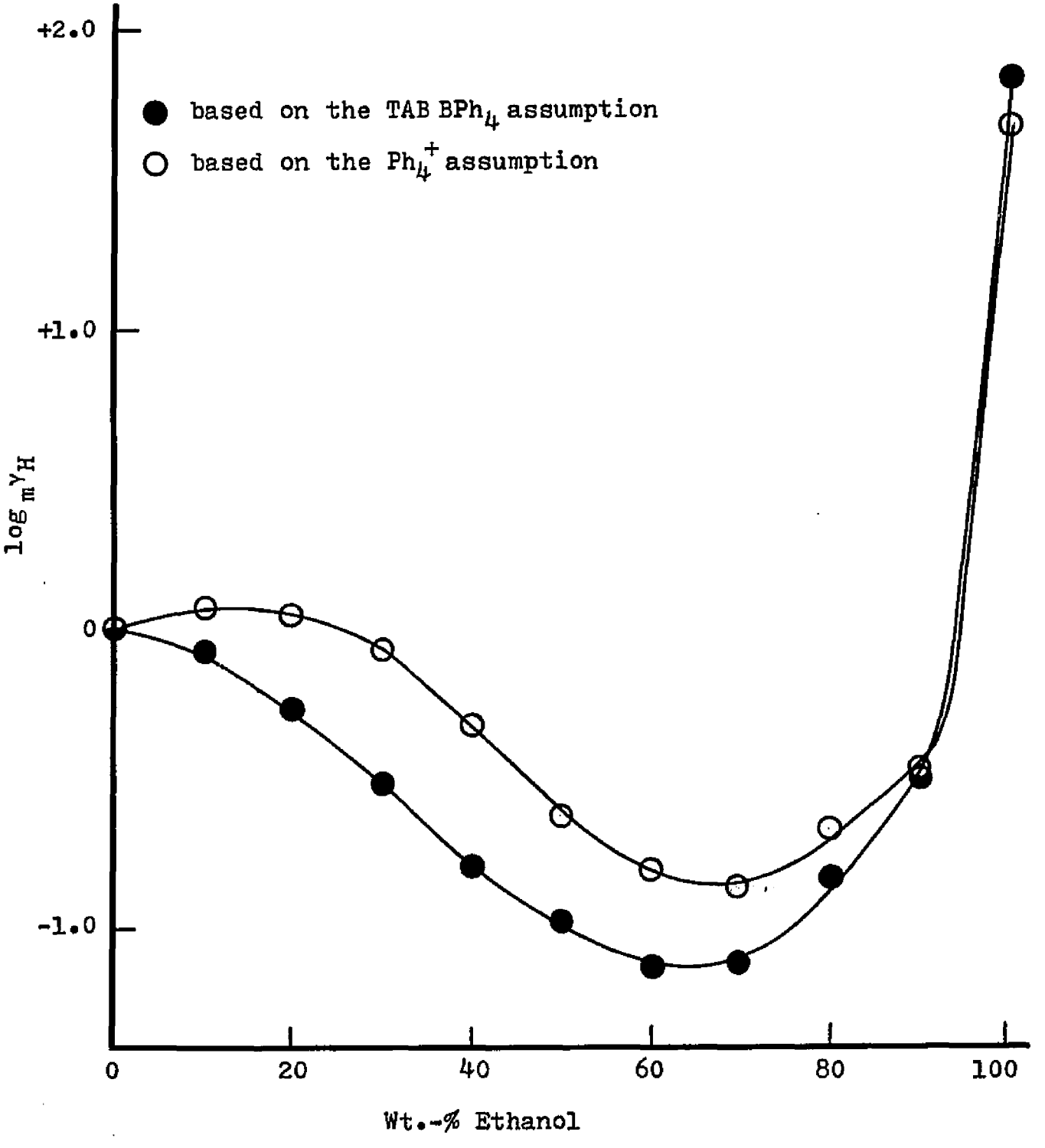


percentage composition of solvent. In all cases studied, there appears to be a reversal or change in solvating powers at around 60 wt.-% ethanol.

Perhaps the best indication of the relative acidity or basicity of ethanol--water solvents is given by the variation of $\log {}_m\gamma_H$ in the solvents. The proton is negligibly small so that changes in solvent rigidity will not affect the degree to which protons can enter the solvent structure. In other words, the medium effect for the proton will not include a neutral component. The entire medium effect for the proton can be attributed to the change in proton solvating power or the basicity of the solvents. Medium effects for the proton, $\log {}_m\gamma_H$, in ethanol--water solvents are listed in Table 68 and are presented in Figure 8. The curve illustrates the classical dip (4, 114) in the $\log {}_m\gamma_H$ versus percent alcohol curve.

Up to $\sim$ 60 wt.-% ethanol, values of $\log {}_m\gamma_H$ continually decrease. A minimum is reached between 60 and 70 wt.-% ethanol after which values for $\log {}_m\gamma_H$ increase up to 90 wt.-% ethanol at about the same rate as from 10 to 60 wt.-%. Finally, between 90 and 100 wt.-% ethanol, there is a tremendous increase in the value of $\log {}_m\gamma_H$. As a matter of fact, the value even changes sign jumping from $\sim$ -0.5 to $\sim$ +2 log units. This drastic change in $\log {}_m\gamma_H$ from 90 to 100 %

Figure 8. Medium Effects, $\log_m \gamma$, for H^+ Ion in Ethanol--Water Solvents. Water is the Reference Solvent. 25°C, Molal Scale.



ethanol indicates a very great change in the basicity of ethanol--water solvents in this region. Apparantly, as long as there are some unbound water molecules around, the protons remain solvated quite strongly and numerical values of $\log {}_{m}\gamma_{H}$ are negative. In the region between 90 and 100 wt.-% ethanol, any remaining unbound water molecules are removed and $\log {}_{m}\gamma_{H}$ increases to its energetically disfavored value in pure ethanol.

Why are values for $\log {}_{m}\gamma_{H}$ negative in solvents containing 10 to 90 wt.-% ethanol? This can best be answered by looking at the availability of basic sites in the solvent. In the case of water molecules, protons bond to the electronegative oxygen. In alcohol, the same is true. On first thought, it would seem that alcohol can solvate protons better than water due to the inductive effect of the alkyl groups (152). However, there are other considerations. Smaller water molecules can pack themselves around the proton more easily than alcohol molecules can. Thus, in water, the proton can be adjacent to a few water molecules simultaneously (77). In alcohol, the bulkiness of the molecules prevent them from accumulating around the same proton. The steric effects are just as important for solvent molecules in the second and third solvation spheres of the proton. More of the smaller water molecules can pack into the second and third solvation

spheres. Thus, in solvents where many free water molecules are available for solvation, $\log {}_m\gamma_H$ is negative. In solvents containing from 10 to 90 wt.-% ethanol, there are fewer water "icebergs" forming, alcohol molecules are disrupting the three-dimensional water network, and there are more unbound water molecules available for proton solvation.

Why the minimum in the $\log {}_m\gamma_H$ versus wt.-% ethanol curve? The minimum occurs because at this point, the solvent possesses a maximum number of mobile basic sites for bonding with protons. Before the minimum in the curve is reached, i.e. in the range between water and 60 wt.-% ethanol, water molecules are tied up in "iceberg" formation. Beyond the minimum, the abundance of water molecules has decreased to the extent that they are no longer available for proton solvation. The minimum in the $\log {}_m\gamma_H$ versus wt.-% ethanol curve is certainly not unique. Paabo, Bates, and Robinson (74) report a similar minimum for $\Delta\ pK_a$ of ammonium ion versus wt.-% methanol. In this case, $\Delta\ pK_a$ of ammonium can be equated to $(\log {}_m\gamma_H + \log {}_m\gamma_{NH_4(el)})$ and it should follow the same general trend as $\log {}_m\gamma_H$. Bates reports (10) that this minimum, which is characteristic of the medium effect for the proton and $\Delta\ pK_a$ of ammonium ions in alcohol--water mixtures, does not appear for $\Delta\ pK_a$ of p-nitroanilinium ion in methanol--

propylene glycol solvents. Braude and Stern (152) also report that this minimum in solvent basicity does not appear for mixtures of organic solvents. Thus, the minimum can be attributed to a certain structure or solvent basicity which is to be found only in aqueous solvent mixtures. The water component is responsible for the dip in Figure 8. Water seems to have an unusually strong influence on acid-base processes taking place in solvent mixtures where water is one of the components.

Braude and Stern (152) determined values for the Hammett acidity function, H_o, in ethanol--water solvents using hydrochloric acid solutions and m- and p-nitroaniline as indicators. The general relationship between the medium effect for the proton, $\log {}_m\gamma_H$, and the H_o function for a nonaqueous solution of HCl of molality m_{HCl} with a degree of dissociation α is:

$$\log {}_m\gamma_H = -H_o - \log m_{HCl} - \log \alpha - \log {}_s\gamma_H + \log \frac{{}_s\gamma_{BH^+}}{{}_s\gamma_B} + \log \frac{{}_m\gamma_{BH^+}}{{}_m\gamma_B} \qquad (224)$$

where BH^+ and B represent the cationic indicator acids and their conjugate bases, respectively, and the subscripts s and m refer to the salt effect and medium effect activity coefficients, respectively. Assuming that

the last four terms on the right hand side of Equation 224 are negligible, the medium effect for the proton, $\log {}_m\gamma_H$, will be given by $(- H_o - \log m_{HCl})$. This is not a bad assumption since $\log {}_s\gamma_H$ is close to zero for dilute solutions, and the last two terms are also expected to be close to zero for partially aqueous solutions. The last term would actually be equal to $\log {}_m\gamma_{BH^+(el)}$ if the size of the cationic acid is large. Values of $(- H_o - \log m_{HCl})$ in ethanol--water solvents calculated from the data of Braude and Stern are listed in Table 75 along with values of $\log {}_m\gamma_H$ obtained from the tetraphenyl assumption. The Hammett function $(- H_o - \log m_{HCl})$ closely follows the values of $\log {}_m\gamma_H$ obtained from the Ph_4^+ assumption up to $\sim$ 60 wt.-% ethanol and qualitatively follows the general trend in $\log {}_m\gamma_H$ throughout the ethanol--water solvent system. The Hammett function exhibits the expected minimum corresponding to a maximum solvent basicity at around 80 wt.-% ethanol. It also yields a positive value of +0.39 log units for the medium effect of the proton in ethanol, corroborating results obtained from reference-electrolyte methods that water is a stronger base than ethanol. The deviation of the Hammett function from $\log {}_m\gamma_H$ in solvents having more than 60 wt.-% ethanol can be attributed to decrease in the validity of the assumption that the last four terms on the

Table 75. Medium Effects for the Proton in Ethanol--Water Solvents Based on the Ph_4^+ Assumption and the Hammett Acidity Function, H_o. 25°C, Molal Scale.

wt.-% ethanol	$\log {}_m\gamma_H$ Ph_4^+ assumption	$(-H_o - \log m_{Cl})$
0.0	0.0	-0.01
10.0	0.08 ± 0.02	----
20.0	0.06 ± 0.03	-0.18
30.0	-0.06 ± 0.02	----
40.0	-0.32 ± 0.02	-0.52
50.0	-0.62 ± 0.04	----
60.0	-0.80 ± 0.03	-1.03
70.0	-0.86 ± 0.04	-1.17
80.0	-0.67 ± 0.04	-1.25
90.0	-0.46 ± 0.11	-1.23
100.0	+1.68 ± 0.04	+0.39

right hand side of Equation 224 are neglibible. In solutions containing a large percentage of ethanol, the degree of dissociation, α, is expected to be less than unity (55) and the term $\log ({}_m\gamma_{BH^+}/{}_m\gamma_B)$ is expected to be quite appreciable, having a value of +1.2 in ethanol for a cationic acid 3 Å in size as calculated from the Born equation. Indeed, $(-H_o - \log m_{HCl})$ is expected to be smaller than $\log {}_m\gamma_H$ by an amount corresponding to the last four terms in Equation 224.

The variation of the Hammett function $(-H_o - \log m_{HCl})$ in ethanol--water solvents and the general agreement between it and values of $\log {}_m\gamma_H$ obtained from the Ph_4^+ assumption is extremely convincing evidence for the validity of the reference-electrolyte assumptions.

The variation of the basicity of alcohol--water mixtures has been used (114) to interpret variations in medium effects of anions and cations. According to Franks and Ives (114), cation solvation becomes more stable and anion solvation becomes less stable in alcohol--water mixtures of enhanced basicity. Cation solvation is defined by Franks and Ives as lone-pair donation from oxygen atoms of solvent molecules and anion solvation as proton donation from hydroxyl groups of solvent molecules. Although this is a simplistic view of solvation, variations in $\log {}_m\gamma_K$

$\log {}_m\gamma_{Tl}$ and $\log {}_m\gamma_H$ in ethanol--water solvents can be interpreted in terms of solvent basicities. Variations of $\log {}_m\gamma_{Pi}$ in ethanol--water solvents (Figure 5) are opposite to what is expected on the basis of solvent basicity. Instead of a maximum in Figure 5, a minimum appears. Chloride ion medium effects do not exhibit any changes that could be associated with solvent basicities. Franks and Ives view of solvation of cations seems to be consistent with the results obtained in this study. However, anion solvation does not appear to be greatly dependent on the basicity of the solvent.

It is interesting how one can obtain misleading information about the relative basicities of ethanol and water from studying only parts of the ethanol--water solvent system. Looking at the variation of $\log {}_m\gamma_H$ from water to 50 wt.-% ethanol, (Figure 8), it is logical to conclude that ethanol is more basic than water because addition of ethanol to water increases the basicity of the mixture. Looking at the variation of $\log {}_m\gamma_H$ from 100 to 60 wt.-% ethanol, one will arrive at the opposite conclusion--that water is the more basic solvent. Which solvent is more basic? To answer this, we have to know the medium effect for the proton in either solvent using the other as a reference. From this study, we conclude

that $\log_m \gamma_H$ in 100 % ethanol is +1.68 or +1.84 based on the Ph_4^+ and TAB BPh_4 assumptions, respectively. Thus, liquid water is more basic than liquid ethanol. The most surprising piece of information resulting from research based on reference-electrolyte assumptions is that 65 wt.-% ethanol is the most basic ethanol--water solvent, being more basic than pure liquid water or pure liquid ethanol.

Comparison with literature values.

Medium effects for single ions obtained using various methods are often quite different in magnitude and sometimes even in sign. Fortunately, there exists an independent method for estimating the order of magnitude of medium effects for the proton. This independent method which was first proposed by Popovych (8, 17) is based on a study of ΔpK_a's of large cationic acids between water and the solvents of interest where ΔpK_a is defined by:

$$\Delta pK_a = pK_a(s) - pK_a(H_2O) \qquad (225)$$

ΔpK_a can also be defined in terms of the medium effects of the acid, $\log {}_m\gamma_{BH^+}$, the conjugate base, $\log {}_m\gamma_B$, and the proton, $\log {}_m\gamma_H$:

$$\Delta pK_a = \log {}_m\gamma_H - \log \frac{{}_m\gamma_{BH^+}}{{}_m\gamma_B} \qquad (226)$$

In the case of large cationic acids, the neutral component of $\log {}_m\gamma_{BH^+}$ is expected to cancel approximately with $\log {}_m\gamma_B$ so that:

$$\Delta pK \cong \log {}_m\gamma_H - \log {}_m\gamma_{BH^+(el)} \qquad (227)$$

where $\log {}_m\gamma_{BH^+(el)}$ is the electrostatic component of the medium effect of the acid BH^+.

The ΔpK_a's of thirteen ammonium and anilinium acids in ethanol as compiled by Bell (175) range from 0.6 to 1.5 with a mean of 1.0. The electrostatic component of $\log {}_m\gamma_{BH^+}$ in ethanol acmounts to about 0.8 to 1.7 log units for ions 4 - 2 Å in size when calculated using the Born equation. Taking an intermediate value of 1.0 for $\log {}_m\gamma_{BH^+(el)}$, we calculate that $\log {}_m\gamma_H$ should have a magnitude of approximately 2 log units in 100 % ethanol. In other words, $\log {}_m\gamma_H$ should be greater than pK_a by about one log unit. Thus, estimates of $\log {}_m\gamma_H$ in 100 % ethanol of $\sim$ 2 log units are definitely "in the ballpark". This method of estimating "order of magnitude" values of $\log {}_m\gamma_H$ based on the ΔpK_a of cationic acids is one that is generally useful.

Medium effects for the proton, $\log {}_m\gamma_H$, in ethanol--water solvents obtained by various methods are listed in Table 74. Values of +1.68 and +1.84 obtained from the Ph_4^+ and TAB BPh_4 assumptions, respectively, are in good agreement with the expected value of $\sim$ 2 predicted from ΔpK_a's of cationic acids. Values of +4.603 obtained from the empirical method of Grunwald and co-workers appear to be outside a reasonable range. The value of 4.05 obtained from Izmaylov's

Table 74. Medium Effects for the Proton, $\log {}_{m}\gamma_{H}$, in Ethanol--Water Solvents. 25°C, Molal Scale.

wt.-% ethanol	This study Ph_4^+ assumption	This study TAB BPh_4 assumption	Popovych and Dill (17) TAB BPh_4 assumption	Gutzbezahl and Grunwald (116)	Aleksandrov and Izmaylov (104) Kr method
0.0	0.0	0.0	0.0	0.0	0.0
10.0	0.08 ± 0.02	-0.06 ± 0.02	-0.06	----	0.090
20.0	0.06 ± 0.03	-0.26 ± 0.02	-0.26	-0.006	0.175
30.0	-0.06 ± 0.02	-0.51 ± 0.02	-0.50	----	-----
35.0	----	----	----	0.017	-----
40.0	-0.32 ± 0.04	-0.79 ± 0.02	-0.82	----	-----
50.0	-0.62 ± 0.04	-0.98 ± 0.02	-1.03	0.211	-----
60.0	-0.80 ± 0.03	-1.13 ± 0.02	-1.14	----	-----
65.0	----	----	----	0.485	-----
70.0	-0.86 ± 0.04	-1.11 ± 0.03	-1.00	----	-----
72.0	----	----	----	----	0.873
80.0	-0.67 ± 0.04	-0.83 ± 0.03	-0.74	1.077	-----
88.5	----	----	----	----	1.50
90.0	-0.46 ± 0.11	-0.50 ± 0.08	-0.51	----	-----
93.5	----	----	----	----	1.86
95.8	----	----	----	----	2.14
98.0	----	----	~0.2	----	2.45
100.0	+1.68 ± 0.04	+1.84 ± 0.03	+1.85	4.603	4.05

method based on the use of proton-transfer constants is also out of the ballpark.

Upon examination of Grunwald and Izmaylov's values for $\log {}_m\gamma_H$ in ethanol--water solvents, (see Table 74), we see that they fail to reflect the expected variation in basicities of these solvents where a maximum solvent basicity (a minimum in $\log {}_m\gamma_H$) at $\sim$ 60 wt.-% ethanol is expected. Values of $\log {}_m\gamma_H$ obtained by Grunwald and Izmaylov are positive throughout the ethanol--water solvent system. On the other hand, the medium effects for the proton in ethanol--water solvents obtained by reference-electrolyte assumptions do reflect expected variations in the basicity of these solvents. In Table 74, there are two columns of values of $\log {}_m\gamma_H$ based on the TAB BPh_4 assumption. One column lists results obtained by Popovych and Dill (17) and the other, results obtained in this study using the data of Popovych and Dill along with the inclusion of some new data from the present study.

Thus, there are five independent methods that give the same results for $\log {}_m\gamma_H$ in ethanol--water solvents. These are the Ph_4P BPh_4, Ph_4As BPh_4, and TAB BPh_4 reference-electrolyte assumptions, results obtained from studying ΔpK_a's of cationic acids, and the Hammett acidity function ($-H_o - \log m_{HCl}$). The reference-electrolyte methods are further verified by the agreement

between values of $\log_{m}\gamma_{K}$ obtained from reference-electrolyte assumptions and similar values obtained from the Stokes - modified Born equation up to 60 wt.-% ethanol.

Medium effects for single ions in 100 % ethanol obtained by different methods are listed in Table 76. Results obtained from Bjerrum and Larsson's $E_j = 0$ assumption (9) and Izmaylov's $1/n^2$ extrapolation method do not agree well with those obtained from the Ph_4^+ and TAB^+ reference-electrolyte assumptions. Medium effects for cations obtained from the Ph_4^+ and TAB^+ assumptions are smaller in magnitude than those obtained from the other two methods listed. Values of $\log_{m}\gamma_{Br}$ obtained from the reference-electrolyte methods are small negative numbers whereas $\log_{m}\gamma_{Br}$ obtained from Bjerrum and Larsson's and Izmaylov's methods are +1.8 and +1.2, respectively.

Medium effects for electroneutral combinations of single ions should add up to the observed experimental values. For example, when the experimental value for $\log_{m}\gamma_{KCl}$ is 6.12, the sum of $\log_{m}\gamma_{K}$ and $\log_{m}\gamma_{Cl}$ should be equal to 6.12. This is exactly the case for medium effects obtained using the Ph_4^+ and TAB BPh_4 assumptions. However, using Bjerrum and Larsson's medium effects, $\log_{m}\gamma_{KCl}$ equals 6.6 and the value obtained for $\log_{m}\gamma_{KCl}$ from Izmaylov's $1/n^2$ extrapolation is

Table 76. Medium Effects for Single Ions in Ethanol. 25°C, Molal Scale.

Ion	Bjerrum and Larsson (9) $E_j = 0$	Izmaylov (103) $1/n^2$ extrapolation	Reference--Electrolyte methods	
			Ph_4^+	TAB BPh_4
H^+	2.5	3.9	1.68 ± 0.04	1.84 ± 0.03
Li^+	2.8	2.9	1.73	1.89
Na^+	3.5	4.2	2.64	2.80
K^+	4.1	4.0	2.67 ± 0.04	2.83 ± 0.03
Rb^+	3.9	4.6	2.69 ± 0.04	2.85 ± 0.04
Cs^+	4.0	3.8	2.48 ± 0.06	2.64 ± 0.06
Ag^+	2.1	3.7	----	----
Cl^-	2.5	1.2	3.45 ± 0.04	3.29 ± 0.03
Br^-	1.8	1.2	-0.21	-0.37
I^-	1.4	0.8	----	----
$TAB^+ = BPh_4^-$	---	---	----	-3.79 ± 0.02
Ph_4^+	---	---	-3.63 ± 0.03	----

5.2. There are similar inconsistencies and much worse for other electroneutral combinations of ions when literature values of $\log_m \gamma$ are used. The experimental value for $\log_m \gamma_{RbBr}$ is +2.48 and medium effects for Rb^+ and Br^- from the reference-electrolyte assumptions add up to this value. However, a value of +5.8 is obtained for $\log_m \gamma_{RbBr}$ from Bjerrum and Larsson's data.

The internal consistency and agreement with experimental values of medium effects for single ions obtained from reference-electrolyte assumptions lend further credibility to the reference-electrolyte methods. Any worthwhile method for evaluating medium effects for single ions should yield results that are in agreement with experimental values. It must be stressed, however, that the presence or absence of internal consistency does not necessarily by itself prove or disprove the validity of an extrathermodynamic method for estimating medium effects for single ions. The presence of internal consistency can assure that the measured thermodynamic quantities are accurate. However, in the case of extrapolation procedures, such as Izmaylov's $1/n^2$ procedure, the lack of agreement of estimated medium effects for single ions with accurate thermodynamic values does prove that the method is not valid.

Methanol.

Calculations by the tetraphenyl-ion assumption.

Medium effects for a large variety of electrolytes and electroneutral combinations of ions are listed in Table 51 in section VII-F-1-c. Medium effects for reference electrolytes in methanol are obtained from the usual calculations:

$$\log {}_m\gamma_{Ph_4P\ BPh_4} = \log {}_m\gamma_{Ph_4P\ Pi} + \log {}_m\gamma_{KBPh_4} - \log {}_m\gamma_{KPi} \qquad (137)$$

$$\log {}_m\gamma_{Ph_4As\ BPh_4} = \log {}_m\gamma_{Ph_4As\ Pi} + \log {}_m\gamma_{KBPh_4} - \log {}_m\gamma_{KPi} \qquad (138)$$

$$\log {}_m\gamma_{TAB\ BPh_4} = \log {}_m\gamma_{TAB\ Pi} + \log {}_m\gamma_{KBPh_4} - \log {}_m\gamma_{KPi} \qquad (139)$$

Once the medium effects are known for the reference electrolytes, the reference-electrolyte assumptions are applied to obtain medium effects for the individual ions:

$$\log {}_m\gamma_{Ph_4P} = \log {}_m\gamma_{BPh_4} = \tfrac{1}{2} \log {}_m\gamma_{Ph_4P\ BPh_4} = -41.0 \qquad (140)$$

$$\log {}_m\gamma_{Ph_4As} = \log {}_m\gamma_{BPh_4} = \tfrac{1}{2} \log {}_m\gamma_{Ph_4As\ BPh_4} = -4.18 \qquad (141)$$

$$\log {}_m\gamma_{TAB} = \log {}_m\gamma_{BPh_4} = \tfrac{1}{2} \log {}_m\gamma_{TAB\ BPh_4} = -4.30 \qquad (142)$$

Values of $\log {}_m\gamma$ forthe reference ions are tabulated in Table 77 along with numerical values of $\log {}_m\gamma$ for other ions calculated by various paths from thermodynamic data. The list of available medium effects in methanol (Table 51) is quite extensive and because of thet, a given ion usually appears in more than one electrolyte. For instance, values of $\log {}_m\gamma$ are listed in Table 51 for $KClO_4$, $KBPh_4$, KPi, KCl, and KBr. Thus, the medium effect for potassium can be calculated in a number of different ways not all of which yield identical results. All medium effects for single ions listed in Table 77 are ultimately based on the tetraphenyl (Ph_4^+) assumption, i.e., the average value of $\log {}_m\gamma_{Ph_4}$ from the reference electrolytes $Ph_4P\ BPh_4$ and $Ph_4As\ BPh_4$. In methanol, $\log {}_m\gamma_{Ph_4}$ has a numerical value of -4.14.

The medium effect for the proton in methanol can be calculated using three combinations of thermodynamic medium effects along with $\log {}_m\gamma_{Ph_4}$. These three calculations are :

Table 77. Medium Effects for Single Ions, $\log_m \gamma$, in Methanol Based on the Average Value of $\log_m \gamma_{BPh_4}$ from the $Ph_4P\,BPh_4$ and the $Ph_4As\,BPh_4$ Assumptions (the Ph_4^+ Assumption). 25°C, Molal Scale.

Ion	$\log_m \gamma$	Electrolytes Used in Calculation
$Ph_4P^+ = BPh_4^-$	-4.10	$Ph_4P\,BPh_4$
$Ph_4As^+ = BPh_4^-$	-4.18	$Ph_4As\,BPh_4$
$TAB^+ = BPh_4^-$	-4.30	$TAB\,BPh_4$
Ph_4^+	-4.14	$Ph_4P\,BPh_4$, $Ph_4As\,BPh_4$
H^+	+1.81	$AgBPh_4$, AgCl, HCl
H^+	+1.77	$CsBPh_4$, CsCl, HCl
H^+	+1.47	$KBPh_4$, KCl, HCl
Li^+	+0.96	$AgBPh_4$, AgCl, HCl, Li-H
Li^+	+0.92	$CsBPh_4$, CsCl, HCl, Li-H
Li^+	+0.62	$KBPh_4$, KCl, HCl, Li-H
Na^+	+1.57	$AgBPh_4$, AgCl, HCl, Na-H
Na^+	+1.53	$CsBPh_4$, CsCl, HCl, Na-H
Na^+	+1.23	$KBPh_4$, KCl, HCl, Na-H

Table 77. (Continued).

Ion	$\log_m \gamma$	Electrolytes Used in Calculation
K^+	+1.80	$CsBPh_4$, $CsClO_4$, $KClO_4$
K^+	+1.63	$KBPh_4$
K^+	+1.57	$RbBPh_4$, $RbClO_4$, $KClO_4$
K^+	+1.37	$CsBPh_4$, CsPi, KPi
K^+	+1.26	$RbBPh_4$, RbPi, KPi
K^+	-0.35	$AgBPh_4$, AgBr, KBr
Rb^+	+4.05	$KBPh_4$, KBr, RbBr
Rb^+	+2.07	$AgBPh_4$, AgBr, RbBr
Rb^+	+2.04	$KBPh_4$, KPi, RbPi
Rb^+	+1.90	$CsBPh_4$, $CsClO_4$, $RbClO_4$
Rb^+	+1.78	$CsBPh_4$, CsPi, RbPi
Rb^+	+1.73	$KBPh_4$, $KClO_4$, $RbClO_4$
Rb^+	+1.67	$RbBPh_4$
Cs^+	+1.90	$KBPh_4$, KPi, CsPi
Cs^+	+1.68	$AgBPh_4$, AgCl, CsCl
Cs^+	+1.64	$CsBPh_4$
Cs^+	+1.53	$RbBPh_4$, RbPi, CsPi,
Cs^+	+1.47	$KBPh_4$, $KClO_4$, $CsClO_4$
Cs^+	+1.41	$RbBPh_4$, $RbClO_4$, $CsClO_4$
Cs^+	+1.38	$KBPh_4$, KCl, CsCl

Table 77. (Continued).

Ion	$\log_m \gamma$	Electrolytes Used in Calculation
Tl^+	+2.95	$KBPh_4$, KBr, TlBr
Tl^+	+1.35	TAB BPh_4, TAB Pi, TlPi
Tl^+	+1.07	Ph_4AsPi, TlPi
Tl^+	+0.97	$AgBPh_4$, AgBr, TlBr
Tl^+	+0.94	$KBPh_4$, KPi, TlPi
Tl^+	+0.90	Ph_4P Pi, TlPi
Tl^+	+0.82	$CsBPh_4$, $CsClO_4$, $TlClO_4$
Tl^+	+0.82	$AgBPh_4$, AgCl, TlCl
Tl^+	+0.78	$CsBPh_4$, CsCl, TlCl
Tl^+	+0.68	$CsBPh_4$, CsPi, TlPi
Tl^+	+0.65	$KBPh_4$, $KClO_4$, $TlClO_4$
Tl^+	+0.59	$RbBPh_4$, $RbClO_4$, $TlClO_4$
Tl^+	+0.57	$RbBPh_4$, RbPi, TlPi
Tl^+	+0.52	$KBPh_4$, KCl, TlCl
Ag^+	+3.52	$KBPh_4$, KBr, AgBr
Ag^+	+1.54	$AgBPh_4$
Ag^+	+1.50	$CsBPh_4$, CsCl, AgCl
Ag^+	+1.24	$KBPh_4$, KCl, AgCl
Bu_4N^+	-5.80	TAB BPh_4, TABPi, Bu_4NPi
Bu_4N^+	-5.52	Ph_4AsPi, Bu_4NPi
Bu_4N^+	-5.39	$KBPh_4$, KPi, Bu_4NPi
Bu_4N^+	-5.35	Ph_4PPi, Bu_4NPi

Table 77. (Continued).

Ion	$\log_m Y$	Electrolytes used in Calculation
Bu_4N^+	-5.13	$CsBPh_4$, CsPi, Bu_4NPi
Bu_4N^+	-5.02	$RbBPh_4$, RbPi, Bu_4NPi
TAB^+	-5.24	$RbBPh_4$, RbPi, TABPi
TAB^+	-5.13	$CsBPh_4$, CsPi, TABPi
TAB^+	-4.91	Ph_4PPi, TABPi
TAB^+	-4.87	$KBPh_4$, KPi, TABPi
TAB^+	-4.74	Ph_4AsPi, TABPi
TAB^+	-4.46	TAB BPh_4 (-8.60)
Cu^+	+1.29	$AgBPh_4$, AgCl, HCl, Cu - H
Cu^+	+1.55	$CsBPh_4$, CsCl, HCl, Cu - H
Cu^+	+0.95	$KBPh_4$, KCl, HCl, Cu - H
Zn^{+2}	+4.40	$AgBPh_4$, AgCl, HCl, Zn - 2H
Zn^{+2}	+4.32	$CsBPh_4$, CsCl, HCl, Zn - 2H
Zn^{+2}	+3.72	$KBPh_4$, KCl, HCl, Zn - 2H
Cd^{+2}	+2.71	$AgBPh_4$, AgCl, HCl, Cd - 2H
Cd^{+2}	+2.63	$CsBPh_4$, CsCl, HCl, Cd - 2H
Cd^{+2}	+2.03	$KBPh_4$, KCl, HCl, Cd - 2H

Table 77. (Continued).

Ion	$\log_m \gamma$	Electrolytes Used in Calculation
Cl^-	+2.46	Ph_4AsPi, KPi, KCl
Cl^-	+2.42	$KBPh_4$, KCl
Cl^-	+2.35	$RbBPh_4$, $RbClO_4$, $TlClO_4$, TlCl
Cl^-	+2.29	Ph_4PPi, KPi, KCl
Cl^-	+2.29	$KBPh_4$, $KClO_4$, $TlClO_4$, TlCl
Cl^-	+2.16	$CsBPh_4$, CsCl
Cl^-	+2.12	$AgBPh_4$. AgCl
Cl^-	+2.04	Ph_4PPi, TlPi, TlCl
Cl^-	+2.00	$KBPh_4$, KPi, TlPi, TlCl
Cl^-	+1.87	Ph_4AsPi, TlPi, TlCl
Cl^-	+1.59	TAB BPh_4, TABPi, TlPi, TlCl
Br^-	+2.41	$KBPh_4$, KCl, TlCl, TlBr
Br^-	+2.36	$RbBPh_4$, RbPi, TlPi, TlBr
Br^-	+2.36	$RbBPh_4$. RbBr
Br^-	+2.34	$RbBPh_4$, $RbClO_4$, $TlClO_4$, TlBr
Br^-	+2.30	$KBPh_4$, $KClO_4$, $RbClO_4$, RbBr
Br^-	+2.28	$KBPh_4$, $KClO_4$, $TlClO_4$, TlBr
Br^-	+2.26	$KBPh_4$, KCl, AgCl, AgBr
Br^-	+2.25	$CsBPh_4$, CsPi, TlPi, TlBr
Br^-	+2.25	$CsBPh_4$, CsPi, RbPi, RbBr
Br^-	+2.15	$CsBPh_4$, CsCl, TlCl, TlBr
Br^-	+2.13	$CsBPh_4$, $CsClO_4$, $RbClO_4$, RbBr
Br^-	+2.11	$AgBPh_4$, AgCl, TlCl, TlBr

Table 77. (Continued).

Ion	$\log_m \gamma$	Electrolytes Used in Calculation
Br^-	+2.11	$CsBPh_4$, $CsClO_4$, $TlClO_4$, TlBr
Br^-	+2.03	Ph_4PPi, TlPi, TlBr
Br^-	+2.00	$CsBPh_4$, CsCl, AgCl, AgBr
Br^-	+1.99	$KBPh_4$, KPi, TlPi, TlBr
Br^-	+1.99	$KBPh_4$, KPi, RbPi, RbBr
Br^-	+1.96	$AgBPh_4$, AgBr
Br^-	+1.86	Ph_4AsPi, TlPi, TlBr
Br^-	+1.58	TAB BPh_4, TABPi, TlPi, TlBr
Br^-	+0.35	$RbBPh_4$, RbPi, KPi, KBr
Br^-	+0.24	$CsBPh_4$, CsPi, KPi, KBr
Br^-	+0.04	$RbBPh_4$, $RbClO_4$, $KClO_4$, KBr
Br^-	-0.02	$KBPh_4$, KBr
Br^-	-0.19	$CsBPh_4$, $CsClO_4$, $KClO_4$, KBr
I^-	+1.36	$KBPh_4$, KCl, AgCl, AgI
I^-	+1.10	$CsBPh_4$, CsCl, AgCl, AgI
I^-	+1.06	$AgBPh_4$, AgI
I^-	-0.92	$KBPh_4$, KBr, AgBr, AgI
NO_3^-	+2.56	$KBPh_4$, KCl, TlCl, $TlNO_3$
NO_3^-	+2.51	$RbBPh_4$, RbPi, TlPi, $TlNO_3$
NO_3^-	+2.49	$RbBPh_4$, $RbClO_4$, $TlClO_4$, $TlNO_3$
NO_3^-	+2.46	$AgBPh_4$, AgCl, TlCl, $TlNO_3$
NO_3^-	+2.43	$KBPh_4$, $KClO_4$, $TlClO_4$, $TlNO_3$

Table 77. (Continued).

Ion	$\log_m Y$	Electrolytes Used in Calculation
NO_3^-	+2.40	$CsBPh_4$, CsPi, TlPi, $TlNO_3$
NO_3^-	+2.30	$CsBPh_4$, CsCl, TlCl, $TlNO_3$
NO_3^-	+2.26	$CsBPh_4$, $CsClO_4$, $TlClO_4$, $TlNO_3$
NO_3^-	+2.18	Ph_4PPi, TlPi, $TlNO_3$
NO_3^-	+2.14	$KBPh_4$, KPi, TlPi, $TlNO_3$
NO_3^-	+2.11	$AgBPh_4$, AgBr, TlBr, $TlNO_3$
NO_3^-	+2.01	Ph_4AsPi, TlPi, $TlNO_3$
NO_3^-	+1.73	TAB BPh_4, TABPi, TlPi, $TlNO_3$
NO_3^-	+0.13	$KBPh_4$, KBr, TlBr, $TlNO_3$
ClO_4^-	+1.33	$KBPh_4$, $KClO_4$
ClO_4^-	+1.39	$RbBPh_4$, $RbClO_4$
ClO_4^-	+1.16	$CsBPh_4$, $CsClO_4$
Pi^-	-0.37	$RbBPh_4$, RbPi
Pi^-	-0.48	$CsBPh_4$, CsPi
Pi^-	-0.70	Ph_4PPi
Pi^-	-0.74	$KBPh_4$, KPi
Pi^-	-0.87	Ph_4AsPi
Pi^-	-1.15	TAB BPh_4, TABPi

Table 77. (Continued).

Ion	$\log_m Y$	Electrolytes Used in Calculation
Ac^-	+2.86	$KBPh_4$, KCl, AgCl, AgAc
Ac^-	+2.60	$CsBPh_4$, CsCl, AgCl, AgAc
Ac^-	+2.56	$AgBPh_4$, AgAc
Ac^-	+0.78	$KBPh_4$, KBr, AgBr, AgAc
Bz^-	+1.56	$KBPh_4$, KCl, AgCl, AgBz
Bz^-	+1.30	$CsBPh_4$, CsCl, AgCl, AgBz
Bz^-	+1.26	$AgBPh_4$, AgBz
Bz^-	-0.72	$KBPh_4$, KBr, AgBr, AgBz

$$\log {}_{m}\gamma_{H} = -\log {}_{m}\gamma_{Ph_4} + \log {}_{m}\gamma_{AgBPh_4} - \log {}_{m}\gamma_{AgCl} + \quad (228)$$

$$+ \log {}_{m}\gamma_{HCl} = +1.81$$

$$\log {}_{m}\gamma_{H} = -\log {}_{m}\gamma_{Ph_4} + \log {}_{m}\gamma_{CsBPh_4} - \log {}_{m}\gamma_{CsCl} + \quad (229)$$

$$+ \log {}_{m}\gamma_{HCl} = +1.77$$

$$\log {}_{m}\gamma_{H} = -\log {}_{m}\gamma_{Ph_4} + \log {}_{m}\gamma_{KBPh_4} - \log {}_{m}\gamma_{KCl} + \quad (230)$$

$$+ \log {}_{m}\gamma_{HCl} = +1.47$$

The six calculations used for arriving at a value for $\log {}_{m}\gamma_{K}$ are :

$$\log {}_{m}\gamma_{K} = -\log {}_{m}\gamma_{Ph_4} + \log {}_{m}\gamma_{CsBPh_4} - \log {}_{m}\gamma_{CsClO_4} + \quad (231)$$

$$+ \log {}_{m}\gamma_{KClO_4} = +1.80$$

$$\log {}_{m}\gamma_{K} = -\log {}_{m}\gamma_{Ph_4} + \log {}_{m}\gamma_{RbBPh_4} - \log {}_{m}\gamma_{RbClO_4} + \quad (232)$$

$$+ \log {}_{m}\gamma_{KClO_4} = +1.57$$

$$\log {}_{m}\gamma_{K} = -\log {}_{m}\gamma_{Ph_4} + \log {}_{m}\gamma_{KBPh_4} = +1.63 \quad (233)$$

$$\log {}_m\gamma_K = -\log {}_m\gamma_{Ph_4} + \log {}_m\gamma_{CsBPh_4} - \log {}_m\gamma_{CsPi} + \log {}_m\gamma_{KPi} = +1.37 \quad (234)$$

$$\log {}_m\gamma_K = -\log {}_m\gamma_{Ph_4} + \log {}_m\gamma_{RbBPh_4} - \log {}_m\gamma_{RbPi} + \log {}_m\gamma_{KPi} = +1.36 \quad (235)$$

$$\log {}_m\gamma_K = -\log {}_m\gamma_{Ph_4} + \log {}_m\gamma_{AgBPh_4} - \log {}_m\gamma_{AgBr} + \log {}_m\gamma_{KBr} = -0.35 \quad (236)$$

Electrolytes whose thermodynamic medium effects were used in the calculation of medium effects for other single ions in methanol are listed in the appropriate places in Table 77. It must be remembered that all medium effects for single ions listed in Table 77 are based on the Ph_4^+ assumption.

Discrepancies among the individual values of $\log {}_m\gamma$ for any one ion are not a reflection on the reference-electrolyte assumption, but are due to inaccuracies in the thermodynamic (experimentally measured) medium effects used in the calculations. Some of the more obvious discrepancies and their possible causes will now be discussed.

The value for $\log {}_m\gamma_{KBr}$ is probably incorrect by

about 2 log units since $\log_{m}\gamma_{Rb}$ calculated using $\log_{m}\gamma_{KBr}$ is 2 log units larger than the next value. Other evidence for the inaccuracy of $\log_{m}\gamma_{KBr}$ can be seen in values for $\log_{m}\gamma_{K}$, $\log_{m}\gamma_{Tl}$, $\log_{m}\gamma_{Ag}$, $\log_{m}\gamma_{Br}$, $\log_{m}\gamma_{I}$, $\log_{m}\gamma_{NO_3}$, $\log_{m}\gamma_{Ac}$, and $\log_{m}\gamma_{Bz}$ (Bz is benzoate), which are all about 2 log units higher or lower than the average of other values. When medium effects of alkali-metal perchlorates, tetraphenylborates, picrates, and chlorides are used to calculate medium effects for single ions, the resulting medium effects cluster within 0.2 log units provided $\log_{m}\gamma_{KBr}$ was not used in the calculation. When medium effects for the silver and thallous salts are used to calculate medium effects for single ions, the results are in excellent agreement (within $\pm$0.25 log units) of the results calculated using alkali-metal salts.

Although most calculations used in Table 77 yield satisfying results, there is still room for improvement. Better, more accurate ion-activity products and standard potential measurements are needed to narrow down the range of medium effects for any one single ion.

Interpretation of results.

Structure of solvent.

Much the same can be said for methanol as was said about ethanol in section VIII-A-3-a. Pure methanol is a structured solvent made up of small linear chains of methanol molecules hydrogen bonded in a manner similar to ethanol. One would expect medium effects for single ions to be similar in the two solvents.

Bates and Robinson (11) found that methanol--water mixtures are similar in basicity characteristics to ethanol--water mixtures. They found that Δ pK_a for o-chloroanilinium and m-nitroanilinium ions went through a minimum when plotted as a function of wt.-% methanol and reached a maximum in 100 % methanol. The Δ pK_a's for these cationic acids should be equal to the medium effect for the proton, $\log {}_m\gamma_H$, when corrected for the term $\log ({}_m\gamma_{BH^+}/{}_m\gamma_B)$ which should be equal to $\log {}_m\gamma_{BH^+(el)}$. From the results of Bates and Robinson, we conclude that methanol--water mixtures are more basic than water ($\log {}_m\gamma_H$ is negative) and pure methanol is less basic than water. In other words, the proton exists in a higher energy state in pure methanol than in pure water. The values of Δ pK_a for cationic acids reach a minimum close to 80 wt.-% methanol and then rise steeply to positive values in

pure methanol. This behavior is similar to that of $\log_m \gamma_H$ in the ethanol--water solvent system.

Using an argument similar to the one used for describing effects of adding ethanol to water, one can say that addition of methanol to water breaks up the highly structured aqueous solvent and makes available a larger number of basic sites on the water. The basicity of the solvent mixtures increases until it reaches a maximum after which, the effects of addition of methanol are greater than the effects of structure breaking and the basicity decreases. The large decrease in basicity in the region between 80 and 100 wt.-% methanol may be due to the structuring of the organic solvent with the resulting inclusion of any available water molecules in the organic matrix thus rendering basic sites on the water unavailable for bonding.

Solvation of solutes.

Similar statements can be made about solvation of solutes in methanol as about the solvation in ethanol in section VIII-A-3-b. There are two or three regions of solvation around each particle. The extent to which solvent molecules are structured in each region depends on the size and charge of the particle. Small ions will be structure promoters. They will orient solvent molecules in the first solvation sphere to a greater degree than large ions and uncharged solutes. The structure of the solvent around large uncharged solutes and ions of small charge and similar dimensions will be similar.

One important piece of information about the relative basicity of methanol and water comes from the work of Kebarle, Haynes, and Collins (176) who determined that protons in solution are preferentially solvated by water molecules as opposed to methanol molecules. They based this conclusion on mass spectrometric results of gas-phase protons in equilibrium with varying methanol--water vapors. Other mass spectrometric evidence (183) indicates that in the gas phase, methanol molecules have a greater basicity than water molecules. The preference for methanol on the part of the proton decreases with increasing number of solvent molecules in a cluster, and in microclusters, including liquid solutions, water is more basic than methanol.

Discussion.

Representative values of medium effects for single ions in methanol had to be chosen somewhat arbitrarily from the data in Table 77. These representative values of $\log {}_{m}\gamma$ for single ions in methanol are listed in Table 78.

Values of $\log {}_{m}\gamma$ for the reference ions were obtained by applying the reference-electrolyte assumption. As was stated earlier, the value of -4.14 for $\log {}_{m}\gamma_{Ph_4}$, which is the average value of $\log {}_{m}\gamma_{\text{reference ion}}$ from the Ph_4P BPh_4 and Ph_4As BPh_4 assumptions, was used to calculate all medium effects for single ions in methanol appearing in Tables 77 and 78. It is interesting to note that $\log {}_{m}\gamma_{Ph_4P}$ and $\log {}_{m}\gamma_{Ph_4As}$ differ by only 0.08 log units, which indicates that the medium effects for these two ions are predominantly determined by size, structure, and surface charge rather than the nature of the central atom. Medium effects for all the reference ions are negative indicating that they are preferentially solvated by the organic solvent.

The medium effect for the proton in methanol, $\log {}_{m}\gamma_{H}$, is listed as +1.68. This is the average of all three values reported in Table 77. There is no valid reason to reject any of the three values or to favor any one of them over the others. The positive value of $\log {}_{m}\gamma_{H}$ indicates that liquid methanol is

Table 78. Representative Values of Medium Effects, $\log_m \gamma$, for Single Ions in Methanol Based on the Ph_4^+ Assumption. 25°C, Molal Scale.

Ion	$\log_m \gamma$
$Ph_4P^+ = BPh_4^-$	-4.10
$Ph_4As^+ = BPh_4^-$	-4.18
$TAB^+ = BPh_4^-$	-4.30
Ph_4^+	-4.14
H^+	+1.68
Li^+	+0.83
Na^+	+1.44
K^+	+1.63
Rb^+	+1.67
Cs^+	+1.64
Tl^+	+0.82
Ag^+	+1.54
Bu_4N^-	-5.44
TAB^+	-4.70
Cu^+	+1.26
Zn^{+2}	+4.11
Cd^{+2}	+2.46
Cl^-	+2.42
Br^-	+2.36
I^-	+1.17
NO_3^-	+2.35
ClO_4^-	+1.29
Pi^-	-0.79
Ac^-	+2.67
Bz^-	+1.37

less basic than liquid water, or that the proton exists in a higher energy state in methanol than in water. It is interesting to note that in ethanol, $\log {}_{m}\gamma_{H}$ is also +1.68. This apparent coincidence testifies to the similarity of the two alcohols.

The tabulated value (Table 78) of +0.83 for $\log {}_{m}\gamma_{Li}$ in methanol is the average of all three values reported in Table 77. The corresponding value in ethanol is +1.73 log units.

The value of +1.44 for $\log {}_{m}\gamma_{Na}$ is also the average of the three calculated values from Table 77. The corresponding value in ethanol is +2.64. It appears that small cations would be preferentially solvated by methanol as opposed to ethanol which would be expected as predicted from the Born equation.

The value of +1.63 for $\log {}_{m}\gamma_{K}$ is the recommended one because it is based on a calculation involving $KBPh_4$ directly. Other values of $\log {}_{m}\gamma_{K}$ listed in Table 77 required at least two additional medium effects in the calculation. Values of $\log {}_{m}\gamma_{K}$ based on the medium effects of alkali-metal perchlorates and tetraphenylborates are +1.80, +1.63, and +1.57 with an average of +1.67. This happens to be within experimental error of the tabulated value of +1.63 for $\log {}_{m}\gamma_{K}$.

The value for $\log {}_{m}\gamma_{Rb}$ of +1.67 listed in Table 78

was chosen because it was calculated in the most direct way, using $RbBPh_4$. A value of +1.73 for $\log {}_m\gamma_{Rb}$ derived from medium effects for $KBPh_4$, $KClO_4$, and $RbClO_4$ is quite close, lending credibility to the tabulated value. The corresponding value in ethanol is +2.69 log units which is consistent with the previous observation that small cations favor methanol over ethanol.

The medium effect $\log {}_m\gamma$ for Cs^+ listed in Table 78 is +1.64. This is the value calculated using $CsBPh_4$. It is close to the value of +1.67 for $\log {}_m\gamma_{Rb}$ just as medium effects for these two ions are similar in ethanol. The medium effect for Cs^+ in ethanol is +2.48 log units.

The medium effect, $\log {}_m\gamma$ for Tl^+ was chosen by averaging all the values listed in Table 77 except those involving $\log {}_m\gamma_{KBr}$. In methanol, $\log {}_m\gamma_{Tl} = +0.82$ and in ethanol, it is +1.61.

A value of +1.54 is listed in Table 78 for $\log {}_m\gamma_{Ag}$. This is the value obtained using $\log {}_m\gamma_{AgBPh_4}$. The value of +1.50 for $\log {}_m\gamma_{Ag}$ calculated using medium effects of $CsBPh_4$, CsCl, and AgCl is satisfyingly close to 1.54.

A value of -5.44 is listed in Table 78 for $\log {}_m\gamma_{Bu_4N}$. This is the average of two values of $\log {}_m\gamma_{Bu_4N}$ calculated using medium effects for Ph_4P Pi and Ph_4As Pi which

were determined experimentally in this study. The Bu_4N^+ ion is large and organic in nature and as such, it is preferentially solvated in organic solvents as opposed to water.

The listed value for $\log {}_m\gamma_{TAB}$ of -4.70 is the average of three values obtained using medium effects of Ph_4P Pi, Ph_4As Pi, and TAB BPh_4. In ethanol, $\log {}_m\gamma_{TAB} = -3.79$ which is about 1 log unit more positive than the value in methanol and in keeping with the observation that cations exist in a higher energy state in ethanol as compared to methanol.

The medium effects for Cu^+, Zn^{+2}, and Cd^{+2} of +1.26, +4.11 and +2.46, respectively, are the average of the values listed in Table 77 for these ions. It is interesting to note that the medium effects for these transition-metal ions are all positive indicating that they do not form specific solvates in methanol.

The value of $\log {}_m\gamma_{Cl} = +2.42$ was calculated using medium effects of $KBPh_4$ and KCl. The same calculation path was used by Popovych (18) to calculate $\log {}_m\gamma_{Cl} = +2.08$ in methanol using the TAB BPh_4 assumption. In Table 77, the value of $\log {}_m\gamma_{Cl} = +2.12$ closely agrees with Popovych's value. It was obtained using medium effects for $AgBPh_4$ and AgCl.

Medium effects for Br^- ion listed in Table 77 range from +2.41 to -0.19 with a median value of +2.11.

The values calculated using $\log {}_m\gamma_{KBr}$ are rejected. The representative value of +2.36 listed in Table 78 is based on the most direct calculation involving medium effects of $RbBPh_4$ and RbBr. An identical value of +2.36 is obtained using medium effects for $RbBPh_4$, RbPi, TlPi, and TlBr. The medium effect for Br^- in ethanol is -0.21 log units, a rather uncertain value since $\log {}_m\gamma_{Cl}$ and $\log {}_m\gamma_I$ are both positive. Medium effects for small negative ions are also positive in methanol indicating preferential solvation by water.

The medium effect for I^- is listed as +1.17 log units in Table 78. This is the average of the first three values of $\log {}_m\gamma_I$ in Table 77. The value of -0.92 was not included in the average because $\log {}_m\gamma_{KBr}$ was used to obtain it. The most direct value of +1.06 obtained using medium effects of $AgBPh_4$ and AgI was not used alone because the value for $\log {}_m\gamma_{AgBPh_4}$ is questionable (8).

The medium effect for NO_3^- is reported in Table 78 as +2.35. This is the average of thirteen values from Table 77. The value of +0.13 obtained via $\log {}_m\gamma_{KBr}$ was not included in the average.

The medium effect for ClO_4^- of +1.29 log units is the average of the two most direct values of -0.87 and -0.70 obtained from medium effects of Ph_4As Pi and Ph_4P Pi, respectively.

Medium effects for Ac^- (acetate ion) and Bz^- (benzoate ion) of +2.67 and +1.37, respectively, are averages of all values listed except those involving $\log {}_m\gamma_{KBr}$. It is interesting to note that these values are positive even though Ac^- and Bz^- are rather large and would be expected to solvate rather easily in organic solvents. Medium effects for other Ac^- and Bz^- salts should be determined so that $\log {}_m\gamma_{Ac}$ and $\log {}_m\gamma_{Bz}$ can be evaluated by alternate paths.

As in ethanol, medium effects for small cations and anions in methanol are positive. In general, they are about one log unit more negative than the corresponding values in ethanol. Thus, ions are more readily solvated in methanol as opposed to ethanol. Medium effects for the proton are similar (+1.68 log units) in both solvents. Although methanol and ethanol have similar basicities, they have dissimilar solvating powers for ions of appreciable size.

Comparison with literature values.

Medium effects for single ions in methanol obtained by various methods are listed in Table 79. The first four rows list medium effects obtained using reference-electrolyte assumptions. Although medium effects obtained by Alexander and Parker (28) should be identical to those obtained by Kolthoff (31), they are not. This results from inaccuracies in experimental values of $\log_m \gamma$ for the electrolytes used. Alexander and Parker's values are probably the most inaccurate since these authors do not correct for non-ideal behavior of their electrolytes with activity coefficients and degrees of dissociation. If we used experimental data of good accuracy throughout, medium effects from the $Ph_4As\ BPh_4$ assumption would be in excellent agreement with those obtained from the Ph_4^+ assumption. In most cases, the agreement is only fair. Except for $\log_m \gamma_{Rb}$ and $\log_m \gamma_{Ag}$, the medium effects determined by Popovych (18) using the TAB BPh_4 assumption are in good agreement with those from the Ph_4^+ assumption.

In general, the medium effects for most cations and anions in methanol based on reference-electrolyte assumptions are positive and medium effects for Pi^- and the reference ions are negative.

Medium effects for cations and anions in methanol evaluated by Izmaylov's $1/n^2$ extrapolation procedure (103)

are positive and, in qualitative agreement with medium effects obtained using reference electrolytes.

Medium effects for cations in methanol obtained by Strehlow (36), using a modified Born equation are negative. Alfenaar and DeLigny (8) also obtained negative values for $\log_m \gamma_{cations}$ in methanol using their extrapolation procedure in which ΔG^o(neut) was corrected for by the inert-gas assumption before extrapolation. Andrews et al., using the linear extrapolation procedure of Feakins and Watson (108) also obtained negative values for $\log_m \gamma_{cations}$ in methanol. Values of $\log_m \gamma_{anions}$ in methanol obtained by Strehlow (36), Alfenaar and DeLigny (8) and Andrews et al. (108) are all more positive than the equivalent values obtained via reference-electrolyte assumptions. As was previously mentioned, values of $\log_m \gamma$ for single ions obtained by extrapolation procedures of Alfenaar and DeLigny and Feakins et al. are not to be trusted due to the inherent inability of these methods to yield accurate results.

Table 79. Medium Effects, $\log_{m}\gamma$, for Single Ions in Methanol. 25°C, Molal Scale.

Method	$\log_{m}\gamma$ H^+	Li^+	Na^+	K^+	Rb^+	Cs^+	Ag^+
Ph_4^+ Assumption	1.68	0.83	1.44	1.63	1.67	1.64	1.54
Alexander and Parker Ph_4As BPh_4 assumption (28)	----	----	----	1.7	----	1.4, 1.3	1.2
Kolthoff, Ph_4As BPh_4 assumption (31)	2.0	----	1.6	1.9	1.9	1.8	1.4
Popovych, TAB BPh_4 assumption (18)	1.84	----	----	1.80	0.89	----	0.78
Pleskov, Rb electrode (37)	0.3	----	----	----	0.0	----	-0.3
Izmaylov, $1/n^2$ extrapolation (103)	3.1	1.6	1.8	2.0	2.8	2.7	3.5
Strehlow, modified Born equation (36)	0.07	----	-0.40	-0.12	-0.06	0.01	----
Alfenaar and DeLigny (8)	-1.45	----	-1.34	-0.90	-0.89	-0.94	----
Andrews et al. (method of Feakins and Watson)(108)	-2.25	-2.89	-2.23	-1.57	----	----	----

Table 79. (Continued).

Method	Cl^-	Br^-	I^-	$\log_m \gamma$ Pi^-	TAB^+	Ph_4As^+	Ph_4^+
Ph_4^+ Assumption	2.42	2.36	1.17	-0.79	-4.70	----	-4.14
Alexander and Parker $Ph_4As\ BPh_4$ assumption (28)	1.9	1.5	0.3, 0.9	-1.2	----	-4.2	----
Kolthoff, $Ph_4As\ BPh_4$ assumption (31)	2.3	2.1	1.3	-0.9	----	-4.2	----
Popovych, TAB BPh_4 assumption (18)	2.08	----	----	-0.95	-4.30	----	----
Pleskov, Rb electrode (37)	3.7	----	----	----	----	----	----
Izmaylov, $1/n^2$ extrapolation (103)	1.0	1.0	0.0	----	----	----	----
Strehlow, modified Born equation (36)	4.00	3.53	2.96	----	----	----	----
Alfenaar and DeLigny (8)	5.69	5.31	4.56	----	----	----	----
Andrews et al. (method of Feakins and Watson)(108)	6.18	5.80	5.04	----	----	----	----

Acetonitrile.

Calculations by the tetraphenyl-ion assumption.

Medium effects for the reference electrolytes $Ph_4P\ BPh_4$ and $Ph_4As\ BPh_4$ in acetonitrile were obtained by the usual indirect method:

$$\log {}_m\gamma_{Ph_4P\ BPh_4} = \log {}_m\gamma_{Ph_4P\ Pi} + \log {}_m\gamma_{KBPh_4} - \log {}_m\gamma_{KPi} = +11.62 \pm 0.08 \quad (137)$$

$$\log {}_m\gamma_{Ph_4As\ BPh_4} = \log {}_m\gamma_{Ph_4As\ Pi} + \log {}_m\gamma_{KBPh_4} - \log {}_m\gamma_{KPi} = +11.44 \pm 0.08 \quad (138)$$

Medium effects for the reference electrolyte TAB BPh_4 were not calculated due to the large solubility (0.5707 molal at 25°C) of TAB BPh_4 in acetonitrile. Applying the reference-electrolyte assumption, we obtain medium effects for the reference ions in acetonitrile:

$$\log {}_m\gamma_{Ph_4P} = \log {}_m\gamma_{BPh_4} = \tfrac{1}{2} \log {}_m\gamma_{Ph_4P\ BPh_4} = -5.81 \pm 0.04 \quad (140)$$

$$\log {}_m\gamma_{Ph_4As} = \log {}_m\gamma_{BPh_4} = \tfrac{1}{2} \log {}_m\gamma_{Ph_4As\ BPh_4} = -5.72 \pm 0.04 \quad (141)$$

A complete error analysis was carried out on the

pK values for electrolytes in acetonitrile determined in this study. The standard deviations in the values of $\log_m \gamma$ for electrolytes and single ions, calculated by the method of propogation of errors, are listed and discussed in sections VII-F-1-e (for electrolytes) and VIII-C-2 (for single ions).

Values of $\log_m \gamma$ for the reference ions obtained from the two assumptions are just about within experimental error so that these values can be averaged for further calculations. The resulting value of -5.77 ± 0.05 log units for the reference ion is termed the medium effect for the tetraphenyl (Ph_4^+) ion in acetonitrile and its further application in evaluating medium effects for single ions is known as the tetraphenyl assumption.

Table 80 lists medium effects for single ions in acetonitrile calculated using the tetraphenyl assumption. Using the data in Table 52 for medium effects for electroneutral combinations of ions, multiple calculation paths were available when calculating medium effects for any one single ion. Table 80 lists the electrolytes whose medium effects were used to calculate values of $\log_m \gamma$ for single ions. It must be remembered that all medium effects for single ions reported in Table 80 are based on the tetraphenyl assumption. The large diversity of values listed for any particular ion is a result of inaccuracies in the experimental data in

Table 80. Medium Effects for Single Ions in Acetonitrile Based on the Average Value of $\log {}_m\gamma_{BPh_4}$ From the $Ph_4P\ BPh_4$ and $Ph_4As\ BPh_4$ Assumptions. 25°C, Molal Scale.

Ion	$\log {}_m\gamma$	Electrolytes Used in Calculation
$Ph_4P^+ = BPh_4^-$	-5.81 ± 0.04	$Ph_4P\ BPh_4$
$Ph_4As^+ = BPh_4^-$	-5.72 ± 0.04	$Ph_4As\ BPh_4$
Ph_4^+	-5.77 ± 0.05	$Ph_4P\ BPh_4$, $Ph_4As\ BPh_4$
H^+	+8.2	Reference 31.
K^+	+2.21	$AgBPh_4$, AgBr, KBr
K^+	+1.46	Ph_4AsPi, KPi
K^+	+1.27	Ph_4PPi, KPi
K^+	+1.24	$CsBPh_4$, $CsClO_4$, $KClO_4$
K^+	+1.09	$RbBPh_4$, $RbClO_4$, $KClO_4$
K^+	$+1.09 \pm 0.07$	$KBPh_4$
K^+	+0.56	$CsBPh_4$, CsPi, KPi
K^+	+0.41	$RbBPh_4$, RbPi, KPi
Rb^+	+2.86	$CsBPh_4$, CsCl, RbCl
Rb^+	+1.71	$AgBPh_4$, AgI, RbI
Rb^+	+1.67	Ph_4AsPi, RbPi

Table 80. (Continued).

Ion	$\log_m \gamma$	Electrolytes Used in Calculation
Rb^+	+1.57	$KBPh_4$, KPi, RbPi
Rb^+	+1.57	$KBPh_4$, KCl, RbCl
Rb^+	+1.54	$AgBPh_4$, AgBr, RbBr
Rb^+	+1.48	Ph_4PPi, RbPi
Rb^+	+1.16	$CsBPh_4$, CsPi, RbPi
Rb^+	+1.13	$AgBPh_4$, AgCl, RbCl
Rb^+	+1.04	$CsBPh_4$, $CsClO_4$, $RbClO_4$
Rb^+	+0.89	$KBPh_4$, $KClO_4$, $RbClO_4$
Rb^+	$+0.89 \pm 0.07$	$RbBPh_4$
Rb^+	+0.42	$KBPh_4$, KBr, RbBr
Cs^+	+1.27	Ph_4AsPi, CsPi
Cs^+	+1.17	$KBPh_4$, KPi, CsPi
Cs^+	+1.08	Ph_4PPi, CsPi
Cs^+	$+0.64 \pm 0.07$	$CsBPh_4$
Cs^+	+0.49	$RbBPh_4$, RbPi, CsPi
Cs^+	+0.49	$RbBPh_4$, $RbClO_4$, $CsClO_4$
Cs^+	+0.65	$KBPh_4$, KCl, CsCl
Cs^+	-1.09	$AgBPh_4$, AgCl, CsCl
Cs^+	-1.33	$RbBPh_4$, RbCl, CsCl
Tl^+	+3.67	$CsBPh_4$, CsCl, TlCl
Tl^+	+2.67	$AgBPh_4$, AgI, TlI
Tl^+	+2.44	$AgBPh_4$, AgBr, TlBr

Table 80. (Continued).

Ion	$\log_m \gamma$	Electrolytes Used in Calculation
Tl^+	+2.38	$KBPh_4$, KCl, TlCl
Tl^+	+2.17	Ph_4AsPi, TlPi
Tl^+	+2.07	$KBPh_4$, KPi, TlPi
Tl^+	+1.98	Ph_4PPi, TlPi
Tl^+	+1.94	$AgBPh_4$, AgCl, TlCl
Tl^+	+1.85	$RbBPh_4$, RbI, TlI
Tl^+	+1.54	$CsBPh_4$, CsPi, TlPi
Tl^+	+1.39	$RbBPh_4$, RbPi, TlPi
Tl^+	+1.32	$KBPh_4$, KBr, TlBr
Tl^+	+0.99	$CsBPh_4$, $CsClO_4$, $TlClO_4$
Tl^+	+0.84	$KBPh_4$, $KClO_4$, $TlClO_4$
Tl^+	+0.84	$RbBPh_4$, $RbClO_4$, $TlClO_4$
Ag^+	-1.90	$CsBPh_4$, CsCl, AgCl
Ag^+	-3.19	$KBPh_4$, KCl, AgCl
Ag^+	-3.63	$AgBPh_4$
Ag^+	-3.87	$RbBPh_4$, RbCl, AgCl
Ag^+	-4.28	$RbBPh_4$, RbBr, AgBr
Ag^+	-4.45	$RbBPh_4$, RbI, AgI
Ag^+	-4.75	$KBPh_4$, KBr, AgBr

Table 80. (Continued).

Ion	$\log_m \gamma$	Electrolytes Used in Calculation
Cl^-	+8.39	$RbBPh_4$, $RbClO_4$, $TlClO_4$, TlCl
Cl^-	+8.39	$KBPh_4$, $KClO_4$, $TlClO_4$, TlCl
Cl^-	+7.53	$RbBPh_4$, RbCl
Cl^-	+7.29	$AgBPh_4$, AgCl
Cl^-	+7.25	Ph_4PPi, TlPi, TlCl
Cl^-	+7.16	$KBPh_4$, KPi, TlPi, TlCl
Cl^-	+7.06	Ph_4AsPi, TlPi, TlCl
Cl^-	+6.85	$KBPh_4$, KCl
Cl^-	+6.67	Ph_4PPi, KPi, KCl
Cl^-	+6.48	Ph_4AsPi, KPi, KCl
Cl^-	+5.56	$CsBPh_4$, CsCl
Cl^-	+5.12	Ph_4PPi, CsPi, CsCl
Cl^-	+5.03	$KBPh_4$, KPi, CsPi, CsCl
Cl^-	+4.93	Ph_4AsPi, CsPi, CsCl
Br^-	+6.63	$RbBPh_4$, RbPi, KPi, KBr
Br^-	+6.48	$CsBPh_4$, CsPi, KPi, KBr
Br^-	+6.43	$RbBPh_4$, $RbClO_4$, $TlClO_4$, TlBr
Br^-	+6.43	$KBPh_4$, $KClO_4$, $TlClO_4$, TlBr
Br^-	+6.28	$CsBPh_4$, $CsClO_4$, $TlClO_4$, TlBr
Br^-	+5.95	$RbBPh_4$, $RbClO_4$, $KClO_4$, KBr
Br^-	+5.95	$KBPh_4$, KBr
Br^-	+5.88	$RbBPh_4$, RbPi, TlPi, TlBr
Br^-	+5.80	$CsBPh_4$, $CsClO_4$, $KClO_4$, KBr

Table 80. (Continued).

Ion	$\log_m \gamma$	Electrolytes Used in Calculation
Br^-	+5.73	$CsBPh_4$, CsPi, TlPi, TlBr
Br^-	+5.48	$RbBPh_4$, RbBr
Br^-	+5.48	$KBPh_4$, $KClO_4$, $RbClO_4$, RbBr
Br^-	+5.33	$AgBPh_4$, AgCl, TlCl, TlBr
Br^-	+5.33	$CsBPh_4$, $CsClO_4$, $RbClO_4$, RbBr
Br^-	+5.29	Ph_4PPi, TlPi, TlBr
Br^-	+5.21	$CsBPh_4$, CsPi, RbPi, RbBr
Br^-	+5.20	$KBPh_4$, KPi, TlPi, TlBr
Br^-	+5.10	Ph_4AsPi, TlPi, TlBr
Br^-	+4.89	$KBPh_4$, KCl, TlCl, TlBr
Br^-	+4.83	$AgBPh_4$, AgBr
Br^-	+4.80	$KBPh_4$, KPi, RbPi, RbBr
Br^-	+4.39	$KBPh_4$, KCl, AgCl, AgBr
Br^-	+3.60	$CsBPh_4$, CsCl, TlCl, TlBr
Br^-	+3.10	$CsBPh_4$, CsCl, AgCl, AgBr
I^-	+3.61	$RbBPh_4$, RbPi, TlPi, TlI
I^-	+3.46	$CsBPh_4$, CsPi, TlPi, TlI
I^-	+3.45	$KBPh_4$, KBr, AgBr, AgI
I^-	+3.21	$RbBPh_4$, RbBr, TlBr, TlI
I^-	+3.15	$RbBPh_4$, RbI
I^-	+2.98	$RbBPh_4$, RbBr, AgBr, AgI
I^-	+2.93	$KBPh_4$, KPi, TlPi, TlI
I^-	+2.62	$KBPh_4$, KCl, TlCl, TlI

Table 80. (Continued).

Ion	$\log_m \gamma$	Electrolytes Used in Calculation
I^-	+2.47	$KBPh_4$, KPi, RbPi, RbI
I^-	+2.47	$KBPh_4$, KCl, RbCl, RbI
I^-	+2.33	$AgBPh_4$, AgI
I^-	+1.89	$KBPh_4$, KCl, AgCl, AgI
I^-	+1.33	$CsBPh_4$, CsCl, TlCl, TlI
I^-	+1.18	$CsBPh_4$, CsCl, RbCl, RbI
NO_3^-	+4.50	$RbBPh_4$, $RbClO_4$, $TlClO_4$, $TlNO_3$
NO_3^-	+4.50	$KBPh_4$, $KClO_4$, $TlClO_4$, $TlNO_3$
NO_3^-	+4.35	$CsBPh_4$, $CsClO_4$, $TlClO_4$, $TlNO_3$
NO_3^-	+4.02	$KBPh_4$, KBr, TlBr, $TlNO_3$
NO_3^-	+3.95	$RbBPh_4$, RbPi, TlPi, $TlNO_3$
NO_3^-	+3.80	$CsBPh_4$, CsPi, TlPi, $TlNO_3$
NO_3^-	+3.55	$RbBPh_4$, RbBr, RlBr, $TlNO_3$
NO_3^-	+3.40	$AgBPh_4$, AgCl, TlCl, $TlNO_3$
NO_3^-	+3.36	Ph_4PPi, TlPi, $TlNO_3$
NO_3^-	+3.27	$KBPh_4$, KPi, TlPi, $TlNO_3$
NO_3^-	+3.17	Ph_4AsPi, TlPi, $TlNO_3$
NO_3^-	+2.96	$KBPh_4$, KCl, TlCl, $TlNO_3$
NO_3^-	+2.90	$AgBPh_4$, AgBr, TlBr, $TlNO_3$
NO_3^-	+1.67	$CsBPh_4$, CsCl, TlCl, $TlNO_3$

Table 80. (Continued).

Ion	$\log_m \gamma$	Electrolytes Used in Calculations
SCN^-	+3.50	$KBPh_4$, $KClO_4$, $TlClO_4$, TlSCN
SCN^-	+3.50	$RbBPh_4$, $RbClO_4$, $TlClO_4$, TlSCN
SCN^-	+3.35	$CsBPh_4$, $CsClO_4$, $TlClO_4$, TlSCN
SCN^-	+3.02	$KBPh_4$, KBr, TlBr, TlSCN
SCN^-	+2.95	$RbBPh_4$, RbPi, TlPi, TlSCN
SCN^-	+2.80	$CsBPh_4$, CsPi, TlPi, TlSCN
SCN^-	+2.64	$RbBPh_4$, RbCl, TlCl, TlSCN
SCN^-	+2.55	$RbBPh_4$, RbBr, TlBr, TlSCN
SCN^-	+2.49	$KBPh_4$, KBr, TlBr, TlSCN
SCN^-	+2.30	$AgBPh_4$, AgCl, TlCl, TlSCN
SCN^-	+2.27	$KBPh_4$, KPi, TlPi, TlSCN
SCN^-	+1.96	$KBPh_4$, KCl, TlCl, TlSCN
SCN^-	+1.90	$AgBPh_4$, AgBr, TlBr, TlSCN
SCN^-	+1.67	$AgBPh_4$, AgI, TlI, TlSCN
SCN^-	+0.67	$CsBPh_4$, CsCl, TlCl, TlSCN
ClO_4^-	+1.37	$KBPh_4$, $KClO_4$
ClO_4^-	+1.37	$RbBPh_4$, $RbClO_4$
ClO_4^-	+1.22	$CsBPh_4$, $CsClO_4$
ClO_4^-	+0.89	$KBPh_4$, KBr, TlBr, $TlClO_4$
ClO_4^-	+0.36	$RbBPh_4$, RbI, TlI, $TlClO_4$
ClO_4^-	+0.14	$KBPh_4$, KPi, TlPi, $TlClO_4$
ClO_4^-	-0.17	$KBPh_4$, KCl, TlCl, $TlClO_4$
ClO_4^-	-0.46	$AgBPh_4$, AgI, TlI, $TlClO_4$

Table 80. (Continued).

Ion	$\log_m \gamma$	Electrolytes Used in Calculation
Pi^-	+0.21	$RbBPh_4$, RbPi
Pi^-	+0.06	$CsBPh_4$, CsPi
Pi^-	-0.38	Ph_4PPi
Pi^-	-0.47 ± 0.07	$KBPh_4$, KPi
Pi^-	-0.57	Ph_4AsPi
Pi^-	-0.78	$KBPh_4$, KCl, TlCl, TlPi
Ac^-	+10.65	$RbBPh_4$, RbI, AgI, AgAc
Ac^-	+9.83	$AgBPh_4$, AgAc
Ac^-	+9.39	$KBPh_4$, KCl, AgCl, AgAc
Ac^-	+8.10	$CsBPh_4$, CsCl, AgCl, AgAc
Bz^-	+7.95	$RbBPh_4$, RbI, AgBz
Bz^-	+7.13	$AgBPh_4$, AgBz
Bz^-	+6.69	$KBPh_4$, KCl, AgCl, AgBz
Bz^-	+5.40	$CsBPh_4$, CsCl, AgCl, AgBz

Table 52. Table 82 lists values of $\log {}_{m}\gamma$ for single ions considered most reliable by this author.

The following eight calculations of $\log {}_{m}\gamma_{K}$ correspond to the eight values listed in Table 80. They are presented as an explanation to Table 80 :

$$\log {}_{m}\gamma_{K} = -\log {}_{m}\gamma_{Ph_4} + \log {}_{m}\gamma_{AgBPh_4} - \log {}_{m}\gamma_{AgBr} + \quad (237)$$
$$+ \log {}_{m}\gamma_{KBr} = +2.21$$

$$\log {}_{m}\gamma_{K} = + \log {}_{m}\gamma_{Ph_4} - \log {}_{m}\gamma_{Ph_4 As\,Pi} + \log {}_{m}\gamma_{KPi} = \quad (238)$$
$$= + 1.46$$

$$\log {}_{m}\gamma_{K} = + \log {}_{m}\gamma_{Ph_4} - \log {}_{m}\gamma_{Ph_4 P\,Pi} + \log {}_{m}\gamma_{KPi} = \quad (239)$$
$$= + 1.26$$

$$\log {}_{m}\gamma_{K} = -\log {}_{m}\gamma_{Ph_4} + \log {}_{m}\gamma_{CsBPh_4} - \log {}_{m}\gamma_{CsClO_4} + \quad (240)$$
$$+ \log {}_{m}\gamma_{KClO_4} = +1.24$$

$$\log {}_{m}\gamma_{K} = - \log {}_{m}\gamma_{Ph_4} + \log {}_{m}\gamma_{RbBPh_4} - \log {}_{m}\gamma_{RbClO_4} + \quad (241)$$
$$+ \log {}_{m}\gamma_{KClO_4} = +1.09$$

$$\log {}_{m}\gamma_{K} = -\log {}_{m}\gamma_{Ph_4} + \log {}_{m}\gamma_{KBPh_4} = +1.09 \qquad (242)$$

$$\log {}_{m}\gamma_{K} = -\log {}_{m}\gamma_{Ph_4} + \log {}_{m}\gamma_{CsBPh_4} - \log {}_{m}\gamma_{CsPi} + \qquad (243)$$
$$+ \log {}_{m}\gamma_{KPi} = +0.56$$

$$\log {}_{m}\gamma_{K} = -\log {}_{m}\gamma_{Ph_4} + \log {}_{m}\gamma_{RbBPh_4} - \log {}_{m}\gamma_{RbPi} + \qquad (244)$$
$$+ \log {}_{m}\gamma_{KPi} = +0.41$$

In many cases, medium effects for a particular single ion calculated using different paths do not differ by much even though one value might involve two or more electrolytes. This is quite interesting and it certainly lends credibility to the accuracy of the medium effects involved in the calculations. It must be pointed out, however, that even agreement among two or more values of $\log {}_{m}\gamma$ for a single ion does not prove that these values are correct. The basic assumption used to obtain the first medium effect for a single ion has to be valid before any of the results can be accepted as correct. In certain instances in Table 80, there are cases of double agreement. For instance, there are two values of +1.57 for $\log {}_{m}\gamma_{Rb}$ and there are also two values of +0.89 for $\log {}_{m}\gamma_{Rb}$.

In cases like this, we cannot chose one value over the other unless an error analysis is performed on the pK values used to calculate medium effects.

Error analysis.

Standard deviations for $\log_m\gamma$ for the reference electrolytes, $d\log_m\gamma$, were determined by the method of propogation of errors using values of $d\log_m\gamma$ for electrolytes given in Table 54 section VII-F-1-e :

$$d\log_m\gamma_{Ph_4P\ BPh_4} = \left[(d\log_m\gamma_{Ph_4P\ Pi})^2 + (d\log_m\gamma_{KBPh_4})^2 + (d\log_m\gamma_{KPi})^2\right]^{\frac{1}{2}} = 0.075 \quad (245)$$

$$d\log_m\gamma_{Ph_4As\ BPh_4} = \left[(d\log_m\gamma_{Ph_4As\ Pi})^2 + (d\log_m\gamma_{KBPh_4})^2 + (d\log_m\gamma_{KPi})^2\right]^{\frac{1}{2}} = 0.075 \quad (246)$$

Values of $d\log_m\gamma$ for the reference ions were then calculated :

$$d\log_m\gamma_{Ph_4P} = d\log_m\gamma_{BPh_4} = \tfrac{1}{2}\, d\log_m\gamma_{Ph_4P\ BPh_4} = 0.038 \quad (247)$$

$$d\log_m\gamma_{Ph_4As} = d\log_m\gamma_{BPh_4} = \tfrac{1}{2}\, d\log_m\gamma_{Ph_4As\ BPh_4} = 0.38 \quad (248)$$

and a value for $d\log_m\gamma_{Ph_4}$ was arrived at in the following manner :

$$d \log_{m}\gamma_{Ph_4} = \left[(d \log_{m}\gamma_{Ph_4P})^2 + (d \log_{m}\gamma_{Ph_4As})^2 \right]^{\frac{1}{2}} = 0.052 \quad (249)$$

In this way, the errors involved in evaluating $\log_{m}\gamma_{Ph_4P}$ and $\log_{m}\gamma_{Ph_4As}$ are propogated to give the standard deviations in $\log_{m}\gamma_{Ph_4}$.

Standard deviations in the medium effect of K^+. Rb^+, and Cs^+ were evaluated to be ± 0.07 log units for all three ions using the following equation:

$$d \log_{m}\gamma_{M} = \left[(d \log_{m}\gamma_{Ph_4})^2 + (d \log_{m}\gamma_{MBPh_4})^2 \right]^{\frac{1}{2}} = \pm 0.07 \quad (250)$$

where M is the alkali metal.

The standard deviation in $\log_{m}\gamma_{Pi}$ was evaluated to be ± 0.07 log units using the equation:

$$d \log_{m}\gamma_{Pi} = \left[(d \log_{m}\gamma_{Ph_4})^2 + (d \log_{m}\gamma_{KBPh_4})^2 + (d \log_{m}\gamma_{KPi})^2 \right]^{\frac{1}{2}} = \pm 0.07 \quad (251)$$

Considering the manner in which errors propogate in the calculations of medium effects for single ions, the good agreement among results in Table 80 is satisfying.

Interpretation of results.

Structure of solvent.

Acetonitrile is a dipolar aprotic solvent and as such, it has very poor hydrogen-bonding abilities. It has a dipole moment of 3.84 D (174) and a dielectric constant of 35.95 (177). It is much less structured a solvent then methanol, which has a dipole moment of only 1.70 D (174) but a dielectric constant of 32.6 (173). If acetonitrile was as structured as methanol, we would expect its dielectric constant to be at least 60.

Solvation in acetonitrile as opposed to solvation in alcohols is much more dependent on the intrinsic nature of the solvent molecules than on the interaction between the particles and solvent clusters.

Solvation of solutes.

There is a diversity of beleifs about solvation of ions in acetonitrile. According to Coetzee and Campion (46), small anions will occupy a position behind the -C≡N group which makes them less susceptible to solvation by more than one solvent molecule. Cations, on the other hand, are believed (46) to occupy positions external to the CH_3CN molecule which allows them to be solvated by more than one molecule simultaneously. Thus, according to Coetzee and Campion, anions should have positive medium effects in acetonitrile and cations--negative or small medium effects.

Luehrs, Iwamoto, and Kleinberg (178) have suggested that halides are solvated very poorly in acetonitrile as compared to methanol or water because of the inavailability of H-bonding in that solvent. Thus, we would expect medium effects for halides to be more positive in acetonitrile than in methanol.

Polarographic measurements can be used to evaluate the extent of solvation of ions. As they become more strongly solvated, cations are reduced at more negative potentials and anions are oxidized at more positive potentials at the D.M.E.. Although comparisons of $E_{\frac{1}{2}}$ among different solvents are difficult due to the uncertainty of liquid-junction potentials at solvent-solvent interfaces, some polarographic studies have

been performed which indicate that the ClO_4^- and Pi^- ions are more strongly solvated in acetonitrile than in water while the reverse is true for the halides, SCN^-, and NO_3^- ions (46). There is also polarographic evidence (15) which indicates that alkali-metal ions are more strongly solvated by water than by acetonitrile. Kolthoff and Coetzee (179, 180) found that cations are generally much less solvated in acetonitrile than in water and that the size of an ion has a much greater effect on its $E_{\frac{1}{2}}$ in acetonitrile than in water. This could be due to the tendency for small ions to fall behind the -C≡N group (46) which prevents solvation by multiple solvent molecules. This also explains the observation (46) that solubilities of salts in acetonitrile are particularly sensitive to the type of anion.

Price (147) believes that in general, electrolytes have low solubilities in acetonitrile because the negative charge of the solvent dipole is dispersed, i.e., the charge is not localized on a favorable electron-donor atom. Thus, cations are not bonded tightly to concentrations of negative charge as they are in water.

According to Parker (50), the poor hydrogen-bonding ability of acetonitrile makes it a very poor solvent for anions. Also, the lack of a localized

negative charge on the CH_3CN molecule makes it a poor cation solvator.

All available theoretical considerations would lead us to postulate that medium effects for anions and cations should be positive in acetonitrile and those for anions should be larger in magnitude in acetonitrile than in alcohols. The proton should be poorly solvated in acetonitrile and thus, it should also have a positive medium effect in that solvent. Ions such as Cu^+ and Ag^+ which undergo specific interaction with the solvent (158, 159) should have negative or very small positive values for $\log_m \gamma$. If the reference-electrolyte methods yield results consistent with these theoretical predictions, the validity of the method will be enhanced a great deal.

Discussion.

Representative values of medium effects for single ions in acetonitrile are listed in Table 81. These are the most reliable values in the opinion of this investigator. These values were abstracted from the listings in Table 80 at times, somewhat arbitrarily. A discussion of the individual medium effects for single ions follows.

Medium effects listed for the reference ions, Ph_4P^+, Ph_4As^+, and BPh_4^- were obtained directly from the reference-electrolyte assumptions using experimental data from this study. As always, the medium effect for Ph_4^+ is the average value obtained from the two reference-electrolyte assumptions Ph_4P BPh_4 and Ph_4As BPh_4. Medium effects for all other ions listed in Table 81 are based on the value of -5.77 ± 0.05 for $\log {}_mY_{Ph_4}$.

The medium effect for the proton, $\log {}_mY_H$, of +8.2 log units was taken directly from the data of Kolthoff and Chantooni (31). It was obtained from pK_a's of acetic and substituted benzoic acids in water and acetonitrile along with knowledge of the medium effects for the acid anions and medium effects for the acids. Medium effects for the acid anions, $\log {}_mY_A$, were obtained from values of $\log {}_mY$ for salts of the acid obtained via the solubility method and

Table 81. Medium Effects, $\log_m \gamma$, for Single Ions in Acetonitrile Based on the Ph_4^+ Assumption. 25°C, Molal Scale.

Ion	$\log_m \gamma$
$Ph_4P^+ = BPh_4^-$	-5.81 ± 0.04
$Ph_4As^+ = BPh_4^-$	-5.72 ± 0.04
Ph_4^+	-5.77 ± 0.05
H^+	+8.2 (31)
Li^+	+5.1
Na^+	+5.6
K^+	$+1.09 \pm 0.07$
Rb^+	$+0.89 \pm 0.07$
Cs^+	$+0.64 \pm 0.07$
Tl^+	+1.74
Ag^+	-3.63
Cu^+	-7.0
Cu^{+2}	-4.4
Ca^{+2}	+20.5
Zn^{+2}	+17.2
Cd^{+2}	+14.2
Pb^{+2}	+16.6
Cl^-	+6.85
Br^-	+5.95
I^-	+2.74
NO_3^-	+3.67
SCN^-	+2.64
ClO_4^-	+1.21
Pi^-	-0.47 ± 0.07
Ac^-	+9.83
Bz^-	+7.13

medium effects for the acids were obtained by the solubility method. The $Ph_4As\ BPh_4$ assumption was used to get values for $\log {}_m\gamma_A$. The value of +8.2 for $\log {}_m\gamma_H$ reported here is corrected to the molal scale. However, no effort was made to adjust $\log {}_m\gamma_H$ to its value based on the Ph_4^+ assumption because medium effects for single ions based on the Ph_4^+ and $Ph_4As\ BPh_4$ assumptions will differ only by 0.05 log units.

As predicted, the $\log {}_m\gamma_H$ is positive in acetonitrile which means that the proton exists in a higher energy state in acetonitrile as compared to water. Thus, acetonitrile is a much poorer solvent for protons than water, ethanol, or methanol. With ethanol or methanol used as a reference solvent, $\log {}_m\gamma_H$ in acetonitrile would still be positive, having a value of +6.6 log units.

The value of +8.2 for $\log {}_m\gamma_H$ in acetonitrile confirms the poor hydrogen-accepting ability of that solvent and the delocalization of the negative charge of the $-C\equiv N$ group. We can now qualitatively predict that acetonitrile would be a poor solvent for cations in general.

Values of $\log {}_m\gamma$ for Li^+ and Na^+ were calculated using the values of $(\log {}_m\gamma_M - \log {}_m\gamma_H)$ (where $M = Li^+$ or Na^+) listed in Table 52 and the value of +8.2 for $\log {}_m\gamma_H$. Medium effects for both ions are positive, as we expect, indicating that they are preferentially

solvated in water. $\log {}_{m}\gamma_{Li} = +5.1$ and $\log {}_{m}\gamma_{Na} = +5.6$. These small ions are overwhelmingly solvated by water. If Kolthoff and Coetzee (179, 180) were correct, a change in ionic size will have a great effect on $\log {}_{m}\gamma$ for other univalent cations and numerical values of $\log {}_{m}\gamma$ for K^+, Rb^+, and Cs^+ whould decrease reflecting their solvation energies in acetonitrile owing to the increased polarizability of these larger ions. Values of $\log {}_{m}\gamma_{K}$, $\log {}_{m}\gamma_{Rb}$, and $\log {}_{m}\gamma_{Cs}$ are indeed much smaller than 5 log units. Medium effects for the alkali-metal and halide ions decrease with increasing ionic size indicating that polarizability and surface charge density of the ions are important factors in determining their values in acetonitrile. These effects are not as evident in methanol or in ethanol, where all the alkali-metal ions have similar medium effects.

A value of 1.09 ± 0.07 was chosen as representative for $\log {}_{m}\gamma_{K}$ in acetonitrile because the medium effects for electrolytes used in calculating it were determined by this investigator. This would be the "traditional" value because it is calculated using $\log {}_{m}\gamma_{KBPh_4}$. Another suggested value for $\log {}_{m}\gamma_{K}$ would be + 1.37 which is the average value obtained using medium effects for $Ph_4As\,Pi$, $Ph_4P\,Pi$, and KPi (see Table 80). Interestingly, another value of +1.09 is obtained for $\log {}_{m}\gamma_{K}$ using medium effects for $RbClO_4$, $RbBPh_4$, and

$KClO_4$. This increases our confidence in the accuracy of the preferred value listed in Table 81.

Potassium is only slightly larger than sodium having an ionic radius of 1.33 Å as compared to 0.97 Å for sodium and yet, its medium effect is 4.5 log units smaller than the medium effect for sodium. Medium effects of Rb^+ and Cs^+ whose radii are 1.47 Å and 1.67 Å, respectively, are only slightly smaller (by 0.2 and 0.5 log units for Rb^+ and Cs^+) than the medium effect for K^+. Apparantly, there is a critical size for univalent cations, between 0.97 and 1.33 Å above which solvation in acetonitrile becomes exceedingly difficult.

A value of 0.89 ± 0.07 was chosen for $\log {}_m\gamma_{Rb}$ in acetonitrile because it was determined in this laboratory and because the least number of electrolytes were involved in its calculation. Other values of $\log {}_m\gamma_{Rb}$ in Table 80 require use of medium effects for more electrolytes, a factor which detracts from the precision of the resulting value. Another value of 0.89 is reported (see Table 80) for $\log {}_m\gamma_{Rb}$ based on medium effects for $KBPh_4$, $KClO_4$, and $RbClO_4$. Curiously enough, there are two identical values of +1.57 on the table also. The values of +1.48 and +1.67 calculated from medium effects for Ph_4P Pi and Ph_4As Pi, respectively, along with $\log {}_m\gamma_{RbPi}$, average out to

+1.58. This would be a recommended value if $\log {}_{m}\gamma_{RbPi}$ were re-evaluated more precisely and the value used here (+1.1) were confirmed.

A value of +0.64 ± 0.07 is listed in Table 81 for $\log {}_{m}\gamma_{Cs}$. This value is determined by the most direct path. Values of 1.27 and 1.08 estimated from medium effects for CsPi, and Ph_4P Pi and Ph_4As Pi, average to +1.18 which would be a recommended value if the medium effect for CsPi (0.70 log units) were independently confirmed.

The value chosen for $\log {}_{m}\gamma_{Tl}$ is +1.74. This is the average of the fifteen values listed in Table 80. It was not possible to calculate $\log {}_{m}\gamma_{Tl}$ more directly because the medium effect for $TlBPh_4$ in acetonitrile is not available.

As expected, $\log {}_{m}\gamma_{Ag}$ is negative. The value of -3.63 listed in Table 81 is the "direct" value estimated using $\log {}_{m}\gamma_{AgBPh_4}$. The negative value for $\log {}_{m}\gamma_{Ag}$ reflects the specific interaction of Ag^{+} with acetonitrile so often reported in the literature (4, 158, 159, 170, 180). The average of all other values (except -1.90 which required use of the questionable value for $\log {}_{m}\gamma_{CsCl}$) of $\log {}_{m}\gamma_{Ag}$ in Table 80 is -4.03 which is also quite credible. There is some objection (4) to using $\log {}_{m}\gamma_{AgBPh_4}$ in medium effect calculations because this silver salt is particularly unstable. However, Kolthoff

and Chantooni (31) recently reported a more reliable value of -9.4 for $\log {}_m\gamma_{AgBPh_4}$ in acetonitrile based on carefully determined values of $K_{sp}(AgBPh_4)$ in water and acetonitrile.

Medium effects for Cu^+ and Cu^{+2} ions are also negative in acetonitrile. Values of -7.0 and -4.4 are listed in Table 81 for $\log {}_m\gamma_{Cu(I)}$ and $\log {}_m\gamma_{Cu(II)}$, respectively. The negative values reflect preferential sovation by acetonitrile as compared to water. These were calculated from standard potentials of copper electrodes (156, 161) in water and acetonitrile using Equation 54 and the value of +8.2 for $\log {}_m\gamma_H$. Medium effects for Ca^{+2}, Zn^{+2}, Cd^{+2}, and Pb^{+2} were determined in a similar manner. Except for Cu^{+2}, all divalent cations studied have large positive medium effects in acetonitrile.

The medium effect for Ca^{+2} is+ 20.5. This is unexpectedly large for an ion with a radius of 0.99 Å that is similar in size to sodium (r_{Na} = 0.97 Å). Zinc, cadmium, and lead ions which have radii of 0.74, 0.97, and 1.2 Å, respectively, also have large positive medium effects of +17.2, +14.2, and +16.6, respectively. Apparantly, an increase in ionic charge from +1 to +2 for ions of $\sim$ 1 Å in size has the effect of increasing the medium effect in acetonitrile by 10 - 15 log units.

The large positive value of +6.85 for $\log {}_m\gamma_{Cl}$ listed

in Table 81 reflects the expected dislike of the halides for acetonitrile. This value was obtained using medium effects for $KBPh_4$ and KCl. All other values for $\log {}_m\gamma_{Cl}$ listed in Table 80 are also positive.

A value of +5.95 is listed in Table 81 for $\log {}_m\gamma_{Br}$. This was chosen because $KBPh_4$ and KBr were used in the calculation. It is a representative value, being near the mean of all twenty-four values presented in Table 80. The value of +5.95 seems to be accurate since the same value was arrived at using medium effects for $RbBPh_4$, $RbClO_4$, $KClO_4$, and KBr. Other values for $\log {}_m\gamma_{Br}$ calculated using $\log {}_m\gamma_{TlBr}$ are also close to +5.95. Low values are obtained for $\log {}_m\gamma_{Br}$ using medium effects for AgBr and an especially low value of +3.10 is obtained when $\log {}_m\gamma_{CsCl}$ and $\log {}_m\gamma_{AgBr}$ are used in the calculation. The twenty-four values for $\log {}_m\gamma_{Br}$ reported in Table 80 are all positive. They range from +3.10 to +6.63. This large spread points out the necessity of determining thermodynamic medium effects more accurately in the future.

The value of +2.74 for $\log {}_m\gamma_{I}$ is the average value obtained using the two most direct calculation paths which give results of +3.15 and +2.33. There is no apparent reason to favor +3.15 over +2.33 so they were averaged. Medium effects for the halides in acetonitrile decrease as the ion gets larger. This reflects the

importance of mutual polarizability of anion and solvent molecules (50) in anion solvation by dipolar aprotic solvents.

Values of medium effects for NO_3^-, SCN^-, Ac^-, and Bz^- ions in Table 81 are averages of all values listed in Table 80. The value of +1.21 for $\log_m \gamma_{ClO_4}$ is the average of the first four values listed in Table 81.

A value of -0.47 ± 0.07 is listed for $\log_m \gamma_{Pi}$. This was calculated from medium effects determined by this investigator. It is a small negative value which is quite surprising. Pi^- does not behave like a normal anion in any of the solvents studied in this investigation. It is the only anion studied (aside from BPh_4^-) that has a negative medium effect in methanol, and acetonitrile. Apparently, its large size and aromatic nature allow it to be readily solvated in organic solvents.

Medium effects for all ions except the reference ions, Ag^+, Cu^+, Cu^{+2}, and Pi^- are positive in acetonitrile indicating that this is a generally poor solvent compared to water. In conclusion, the reference-electrolyte method gives us values of medium effects for single ions which are consistent with chemical considerations.

Comparison with literature values.

Medium effects for single ions in acetonitrile obtained using various assumptions are listed in Table 82. From chemical considerations, we expect the medium effects in acetonitrile to be positive for both anions and cations, except in cases where there is specific interaction with acetonitrile.

The first column in Table 82 lists medium effects obtained using the Ph_4^+ assumption. These have been discussed in section VIII-C-3-c. Medium effects for single ions obtained by Alexander, Parker, and co-workers (28, 30), and Kolthoff and co-workers (31) using the $Ph_4As\ BPh_4$ assumption are listed in the next three columns. We expect good agreement among the values of $\log_m \gamma$ obtained from reference-electrolyte assumptions. Alexander and Parker made use of concentration solubility products rather than ion-activity products in evaluating medium effects of electrolytes and because of this there are some discrepancies between their values of medium effects for single ions and those obtained using the Ph_4^+ assumption in this study. In particular, Alexander and Parker (30) report negative values for $\log_m \gamma$ of K^+, and Cs^+ in acetonitrile.

Kolthoff's value of medium effects for single ions obtained by the $Ph_4As\ BPh_4$ assumption are in good agreement with those from the Ph_4^+ assumption, and so

Table 82. Medium Effects, $\log_m \gamma$, for Single Ions in Acetonitrile. 25°C, Molal Scale.

Ion	Ph_4^+ assumption	Alexander Parker et al. Ph_4As (28)	Alexander Parker et al. BPh_4 (30)	Kolthoff et al. Ph_4As (31)	Kolthoff et al. BPh_4 (31)	Izmaylov $1/n^2$ (103)	Coetzee et al. modified Born (15)	Coetzee et al. modified Born (46)
H^+	8.2	---	---	8.2		5.5	6.76	---
Li^+	5.1	---	---	---		1.8	4.90	---
Na^+	5.6	---	---	2.5		2.5	3.38	3.2
K^+	1.09 ± 0.07	0.8	-0.2	1.5		1.4	2.87	---
Rb^+	0.89 ± 0.07	---	---	1.3		1.6	2.54	---
Cs^+	0.64 ± 0.07	0.0	-0.3	1.0		1.1	---	---
Tl^+	1.74	---	---	1.7		---	---	---
Ag^+	-3.63	-5.2	-5.6	-3.7		-3.0	---	---
Cl^-	6.85	8.3	8.7	7.5		8.0	---	5.6
Br^-	5.95	5.8	6.2	5.7		5.0	---	3.7
I^-	2.74	3.4	3.8	3.6		2.3	---	1.4
NO_3^-	3.67	---	---	3.8		---	---	1.8
SCN^-	2.64	3.3	3.7	---		---	---	0.8
ClO_4^-	1.21	---	---	0.9		---	---	-1.4
Pi^-	-0.47 ± 0.07	-1.1	-0.6	-0.2		---	---	-2.6
$Ph_4As^+ = BPh_4^-$	-5.72 ± 0.04	-5.8	-5.8	-5.6		---	---	---
$Ph_4P^+ = BPh_4$	-5.81 ± 0.04	---	---	---		---	---	---

are Izmaylov's values, based on his $1/n^2$ extrapolation.

The last two columns in Table 82 list values of medium effects for single ions obtained by Coetzee and co-workers (15, 46) using radius-modified Born equations. These are in qualitative agreement with those obtained from the Ph_4^+ assumption.

Additivity of electrostatic and neutral contributions to the medium effect for large ions.

According to Frank and Evans (59), the orientation of solvent molecules around a particle in a structured solvent will always be different than in the bulk solvent. This is true for uncharged as well as charged particles. Comparing the structure of the solvent in the immediate vicinity of a large univalent ion and an uncharged molecule of the same size and structure as the ion, the latter will disturb the adjacent solvent molecules in the same manner as its uncharged molecular analog provided the surface charge density of the ion is small enough so that effects of dielectric saturation are negligible. Beyond the first solvation layer, the electric field of the large ion is expected to have negligible influence on the orientation of solvent molecules so that the solvent structure in this region will be identical to the solvent structure in the same region around the uncharged molecule. If one could chose the appropriate ion-molecule combination (analogs), one could state with certainty that they both affect the solvent in an identical manner.

Thus, the neutral component of the solvation energy of a large reference ion should be identical to the solvation energy of a structurally analogous uncharged particle. In this case, the electrostatic contribution

to the medium effect for the reference ion as determined via the Born equation and the medium effect for its uncharged structural analog, should add up to give the experimentally observed medium effect for the reference ion. In this work, it is postulated that the average value of the medium effects for Ph_4C, Ph_4Si, and Ph_4Ge is equal to the neutral contribution to the medium effects for the reference ions Ph_4P^+, Ph_4As^+, TAB^+, and BPh_4^-. The differences among the medium effects of Ph_4C, Ph_4Si, and Ph_4Ge in any given solvent generally do not amount to more than the experimental error and so their average value is adopted as being characteristic of $\log {}_mY_{(neut)}$ for all tetraphenyl ions in a given solvent. The electrostatic component of $\log {}_mY$ for the large reference ions can be estimated using the Born equation.

Do the neutral and electrostatic components for the medium effects of the reference ions add up to give the experimental values? Is the following equation valid?

$$\log {}_mY_{\text{reference ion}} = \log {}_mY_{(neut)} + \log {}_mY_{(Born)} \quad (91)$$

For each solvent studied in this work, values of $\log {}_mY_{(neut)}$ were added to the electrostatic terms, $\log {}_mY_{(Born)}$, calculated for ions with $r = 4$ Å and $r = 5$ Å from Equation 75. Since the solubilities and thus medium

Table 83. Comparison of Calculated and Observed Medium Effects for Reference Ions. Ethanol is the Reference Solvent. 25°C, Molal Scale.

wt.-% ethanol	$\log {}_{m}Y_{(neut)}$	$\log {}_{m}Y_{(Born)}$ 4Å	5Å	$\log {}_{m}Y_{(calc)_o}$ 4Å	5Å	$\frac{1}{2}\log {}_{m}Y$ of the BPh_4^- of Ph_4P^+	of Ph_4As^+	of TAB^+
60.0	1.37	-0.55	-0.44	0.82	0.93	0.31	0.37	0.83
70.0	0.95	-0.45	-0.36	0.50	0.59	0.18	0.23	0.62
80.0	0.67	-0.32	-0.26	0.35	0.41	0.06	0.10	0.41
90.0	0.34	-0.17	-0.14	0.17	0.20	-0.05	-0.03	0.16
CH_3OH	0.10	-0.32	-0.26	-0.22	-0.16	-0.50	-0.51	-0.51
CH_3CN	-0.33	-0.41	-0.33	-0.74	-0.66	-2.14	-2.14	----

effects for Ph_4C, Ph_4Si, and Ph_4Ge were not available in solvents containing less than 60 wt.-% ethanol, pure ethanol was chosen as the reference solvent. The results of these calculations are compared in Table 83 with the experimentally determined medium effects (referred to ethanol) for Ph_4P BPh_4, Ph_4As BPh_4, and TAB BPh_4. The comparison, which is made for $\frac{1}{2} \log_m Y$ of the reference electrolytes, could be made equally well for the complete electrolytes simply by multiplying all values in columns 5 - 9 by two. Columns 5 and 6 are calculated values for $\log_m Y_{\text{reference ions}}$. They were calculated via

$$\log_m Y_{(\text{calc})} = \log_m Y_{\text{reference ion}} = \log_m Y_{(\text{neut})} + \log_m Y_{(\text{Born})} \qquad (252)$$

In Table 83, the agreement between calculated and experimental medium effects in ethanol--water solvents is excellent for TAB BPh_4, but only fair (within 0.2 - 0.5 log units) for Ph_4P BPh_4 and Ph_4As BPh_4. Fair agreement (within 0.3 log units) is observed between calculated and experimental values of $\log_m Y$ for all three reference electrolytes in methanol. Only in acetonitrile is there a significant discrepancy of 1.4 log units between calculated and experimental values of $\log_m Y_{\text{reference ion}}$. Unless these differences

happen to be fortuitous, they could have an important bearing on the applicability of Equation 91 and the selection of reference electrolytes for the estimation of medium effects for ions. If calculated values of $\log {}_m\gamma_{\text{reference ion}}$ are in closer agreement with values derived from TAB BPh_4 than from reference electrolytes where both ions are of the tetraphenyl type, it suggests that size rather than structure may be the governing factor in chosing reference electrolytes. However, before one rushes to endorse TAB BPh_4 as a superior reference electrolyte, he should bear in mind the observation (see Table 83) that all three reference electrolyte assumptions, $\log {}_m\gamma_{Ph_4P} = \log {}_m\gamma_{BPh_4}$, $\log {}_m\gamma_{Ph_4As} = \log {}_m\gamma_{BPh_4}$, and $\log {}_m\gamma_{TAB} = \log {}_m\gamma_{BPh_4}$, yield identical values for $\log {}_m\gamma_{\text{single ion}}$ provided that neither the reference solvent or the solvent being studied is aqueous.

Of the solvents studied so far, only water differentiates between TAB^+ and the tetraphenyl cations and it is likely that this differentiation as well as the discrepancies between observed and calculated medium effects for Ph_4P BPh_4 and Ph_4As BPh_4 in ethanol--water solvents have a common origin. It has been suggested (80, 113) that the positive charge may not be completely "buried" inside a tetraphenyl cation. An interaction between the fractional charges on its surface and the

solvent dipoles could contribute a solvation-energy component missing from Equation 91. Such interaction is expected to be smaller for the BPh_4^- ion (80) and TAB^+ ion (62). If the solvation energy component responsible for the observed discrepancies between $\log {}_m\gamma_{(calc)}$ and $\log {}_m\gamma_{(experimental)}$ is of the ion-dipole variety, such discrepancies could be accentuated in a comparison between pairs of solvents having appreciably different dipole moments. Such is indeed the case with the medium effects in acetonitrile ($\mu = 3.84$ D) referred to ethanol ($\mu = 1.69$ D). Furthermore, by inspecting the expression for ion-dipole energy, $G = (-Nze\mu n/r^2)$, it is seen that for the "transfer" of an ion from ethanol to acetonitrile it would introduce a negative correction to Equation 91, which could perhaps account qualitatively for the observed discrepancy of -1.4 log units in Table 83. We lack the knowledge of the various solvation parameters to draw any quantitative conclusions.

The difference between the dipole moments of ethanol and water is much smaller, but even here it may not be coincidental that the observed medium effects of the tetraphenyl cations in ethanol--water solvents are consistently negative with respect to their calculated values. On the other hand, the dipole moments of ethanol and methanol are identical and it

is interesting that these solvents do not differentiate between the TAB^+ and the tetraphenyl cations.

Additional tests of Equation 91 for pairs of solvents with practically identical dipole moments can be made using Parker and Alexander's (26) data for the medium effects of Ph_4C and $Ph_4As\ BPh_4$ in N,N-dimethylformamide (DMF) and N,N-dimethylacetamide (DMAC). For the transfer from acetonitrile to DMF, $\log {}_m\gamma_{Ph_4C} = -1.1$ and $\frac{1}{2}\log {}_m\gamma_{Ph_4As\ BPh_4} = -1.0$, which would require a Born contribution of +0.1. For an ion with $r = 4$ Å, the value of $\log {}_m\gamma_{(Born)}$ is +0.3. The transfer from acetonitrile to DMAC involves a pair of solvents with practically equal dipole moments and dielectric constants. Thus, if Equation 91 holds here, the medium effect, $\log {}_m\gamma$, should be determined solely by $\log {}_m\gamma_{(neut)}$. Indeed, we find that $\log {}_m\gamma_{Ph_4C} = -0.9$ and $\frac{1}{2}\log {}_m\gamma_{Ph_4As\ BPh_4} = -1.0$.

We can see from the data in Table 83 that the interaction of the reference ions with the solvents studied is predominantly nonelectrostatic. Indeed, it is generally accepted (4, 8) that the neutral contribution to solvation energy of a large ion is proportional to r^2 whereas the electrostatic contribution is proportional to r^{-1}.

Further proof of the nonelectrostatic nature of solvation for large ions comes from the study of medium

effects for ferrocene. Medium effects for ferrocene, $\log {}_{m}\gamma_{Foc}$, are listed in Table 50 along with calculated values of $\log {}_{m}\gamma_{(Born)}$ for an ion the size of ferrocene (3.8 Å) (8) and $\log {}_{m}\gamma_{(calc)}$ which is the sum of $\log {}_{m}\gamma_{Foc}$ and $\log {}_{m}\gamma_{(Born)}$. In Table 50, $\log {}_{m}\gamma_{(calc)}$ is the predicted value for the medium effect of the ferricinium ion. While the Born electrostatic contribution to $\log {}_{m}\gamma$ for ferricinium ion in 100 % ethanol is +0.9, the calculated value of -2.5 for the whole $\log {}_{m}\gamma$ indicates a nonelectrostatic contribution of -3.4 log units for the medium effect of ferricinium ion. This neutral contribution to $\log {}_{m}\gamma$ for large ions should become proportionately larger as the ion increases in size (4, 8).

The present study provides a qualified endorsement for the formulation of $\log {}_{m}\gamma$ for a large ion as a composite of a Born electrostatic contribution and a $\log {}_{m}\gamma_{(neut)}$ derived from experimental data on suitable uncharged analogs. However, such formulation seems to fail for pairs of solvents with appreciably different dipole moments. It should be stressed, however, that before any definitive conclusions can be drawn, we need to know the distances to which dielectric saturation extends in different nonaqueous solvents, and these are likely to be greater than the 4 - 5 Å characteristic of aqueous solutions.

A single e.m.f. series for ethanol--water solvents, methanol, and acetonitrile.

Now that we have knowledge of medium effects for the proton in ethanol--water solvents, methanol, and acetonitrile, we can refer the standard potentials of the hydrogen electrode (SHE) in any of these solvents to the SHE in water as their single arbitrary zero point:

$$ {}_{w}E^{o}(H,SH) = 2.303\frac{RT}{F}\log {}_{m}\gamma_{H} + {}_{w}E^{o}(H,H_2O) \qquad (253) $$

where ${}_{w}E^{o}(H,SH)$ is the potential of the SHE in solvent SH on the aqueous e.m.f. scale referred to the SHE potential in water, and ${}_{w}E^{o}(H,H_2O)$, has the usual value of zero volts. Values of ${}_{w}E^{o}(H,SH)$ in ethanol--water solvents, methanol, and acetonitrile calculated via Equation 253 are compiled in Table 84.

Any conventional potential, referred to the arbitrary zero point of the SHE in a given solvent, can be converted to its counterpart on the aqueous scale by adding to it algebraically the value of ${}_{w}E^{o}(H,SH)$ characteristic of that solvent:

$$ {}_{w}E^{o}(i,SH) = {}_{s}E^{o}(i,SH) + {}_{w}E^{o}(H,SH) \qquad (254) $$

In ethanol--water solvents of greater basicity

Table 84. Standard Potentials of Hydrogen Electrodes In Ethanol--Water Solvents, Methanol, and Acetonitrile. Referred to ${}_wE^\circ(H,H_2O) = 0$. 25°C, Molal Scale.

wt.-% ethanol	${}_wE^\circ(H,s)$, millivolts Ph_4^+ assumption	${}_wE^\circ(H,s)$, millivolts TAB BPh_4 assumption
0.0	0	0
10.0	5	-4
20.0	4	-15
30.0	-4	-30
40.0	-19	-47
50.0	-37	-58
60.0	-47	-66.8
70.0	-51	-65.7
80.0	-40	-49
90.0	-27	-30
100.0	+99.4	+109
CH_3OH	+99.4	--
CH_3CN	+485	--

than water, all potentials undergo a negative shift when transferred from the nonaqueous to the aqueous e.m.f. series. In pure ethanol, potentials on the single scale will be about 0.1 volt more positive than potentials on the conventional scale. The same is true for standard potentials in methanol because the medium effects for the proton in methanol and ethanol are numerically identical (+1.68 log units, based on the Ph_4^+ assumption). Conventional standard potentials in acetonitrile will be about 0.5 volt more negative than their corresponding aqueous values.

A unified pH scale for ethanol--water solvents, methanol, and acetonitrile.

Using the values of $\log {}_{m}\gamma_{H}$ in Tables 68, 78, and 81, any pa_{H}^{*} value referred to infinite dilution in a given ethanol--water solvent, methanol, or acetonitrile can be converted to its counterpart on a single pa_{H} scale referred to the aqueous standard state:

$$pa_{H} = pa_{H}^{*} - \log {}_{m}\gamma_{H} \qquad (18)$$

For example, in ethanol, methanol, and acetonitrile, solutions of a given pa_{H}^{*} will have a pa_{H} lower by 1.68, 1.68, and 8.2 units (Ph_{4}^{+} assumption), respectively. Solutions in these solvents will be more acidic than an aqueous solution of the same nominal pH. Solutions in ethanol--water solvents having an ethanol composition between $\sim$ 30 and $\sim$ 90 wt.-% ethanol will have an aqueous pa_{H} that is higher than their pa_{H}^{*}, i.e., they will be more basic on the single aqueous scale.

Values of liquid-junction potentials at aqueous-nonaqueous interfaces.

It is well known (4, 12, 18, 53) that the e.m.f. of a cell composed of an aqueous and a nonaqueous SHE is a function of both the $\log_m \gamma_H$ and the liquid-junction potential, E_j. This function is involved in the interpretation of pH measurements made in nonaqueous solvents with electrodes standardized against aqueous buffers. Bates, Paabo, and Robinson (22) have determined experimentally values of $(\bar{E}_j - \log_m \gamma_H)$ for dilute buffer solutions in ethanol--water solvents in contact with 3.5M aqueous KCl, where $\bar{E}_j$ (in pH units) is the liquid-junction error in a pH measurement, which is essentially equal to the E_j at the nonaqueous (buffer)--aqueous (3.5M KCl) interface. Similar values are available for methanol from the data of DeLigny and Rehbach (184).

Using values for $\log_m \gamma_H$ in ethanol--water solvents and methanol determined in this study and values for $(\bar{E}_j - \log_m \gamma_H)$ determined by Bates, Paabo and Robinson (22) and DeLigny and Rehbach (184), values for the liquid-junction potential between 3.5M aqueous KCl and buffers in ethanol--water solvents and methanol can be evaluated. These values are listed in Table 85 along with the appropriate values of $\log_m \gamma_H$ and $(\bar{E}_j - \log_m \gamma_H)$.

The liquid-junction potential between aqueous 3.5M

Table 85. Liquid-Junction Potentials Between 3.5M Aqueous KCl and Buffers in Ethanol--Water Solvents and Methanol at 25°C.

wt.-% ethanol	$(\bar{E}_j - \log {}_m\gamma_H)(21)$	$\log {}_m\gamma_H$ interpolated		E_j pH units		E_j millivolts	
		Ph_4^+ [a]	TAB^+ [b]	Ph_4^+	TAB^+	Ph_4^+	TAB^+
0.0	0.000	0.00	0.00	0.00	0.00	0	0
16.2	0.003	0.08	-0.17	0.08	-0.17	5	-10
33.2	0.086	-0.12	-0.61	-0.03	-0.52	-2	-31
52.0	0.221	-0.68	-1.02	-0.46	-0.80	-27	-41
73.4	0.196	-0.83	-1.03	-0.63	-0.83	-37	-49
85.4	-0.032	-0.53	-0.66	-0.56	-0.69	-33	-41
100.0	-2.91	1.68	1.84	-1.23	-1.07	-72.8	-63.3
CH_3OH	-3.26	1.68	1.82	-1.58	-1.44	-93.5	-85.3

KCl and 100 % ethanol is quite appreciable having a value of -1.23 pH units (Ph_4^+ assumption) which corresponds to -72.8 millivolts. Thus, the liquid-junction potential at the interface between aqueous and nonaqueous solutions cannot be suppressed with a concentrated salt bridge. The same is true for $\overline{E}_j$ between water and 3.5M KCl in methanol where $\overline{E}_j$ has a value of -1.58 pH units (Ph_4^+ assumption).

Conclusions.

At this time, reference-electrolyte methods provide the best means for evaluating medium effects for single ions. Values of medium effects for single ions based on the reference-electrolyte assumptions $\log {}_m\gamma_{Ph_4P} = \log {}_m\gamma_{BPh_4}$, $\log {}_m\gamma_{Ph_4As} = \log {}_m\gamma_{BPh_4}$, and $\log {}_m\gamma_{TAB} = \log {}_m\gamma_{BPh_4}$, are in agreement with chemical considerations and, have been independently verified by use of Hammett acidity functions, H_o, and the Stokes' modified Born equation.

While it is presently difficult to make a final choice between the combined Ph_4P BPh_4--Ph_4As BPh_4 assumption (the Ph_4^+ assumption) and the TAB BPh_4 assumption, the former is favored on the grounds that for the solvents studied here, $\log {}_m\gamma_{Ph_4P} = \log {}_m\gamma_{Ph_4As}$, which in turn makes the assumption of their equality to $\log {}_m\gamma_{BPh_4}$ seem very plausible.

Recommendations for future studies.

A critical review of solubility and e.m.f. data in nonaqueous solvents would certainly be desirable in light of the lack of internal consistency of much of the data available in the literature (see Tables 77 and 80). There is also a need to determine the radii of the reference ions Ph_4P^+, Ph_4As^+, TAB^+, and BPh_4^- to a greater degree of accuracy.

It would be of great interest to evaluate medium effects for the proton in methanol--water solvents to see if the variation in basicity of these solvents parallels the variation in ethanol--water solvents. It would also be interesting to see how medium effects for the Li^+ ion vary in alcohol--water solvents and how it compares with the proton.

Independent theoretically sound methods for evaluating medium effects for single ions based on modified redox functions (see section IV-F-1) should be investigated further. Kinetic studies might also prove useful in the evaluation of medium effects for single ions and in testing their physical reality. The area of estimating absolute single-electrode potentials could also lead to more accurate values of ${}_m\gamma$'s (37, 181). Indeed, an accurate experimental method for evaluation of single-electrode potentials would provide a most acceptable solution to the problems of establishing

solvent-independent e.m.f., and ion-activity scales and evaluating liquid-junction potentials between pairs of dissimilar solvents.

Appendix A - 1.

Densities of Ethanol--Water Solvents, Methanol, and Acetonitrile at 25°C (131).

wt.-% ethanol	Density (g/ml)
0.0	0.997077
2.0	0.993359
5.0	0.988166
6.0	0.986563
10.0	0.980434
15.0	0.973345
20.0	0.966392
25.0	0.958946
30.0	0.950672
35.0	0.941459
40.0	0.931483
45.0	0.920850
50.0	0.909852
55.0	0.898502
60.0	0.886990
65.0	0.875269
70.0	0.863399
75.0	0.851336
80.0	0.839114
85.0	0.826596
90.0	0.813622
95.0	0.799912
98.0	0.791170
99.0	0.788135
100.0	0.785058
CH_3OH	0.7865 (129)
CH_3CN	0.7767 (177)

Appendix A - 2.

Dielectric Constants of Ethanol--Water Solvents, Methanol, and Acetonitrile at 25°C (173).

wt.-% ethanol	D
0.0	78.5
10.0	72.8
20.0	67.0
30.0	61.1
40.0	55.0
50.0	49.0
60.0	43.4
70.0	38.0
80.0	32.8
90.0	28.1
100.0	24.3
CH_3OH	32.63 (174)
CH_3CN	35.95 (177)

Appendix A - 3.

Viscosity of Ethanol--Water Solvents at 25°C (182).

wt.-% ethanol	Viscosity, in millipoise
0.0	8.949
10.0	13.28
20.0	18.08
30.0	22.03
40.0	23.74
45.0	23.87
50.0	23.68
60.0	22.32
70.0	20.25
80.0	17.38
90.0	14.22
100.0	11.01

Appendix B - 1.

FORTRAN Computer Program--Shedlovsky Equation.

```
      SIGKA=SQRT(SUMKA/(G-1.))
      SIGQZ=SQRT(SUMQZ/(G-1.))
      DO68 J=1,N
   68 WRITE(3,1068)CONC(J),Q(J),Y(J),X(J)
 1068 FORMAT(F12.5,4X,F8.3,5X,E12.5,4X,F11.4)
      WRITE(3,1072)
 1072 FORMAT(//51H   ACTIVITY COEFF.  DEGREE OF DISSOC.  DELTA LAMBDA)
      DO 73 J=1,N
   73 WRITE(3,1073)ESQRD(J),GAMMA(J),DELQ(J)
 1073 FORMAT(3X,F10.4,F18.4,F17.4)
      WRITE(3,1070)XLPLU,XK
 1070 FORMAT(/10X,14HLAMBDA ZERO # F8.3,5X,5HKA # F10.4)
      WRITE(3,1078)SIGQZ,SIGKA
 1078 FORMAT(10X,15HSTANDARD DEV. #F8.4,4X,15HSTANDARD DEV. #F8.4)
      WRITE(3,1071)WP,XKD
 1071 FORMAT(10X,16HWALDEN PRODUCT #F7.4,4X,5HKD # E11.4)
      GO TO 100
   89 NPROB=NDONE+1
      WRITE(3,1090)NPROB,NCYC
 1090 FORMAT(I5,5X,I5,5X,30H          ITERATION DIVERGING//)
  100 NDONE =NDONE +1
      GO TO 1
      END
```

TRAN IV 360N-FO-479 3-3 MAINPGM DATE 11/12/70 TIME 21.05.5

```
      WRITE(3,1009)
 1009 FORMAT(55H CONCENTRATION    LAMBDA    1/LAMBDA X S%Z<    C F S%Z<)
      NPROB=0
      NDONE=0
      NCYC=0
      SQRDT = SQRT(D*T)
      A = 1.8246E+06/(SQRDT**3)
      ALPHA=0.8204E+06/(SQRDT**3)
      BETA=82.501/(SQRDT*ETA)
   15 S = (ALPHA*QZ)+BETA
      CONST=((1./QZ)**1.5)*S
      DO30 J=1,N
      PROD(J)=SQRT(CONC(J)*Q(J))
      Z(J)=CONST*PROD(J)
      GAMMA(J)=(Q(J)/QZ)*((0.5*Z(J)+SQRT(1.+(0.25*Z(J))**2))**2)
      FSQRD(J) = EXP(-4.60518*A*SQRT(CONC(J)*GAMMA(J)))
      SZ(J)=(.5*Z(J)+SQRT(1.+(.25*Z(J))**2))**2
      Y(J)=1./(Q(J)*SZ(J))
   30 X(J)=CONC(J)*Q(J)*FSQRD(J)*SZ(J)
      SUMY=0.
      SUMX=0.
      SUMXY=0.
      SUMXX=0.
      DO40 J=1,N
      SUMY=SUMY+Y(J)
      SUMX=SUMX+X(J)
      SUMXX=SUMXX+X(J)**2
   40 SUMXY=SUMXY+Y(J)*X(J)
      G=N
      DENOM=SUMX**2-G*SUMXX
      SLOPE=(SUMX*SUMY-G*SUMXY)/DENOM
      CEPT=(SUMX*SUMXY-SUMY*SUMXX)/DENOM
      XLPLU=1./CEPT
      DIFF=ABS(XLPLU-QZ)
      IF(TOL*XLPLU-DIFF)65,69,69
   65 QZ=XLPLU
      NCYC=NCYC+1
      IF(MAXCY-NCYC)89,89,15
   69 NPROB = NDONE+1
      NCYC=NCYC+1
      XKD=1./(SLOPE*XLPLU**2)
      XK=1./XKD
      WP=ETA*XLPLU
      SUMKA=0.
      SUMQZ=0.
      DO 80 J=1,N
      CALKA(J)=((Y(J)-(1./QZ))*(QZ**2))/X(J)
      CALQZ(J)=(1.+SQRT(1.+4.*Y(J)*XK*X(J)))/(2.*Y(J))
      CALY(J)=SLOPE*X(J)+CEPT
      DELQ(J)=Q(J)-1./(CALY(J)*SZ(J))
      DKASQ=(CALKA(J)-XK)**2
      SUMKA=SUMKA+DKASQ
      DQZSQ=(CALQZ(J)-QZ)**2
   80 SUMQZ=SUMQZ+DQZSQ
```

```
ORTRAN IV 360N-FO-479 3-3        MAINPGM          DATE   11/12/70     TIME    21.05.

      C     CONDUCTANCE CALCULATION *SHEDLOVSKY METHOD*
      C
      C     CALCULATION OF CONCENTRATION AND EQUIVALENT CONDUCTANCE
      C
      C     VALUES OF CONSTANTS FROM FUOSS AND ACCASCINA, ELECTROLYTIC COND.
      C     N = NUMBER OF DATA POINTS  MAXCY = MAXIMUM NO. OF ITERATIONS
      C     TOL = TOLERANCE  D = DIELECTRIC CONSTANT  T = ABSOLUTE TEMP.
      C     OZ = ESTIMATE OF LAMBDA ZERO  ETA = VISCOSITY IN POISE
      C     Q = EQUIVALENT CONDUCTANCE  CONC = 1000CONC
      C     CSOL, COND = MEASURED CONDUCTANCE * 10**6
      C     WTSTK=WT OF STOCK SOLUTION, DWT=DENSITY OF WEIGHTS
      C     WTSOL=WT OF SOLUTION PREPARED, V1=VOLUME OF STOCK SOLUTION USED
      C     DAIR1=DENSITY OF AIR FOR BUOYANCY CORRECTION OF STOCK SOLUTION
      C     DAIR2=DENSITY OF AIR FOR BUOYANCY CORRECTION OF SOLUTION PREPARED
      C
            DIMENSION Q(50),CONC(50),Z(50),PROD(50),GAMMA(50),FSQRD(50),X(50)
            DIMENSION Y(50),SZ(50),CALKA(50),CALOZ(50),CALY(50),DELQ(50)
          1 WRITE(3,1001)
       1001 FORMAT(43H1CONDUCTANCE CALCULATION, SHEDLOVSKY METHOD//)
            READ(2,1002)
       1002 FORMAT(55H                                                    )
            WRITE(3,1002)
            READ(2,101)MAXCY,TOL,ICAL
        101 FORMAT(I5,F10.0,5X,I5)
            READ(2,1003)N,OZ,D,T,ETA
       1003 FORMAT(I5,5X,4F10.0)
            IF(ICAL)5,5,2
          2 READ(2,102)SAMPL,STWT,STVOL,DAIR,DWT3
        102 FORMAT(5F10.0)
            STWT=STWT+ (STVOL-(STWT/DWT3))*DAIR
            CSTK=SAMPL/STWT
            READ(2,103)XMW,CELLC,CSOL,DWT,      DSOLV,DAIR1,DAIR2
        103 FORMAT(7E10.0)
            CSOL=CSOL*1.0E-06
            DO 10 J=1,N
            READ(2,1004)WTSTK,WTSOL,V1,COND
       1004 FORMAT(4F10.0)
            WTSTK=WTSTK+((V1-(WTSTK/DWT))*DAIR1)
            WTSOL=WTSOL+((100.-(WTSOL/DWT))*DAIR2)
            C=(CSTK*WTSTK/XMW)/((WTSOL/DSOLV)*1.0E-03)
            COND=COND*1.0E-06
            COND=COND-CSOL
            Q(J)=CELLC*COND
            Q(J)=1000.*Q(J)/C
         10 CONC(J)=C
            GO TO 7
          5 DO 6 J=1,N
            READ(2,1005)CONC(J),Q(J)
       1005 FORMAT(2E10.0)
          6 CONC(J) = 0.0001*CONC(J)
          7 WRITE(3,1007)MAXCY,TOL,OZ
       1007 FORMAT(/7H MAXCY#I4,8H   TOL #F7.4,23H  INITIAL LAMBDA ZERO #F6.2)
            WRITE(3,1008)D,T,ETA
       1008 FORMAT(14H DIELEC CONST#F6.2,9H   TEMP #F7.2,11H   VISCOS #F8.5/)
```

Appendix B - 2.

Computer Program (FORTRAN) for Evaluating $\log(\alpha_I C_I / \alpha_o C_o)$ From C_I, C_o, C_{LiCl}, and K_A.

log 1


```
      IMPLICIT REAL*8(A-H,O-Z)
C     ANALYSIS OF SOLUBILITY DATA(DETERMINATION OF ACTIVITY COEFFICIENT)
C
C     XK1,XK2,XK3 = ASSOCIATION CONSTANTS, =0. IF COMPLETE DISSOCIATION
C     A = DEBYE-HUCKEL A
C     D = DIELECTRIC CONSTANT
C     DSOLV = DENSITY OF SOLVENT
C     TOL = TOLERANCE (PERCENT)
      DIMENSION FSQRD(20),CL1(20),A1P(20),B1P(20),P(20),A1C(20),B1C(20)
      DIMENSION CL(20),PI(20),XLI(20),AC(20),CKP(20),CLC(20),X(20),Y(20)
      DIMENSION ALPHA(20)
    1 WRITE(3,1001)
 1001 FORMAT('1DETERMINATION OF ACTIVITY COEFFICIENT FROM SOLUBILITY')
      READ(1,1002)
 1002 FORMAT(55H                                                      )
      WRITE(3,1002)
      READ(1,1003)N,D,T,XK1,XK2,XK3,DSOLV,TOL
 1003 FORMAT(I5,5X,7F10.0)
      DO 5 I=1,N
    5 READ(1,1005)CKP(I),CLC(I)
 1005 FORMAT(E10.0,F10.0)
      TOL=TOL*.01
      SQRDT=DSQRT(D*T)
      A=1.8246E+06/(SQRDT**3)
      IF(XK1)54,400,10
   10 IF(XK2)54,20,30
   20 IF(XK3)54,300,200
   30 IF(XK3)54,600,100
C     START CALCULATION 1
  100 WRITE(3,1100)
 1100 FORMAT(14H CALCULATION 1/)
      DO 199 I=1,N
      FSQRD(I)=1.
      CL1(I)=CLC(I)
C     USE CL TO CALCULATE POTASSIUM
  110 A1P(I)=(XK1*XK3*(FSQRD(I)**2)*CL1(I)) +XK1*FSQRD(I)
      B1P(I)=(XK3*FSQRD(I)*CL1(I))+1.
      P(I)=(-B1P(I)+DSQRT((B1P(I)**2)+4.*A1P(I)*CKP(I)))/(2.*A1P(I))
      IF(CLC(I))53,119,120
  119 CL(I)=0.
      GO TO 175
  120 A1C(I)=(XK2*XK3*(FSQRD(I)**2)*P(I))+XK2*FSQRD(I)
      B1C(I)=(XK3*FSQRD(I)*P(I))+1.
      CL(I)=(-B1C(I)+((B1C(I)**2)+4.*A1C(I)*CLC(I))**0.5))/(2.*A1C(I))
      DIFF=DABS(CL1(I)-CL(I))
      IF(TOL*CL1(I)-DIFF)170,175,175
  170 CL1(I)=CL(I)
      GO TO 110
  175 PI(I)=CKP(I)/((XK1*FSQRD(I)*P(I))+1.)
      XLI(I)=CLC(I)/((XK2*FSQRD(I)*CL(I))+1.)
      AC(I)=(P(I)+CL(I)+XLI(I)+PI(I))/2.
      FS=DEXP(-4.60518*A*DSQRT(AC(I)))
      IF(DABS(FSQRD(I)-FS)-.0001)199,199,185
  185 FSQRD(I)=FS
```

```
      GO TO 110
  199 CONTINUE
      GO TO 500
C     START CALCULATION 2
  200 WRITE(3,1200)
 1200 FORMAT(14H CALCULATION 2/)
      DO 299 I=1,N
      FSQRD(I)=1.
      CL1(I)=CLC(I)
C     USE CL TO CALCULATE PI
  210 A1P(I)=XK1*FSQRD(I)
      B1P(I)=XK1*FSQRD(I)*CL1(I)-XK1*FSQRD(I)*CLC(I)+1.
      PI(I)=(-B1P(I)+DSQRT((B1P(I)**2)+4.*A1P(I)*CKP(I)))/(2.*A1P(I))
      IF(CLC(I))53,219,220
  219 CL(I)=0.
      GO TO 275
  220 A1C(I)=XK3*FSQRD(I)
      B1C(I)=XK3*FSQRD(I)*PI(I)-XK3*FSQRD(I)*CLC(I)+1.
      CL(I)=(-B1C(I)+(((B1C(I)**2)+4.*A1C(I)*CLC(I))**0.5))/(2.*A1C(I))
      DIFF=DABS(CL1(I)-CL(I))
      IF(TOL*CL1(I)-DIFF)270,275,275
  270 CL1(I)=CL(I)
      GO TO 210
  275 AC(I)=PI(I)+CL(I)
      FS=DEXP(-4.60518*A*DSQRT(AC(I)))
      IF(DABS(FSQRD(I)-FS)-.0001)299,299,285
  285 FSQRD(I)=FS
      GO TO 210
  299 CONTINUE
      GO TO 500
C     START CALCULATION 3
  300 WRITE(3,1300)
 1300 FORMAT(14H CALCULATION 3/)
      DO 399 I=1,N
      FSQRD(I)=1.
  310 PI(I)=(-1.+DSQRT(1.+4.*XK1*FSQRD(I)*CKP(I)))/(2.*XK1*FSQRD(I))
      P(I)=PI(I)
      XLI(I)=CLC(I)
      CL(I)=CLC(I)
      AC(I)=(XLI(I)+P(I)+CL(I)+PI(I))/2.
      FS=DEXP(-4.60518*A*DSQRT(AC(I)))
      IF(DABS(FSQRD(I)-FS)-.0001)399,399,385
  385 FSQRD(I)=FS
      GO TO 310
  399 CONTINUE
      GO TO 500
C     START CALCULATION 4
  400 WRITE(3,1400)
 1400 FORMAT(14H CALCULATION 4/)
      DO 499 I=1,N
      AC(I)=CKP(I)+CLC(I)
      PI(I)=CKP(I)
  499 CONTINUE
      GO TO 500
```

```
C     START CALCULATION 5
  600 WRITE(3,1600)
 1600 FORMAT(14H CALCULATION 5/)
      DO 699 I=1,N
      FSQRD(I)=1.
  610 PI(I)=(-1.+DSQRT(1.+4.*XK1*FSQRD(I)*CKP(I)))/(2.*XK1*FSQRD(I))
      CL(I)=(-1.+DSQRT(1.+4.*XK2*FSQRD(I)*CLC(I)))/(2.*XK2*FSQRD(I))
      AC(I)=PI(I)+CL(I)
      FS=DEXP(-4.60518*A*DSQRT(AC(I)))
      IF(DABS(FSQRD(I)-FS)-.0001) 699,699,685
  685 FSQRD(I)=FS
      GO TO 610
  699 CONTINUE
  500 DO 599 I=1,N
      X(I)=DSQRT(AC(I))
      ALPHA(I)=PI(I)/CKP(I)
  599 Y(I)=(DLOG(ALPHA(I)*CKP(I)/(ALPHA(1)*CKP(1))))/2.30258
      ALPHO=PI(1)/CKP(1)
      TOL=TOL/.01
      WRITE(3,1032)N,D,T
 1032 FORMAT(4H N #I3,9X,15HDIELECT.CONST #F6.2,9X,13HTEMPERATURE #F7.2)
      WRITE(3,1033)DSOLV,TOL
 1033 FORMAT(21H DENSITY OF SOLVENT #F8.5,17X,5HTOL #F6.4)
      WRITE(3,1034)XK1
 1034 FORMAT(39H ASSOCIATION CONSTANT FOR ELECTROLYTE #F8.2)
      WRITE(3,1036)XK2
 1036 FORMAT(40H ASSOCIATION CONSTANT FOR SOLVENT SALT #F8.2)
      WRITE(3,1037)XK3
 1037 FORMAT(44H ASSOCIATION CONSTANT FOR INTERFERING SALT #F8.2)
      WRITE(3,1038)A
 1038 FORMAT(29H THEORETICAL DEBYE-HUCKEL A #E12.5/)
      WRITE(3,1040)
 1040 FORMAT(52H  SOLUBILITY    CONC%LICL<  LOG%          <   SQRT%I<)
      DO 42 I=1,N
   42 WRITE(3,1042)CKP(I),CLC(I),Y(I),X(I)
 1042 FORMAT(1X,E11.4,F11.5,F15.4,F14.5)
      WRITE(3,1046)ALPHO
 1046 FORMAT(/43H DEGREE OF DISSOCIATION %IN PURE SOLVENT< #F7.4)
      READ(1,1000)DUMMY
 1000 FORMAT(F10.0)
      WRITE(3,1060)(X(I),Y(I),I=1,N)
 1060 FORMAT(F6.4,F6.4)
      GO TO 1
   53 WRITE(3,1053)
 1053 FORMAT(/45H CONCENTRATION OF SOLVENT SALT LESS THAN ZERO)
      GO TO 12
   54 WRITE(3,1054)
 1054 FORMAT(/36H ASSOCIATION CONSTANT LESS THAN ZERO)
   12 N=N+1
      DO 14 I=1,N
   14 READ(1,1101)
 1101 FORMAT(1H )
      GO TO 1
      END
```

Appendix B - 3.

Least-Square-Fit Analysis for Evaluating Activity Coefficients (FORTRAN).

```
ORTRAN IV 360N-FO-479 3-4          MAINPGM          DATE    03/01/71      TIME    18.29

      C PROGRAM DBAK, MODIFICATION OF LSFTI FOR POLYNOMIAL UP TO X**4,
      C INPUT DATA IDENTICAL WITH LSFTI EXCEPT THAT ALL Y IN COLUMNS 1 TO 10,
      C ALL X IN COLUMNS 11 TO 20.  PROGRAM SET TO CALCULATE X SQUARED AND
      C X CUBED  MODIFIED BY AL KIRSCH  THANK YOU AL KIRSCK
      C
      C          PROGRAM LSFTI ---  TO LEAST-SQUARES-FIT DATA ON INDEPENDENT
      C               VARIABLE Y INTO A FORM
      C                      Y = A*X1 + B*X2 + C*X3 + ... + E*X5
      C               WHERE X1,X2, ETC. ARE  INDEPENDENT VARIABLES .
            DOUBLE PRECISION Y(50),EY(50),X(50,5),A(5),EINT(5),EEXT(5),
           1RECORD(36)
            CALL SETCLK(5)
          1 READ(1,1001)IND,NI,NP,IFPT,IFSE,IDATA
       1001 FORMAT(6I3)
            IF(IND+9)500,2,500
        500 CALL EXIT
          2 READ(1,1002)(RECORD(I),I=1,36)
       1002 FORMAT(12A6)
            WRITE(3,3001)(RECORD(I),I=1,12)
       3001 FORMAT(1H112A6)
            WRITE(3,1002)(RECORD(I),I=13,36)
            IF(IDATA)5,5,3
          3 DO 4 I=1,NP
      C
      C     THIS IS MODIFICATION OF LSFTI FOR POLYNOMIAL.
      C
          4 READ(1,1003)Y(I),X(I,2)
       1003 FORMAT(2F10.5)
            DO 5555 I=1,NP
            X(I,1)=1.000000
       5555 EY(I)=1.000000
            DO 5556 II=3,NI
            JJ=II-1
            DO 5556 KK=1,NP
       5556 X(KK,II)=X(KK,2)**JJ
      C
          5 CALL LSF(Y,EY,X,NI,NP,IFPT,IFSE,A,EINT,EEXT)
            GOTO 1
            END
```

```
ORTRAN IV 360N-FO-479 3-4          LSF                DATE    03/01/71      TIME    18.29.

      SUBROUTINE LSF(Y,EY,X,NI,NP,IFPT,IFSE,A,EINT,EEXT)
C         LSF-PROGRAM IN FORTRAN IV FOR B.C. COMPUTER (IBM360/40 WITH
C         32K MEMORY).  IN THE LIST OF ARGUMENTS ABOVE, Y THRU IFSE ARE
C         INPUT TO THE SUBROUTINE, AND THE LAST 3 ARE OUTPUT.
C         MAX. NUMBER OF EXPT'L PTS IS 50.
C         Y(I)    = DEPENDENT VARIABLE, I-TH POINT.
C         EY(I)   = DEVIATION ON Y(I)
C         X(I,J) = J-TH INDEPENDENT VARIABLE, I-TH PT.  J UP TO 5.
C         NI      = NO. OF INDEP. VARIABLES.
C         NP      = NO. OF EXPT'L PTS.
C         IFPT    = 1 IF X(I,J) ARE TO BE PRINTED.
C         IFSE    = 1 IF THE SIMULTANEOUS EQN'S ARE TO BE PRINTED.
C         A(J)    = J-TH BEST-FIT COEFFICIENT.
C         EINT(J)= INTERNAL DEVIATION ON A(J)
C         EEXT(J)= EXTERNAL DEVIATION ON A(J)
      DOUBLE PRECISION Y(50),EY(50),X(50,5),A(5),EINT(5),EEXT(5),W(50),
     1P(5,10),Q(5),B(5,50),S(50),E(50),DC(50)
      DIMENSION NG(2)
      IF(IFPT)3,3,1
    1 WRITE(3,3001)
 3001 FORMAT(//79H0   I       X(I,1)         X(I,2)         X(I,3)         X
     1(I,4)         X(I,5)      I)
      DO 2 I=1,NP
    2 WRITE(3,3002)I,(X(I,J),J=1,5),I
 3002 FORMAT(I5,5F14.8,I4)
    3 DO 4 I=1,NP
    4 W(I)=1.0D0/EY(I)**2
      DO 6 J=1,NI
      DO 6 K=J,NI
      P(J,K)=0.0D0
      DO 5 I=1,NP
    5 P(J,K)=P(J,K)+W(I)*X(I,J)*X(I,K)
      P(K,J)=P(J,K)
    6 CONTINUE
      NI1=NI+1
      DO 11 J=1,NI
      DO 11 K=NI1,10
   11 P(J,K)=0.0D0
      IF(IFSE)12,12,7
    7 DO 9 K=1,NI
      Q(K)=0.0D0
      DO 8 I=1,NP
    8 Q(K)=Q(K)+W(I)*Y(I)*X(I,K)
    9 CONTINUE
      WRITE(3,3003)
 3003 FORMAT(//57H THE SIMULTANEOUS EQUATIONS FOR COEFFICIENTS A(J) FOLL
     1OW.)
      WRITE(3,3004)
 3004 FORMAT(//110H       *A(1)                *A(2)                *A(3)
     1          *A(4)                *A(5)          =   CONSTANTS)
      DO 10 K=1,NI
   10 WRITE(3,3005)(P(K,J),J=1,5),Q(K)
 3005 FORMAT(2X,E15.8,4(4X,E15.8),5H    =E15.8)
   12 NG(1)=NI
```

```
      NG(2)=-1
      CALL GAJ03(NG,P)
      DO 14 J=1,NI
      JA=J+NI
      DO 13 K=1,NI
   13 P(K,J)=P(K,JA)
   14 CONTINUE
      DO 16 J=1,NI
      DO 16 I=1,NP
      B(J,I)=0.0D0
      DO 15 K=1,NI
   15 B(J,I)=B(J,I)+P(K,J)*X(I,K)
   16 CONTINUE
      DO 18 J=1,NI
      A(J)=0.0D0
      DO 17 I=1,NP
   17 A(J)=A(J)+B(J,I)*W(I)*Y(I)
   18 EINT(J)=DSQRT(P(J,J))
      DO 20 I=1,NP
      S(I)=0.0D0
      DO 19 J=1,NI
   19 S(I)=S(I)+A(J)*X(I,J)
      E(I)=Y(I)-S(I)
   20 DC(I)=E(I)/EY(I)
      AK=NP-NI
      AJ=0.0D0
      DO 21 I=1,NP
   21 AJ=AJ+W(I)*E(I)**2
      DO 22 J=1,NI
   22 EEXT(J)=DSQRT(AJ*P(J,J)/AK)
      WRITE(3,3006)
 3006 FORMAT(////80H COMPARISON OF INPUT DATA WITH THE BEST-FIT CURVE FO
     1LLOWS.  RESIDUE = Y(I) - LSF)
      WRITE(3,3007)
 3007 FORMAT(//62H     I    INPUT Y(I)  INPUT EY(I)  RESIDUE/EY(I)  Y FROM
     1 LSF    I)
      DO 23 I=1,NP
   23 WRITE(3,3008)I,Y(I),EY(I),DC(I),S(I),I
 3008 FORMAT(I5,F12.6,F13.6,F13.3,3X,F12.6,I4)
      WRITE(3,3009)
 3009 FORMAT(////74H THE LEAST-SQUARES FIT COEFFICIENTS A(J) AND INT. &
     1EXT DEVIATIONS FOLLOW.)
      WRITE(3,3010)
 3010 FORMAT(//45H              A(J)         INT.DEV.      EXT.DEV.)
      DO 24 J=1,NI
   24 WRITE(3,3011)A(J),EINT(J),EEXT(J)
 3011 FORMAT(/8X,E12.5,E13.4,E13.4)
      RETURN
      END
```

```
      SUBROUTINE GAJ03(NG,AMAT)
CGAJ03    THIS IS A MODIFICATION OF GAJ03 ORIGINALLY WRITTEN BY S. EHREN
C     -SON IN FORTRAN II AND IS TO BE CALLED BY LSFAM.
      DOUBLE PRECISION AMAT(5,10),A
      DIMENSION NG(2),K1C(5)
    1 NS1=1                                                          GAJ001
      DO 17 NC=1,15                                                  GAJ001
      N=NG(NC)
      IF(N)12,12,6
    6 M=N+1
      IF(NG(2))2,3,3
    2 K=2*N
      DO 5 I=1,N
      L=I+N
      DO 4 J=M,K
    4 AMAT(I,J)=0.0D0
    5 AMAT(I,L)=1.0D0
      M=K
    3 NSN=NS1+N-1
      DO 9 L=1,N
      A=0.0D0
      DO 7 K=1,N
      I=K+NS1-1
      IF(DABS(AMAT(I,K))-DABS(A))7,7,8
    8 K1=K
      A=AMAT(I,K1)
    7 CONTINUE
      K1C(L)=K1
      K2=K1+NS1-1
      DO 9 I=NS1,NSN
      IF(I-K2)10,9,10
   10 DO 11 J=1,M
      DO 13 L1=1,L
      IF(K1C(L1)-J)13,11,13
   13 CONTINUE
      IF(K)14,14,15
   15 AMAT(K2,J)=AMAT(K2,J)/A
   14 AMAT(I,J)=AMAT(I,J)-AMAT(I,K1)*AMAT(K2,J)
   11 CONTINUE
      K=0
    9 AMAT(I,K1)=0.0D0
   17 NS1=NS1+N
   12 RETURN
      END
```

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