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MEDIUM EFFECTS FOR ELECTROLYTES IN ETHANOL-WATER MIXTURES

by

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To my wife Ilse, for her
patience and understanding
throughout this work.

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Table of Contents

Page

Approval Page.. ii

Dedication... iii

Acknowledgements..................................... iv

Table of Contents.................................... v

List of Tables....................................... vii

List of Figures...................................... x

I. General Considerations............................ 1
  A. Outline of the Problem.......................... 2
  B. The Medium Effect............................... 6
    1. Definition and Significance................... 6
    2. Medium Effects for Single Ions................ 10
    3. Experimental Determination of Medium Effects.. 13
      a. Solubility Method
      b. E.M.F. Method
      c. Medium Effects for Single Ions
  C. Previous Approaches to the Problem.............. 20
    1. The Method of Bjerrum and Larsson............. 20
    2. Pleskov's Normal Element Method............... 26
    3. The Method of Strehlow........................ 30
    4. Grunwald's Empirical Method................... 35
    5. Izmaylov's Three Approaches................... 38
    6. Other More Recent Approaches.................. 47
  D. The Present Approach............................ 51

II. Experimental Methods............................. 56
  A. Synthesis of Electrolytes and Preparation of Solvents.... 57
    1. Introduction.................................. 57
    2. Experimental.................................. 57
      a. Lithium Picrate
      b. Potassium Picrate
      c. Potassium Tetraphenylborate
      d. Triisoamyl-n-butylammonium Iodide
      e. Triisoamyl-n-butylammonium Picrate
      f. Triisoamyl-n-butylammonium Tetraphenylborate
      g. Preparation of Solvents

Page

B. Solubility Studies.......................... 62
    1. Introduction.......................... 62
    2. Experimental.......................... 63
    3. Results and Discussion................. 64
C. Electrolytic Conductance Studies............ 74
    1. Introduction.......................... 74
    2. Experimental.......................... 75
    3. Results and Discussion................. 77
D. Determination of Activity Coefficients....... 100
    1. Introduction.......................... 100
    2. Experimental.......................... 100
    3. Results and Discussion................. 101
E. Potentiometry Studies....................... 109
    1. Introduction.......................... 109
    2. Experimental.......................... 110
    3. Results and Discussion................. 116

III. Interpretation and Application of Over-All Results.. 124
A. Medium Effects for Electrolytes............... 125
B. Medium Effects for Single Ions................ 136
C. Interpretation of pH Scales and Estimation of Liquid-Junction Potentials................ 152
D. Correlation of E.M.F. Series.................. 159
E. Summary...................................... 164

Appendix A. Physical Properties of Ethanol-Water Mixtures at 25°C................................ 168
Density of Ethanol-Water Mixtures at 25°C........ 169
Dielectric Constant of Ethanol-Water Mixtures at 25°C................................ 170
Viscosity of Ethanol-Water Mixtures at 25°C...... 171

Appendix B. Fortran Computer Program Listings........ 172

Bibliography.. 188

Autobiographical Statement.......................... 193

List of Tables

Table Number	Title	Page
I	Single-Ion Medium Effects in Absolute Ethanol at 25°C, According to Bjerrum and Larsson.....	24
II	Standard Potential Series Obtained by Pleskov.	29
III	Standard Potentials of Rubidium in Various Solvents Referred to $E^{\circ}_{H} = 0$ in Water..........	32
IV	Standard Potential of Hydrogen Electrode at 25°C Obtained by Various Methods..............	34
V	Medium Effects for Hydrogen Ion Obtained by Grunwald in Ethanol-Water Mixtures at 25°C....	37
VI	Selected Single-Ion Medium Effects Obtained by Izmaylov................................	44
VII	Comparison of Sums of Izmaylov's Single-Ion Medium Effects with Experimentally Observed Values for Electrolytes in Methanol...........	46
VIII	Molar Absorptivities of Picrate and Tetraphenylborate Ions at 25°C......................	66
IX	Solubilities of Electrolytes in Ethanol-Water Mixtures at 25°C..........................	69
X	Conductance of Electrolytes in Ethanol-Water Mixtures at 25°C..............................	78
XI	Conductance Parameters and Constants Obtained at 25°C.....................................	93
XII	Degree of Dissociation of TABPi in 81.8 Weight-Percent Ethanol as Obtained by the Fuoss and by the Shedlovsky Method............	99
XIII	Experimental Mean Molar Activity Coefficients for KPi, TABPi, $K(BPh_4)$ and $TAB(BPh_4)$ in Ethanol-Water Mixtures at 25°C................	106

Table Number	Title	Page
XIV	Mean Molal Activity Coefficients for KPi, TABPi, K(BPh$_4$) and TAB(BPh$_4$) in Ethanol-Water Mixtures at 25°C Obtained by Interpolation	108
XV	Standard Potential of Cell (IV) in Water at 25°C	119
XVI	Standard Potential of Cell (IV) in Ethanol-Water Mixtures at 25°C	120
XVII	Molal Standard Potential of Potassium Electrode in Ethanol-Water Mixtures at 25°C	123
XVIII	Logarithm of Medium Effects for Electrolytes in Ethanol-Water Mixtures at 25°C	126
XIX	Logarithm of Medium Effects for Electrolytes in Ethanol-Water Mixtures at 25°C	130
XX	Molal Solubility Product for TAB(BPh$_4$) in Water at 25°C Obtained via Equation (116)	135
XXI	Logarithm of Medium Effects for Single Ions in Ethanol-Water Mixtures at 25°C	138
XXII	Comparison of Logarithm of Ionic Medium Effects Obtained by Different Authors in Ethanol at 25°C	140
XXIII	Comparison of Logarithm of Medium Effects for the Hydrogen Ion in Ethanol-Water Mixtures Estimated by Different Methods	142
XXIV	Comparison of Logarithms of Medium Effects for the Hydrogen Ion in Methanol-Water Mixtures Estimated by Different Methods	143
XXV	Comparison of Experimentally Obtained Medium Effects for Potassium and Chloride Ions with Their Theoretical Value	150
XXVI	pH of Solutions in Ethanol-Water Mixtures Expressed on the Aqueous Scale at 25°C	154
XXVII	Liquid-Junction Potentials at Aqueous-Nonaqueous Interphases at 25°C	157
XXVIII	Standard Potentials of Hydrogen and Potassium Electrodes in Ethanol-Water Mixtures at 25°C	160

Table Number	Title	Page
XXIX	Comparison of Molal Standard Potentials in Ethanol at 25°C on Aqueous and Nonaqueous Scales	163
XXX	Density of Ethanol-Water Mixtures at 25°C	169
XXXI	Dielectric Constant of Ethanol-Water Mixtures at 25°C	170
XXXII	Viscosity of Ethanol-Water Mixtures at 25°C	171

List of Figures

Figure Number	Title	Page
1	Determination of hydration energy of hydrogen ion according to Izmaylov......................	43
2	Molar absorptivities of KPi and TABPi in ethanol-water mixtures at 25°C................	65
3	Molar solubilities of picrates and tetraphenylborates in ethanol-water mixtures at 25°C.....	70
4	Typical y - x plot for LiCl in 92.3 wt.-% ethanol.......................................	90
5	Log K_A vs. 1/D plot for the electrolytes studied.......................................	95
6	Comparison of association constants obtained by the Fuoss and by the Shedlovsky methods....	97
7	Comparison of activity coefficients obtained experimentally with those obtained via the Debye-Hückel limiting law......................	107
8	Cell used for potentiometric measurements.....	114
9	Logarithm of medium effects for electrolytes studied in ethanol-water mixtures at 25°C.....	133
10	Logarithm of medium effects for single ions in ethanol-water mixtures at 25°C............	137
11	Comparison of experimentally obtained medium effects for potassium and chloride ions with their theoretical values......................	151
12	pa_H^* and pa_H for solutions in Table XXVI.......	155

Part I. General Considerations.

Outline of the Problem

As of now there are no generally accepted solutions to the following three interrelated problems:

1) the establishment of a single scale for pH and for all other ion activities, referred to their aqueous standard states;

2) the determination of standard potentials, E°, in nonaqueous solvents on a single scale referred to $E^\circ_H = 0$ in water;

3) the estimation of liquid-junction potentials at aqueous-nonaqueous interphases.

The purpose of this research is to demonstrate a new approach towards a possible solution to the above problems, using ethanol-water mixtures as the media for the study.

The activity of a solute, a_i, is commonly referred to infinite dilution in a given solvent as the standard state:

$$a_i = m_i \, {}_s\gamma_i \tag{1}$$

Here the subscript i denotes the solute, m_i, its molality and ${}_s\gamma_i$, its "salt effect" activity coefficient, which approaches unity at infinite dilution in the given solvent. Similarly, standard potentials in any solvent are commonly referred to the standard potential of the hydrogen electrode, which is arbitrarily assigned the value of zero volts in the given solvent. These conventions result in as many different standard states for any given solute and as many different standard reference potentials as we have solvents and solvent combinations. Potentially, this means an infinite number of separate e.m.f. series - scales and series which have no apparent direct interrelation. Such activity scales and standard potential series in each solvent are isolated "worlds" of their own, so to speak. This unsatisfactory state has apparently come about through a lack of foresight in establishing activity scales in different solvents and a lack of fundamental knowledge necessary to correlate these scales.

Initially, water was the only solvent in common use. As the chemistry of electrolytes expanded, chemists found water to be insufficient for their needs and interests. Turning to other solvents, they set up activity scales following much the same procedure as was used for aqueous solutions, i.e., the infinitely dilute solution in a given solvent was adopted as the standard state. As a result, we are now confronted with the problem of correlating electrochemical and other physico-chemical data which were obtained in water and in nonaqueous solvents on unrelated scales.

We can illustrate the problem of such correlation on the example of the activity scale of the hydrogen ion, or the pH scale. The question arises whether in an aqueous solution of a certain pH, let us say pH 4.0 as expressed on the aqueous scale, the hydrogen ion has the same activity as in a given nonaqueous solution of pH 4.0 as expressed on the nonaqueous scale. More briefly, is a solution of pH 4.0

in a given nonaqueous solvent more or less acidic than a solution of pH 4.0 in water? Although the answer to this question will not be offered at this point, it soon becomes apparent that in order to correlate this type of data obtained in different solvents, one must establish a single scale of activities and a single series of standard potentials, independent of solvent. Once the activities and standard potentials are expressed on this common scale, a direct comparison can be made between data obtained in different solvents.

In searching for a common scale we find the aqueous activity and standard potential scales to be most suitable reference points, because most of the chemistry of electrolytes has already been carried out in water. In principle, therefore, we can establish a single scale of activities in all solvents referred to the aqueous standard state and a single series of standard potentials in all solvents referred to $E^\circ_H = 0$ in water. The standard potential of hydrogen in any solvent other than water will normally assume a value other than zero.

Once water is chosen as a reference, the problem reduces to one of expressing activities and standard potentials in nonaqueous media on their aqueous scales. It should be pointed out here that the solution to any one of the above three problems will render all of them solved. Therefore, once the activities and standard potentials in nonaqueous media are expressed on their aqueous scale, the estimation of liquid-junction potentials will follow automatically.

The parameters which provide the solution to the three interrelated problems mentioned above are the so-called *medium effects* for single ions. These are considered in detail in the next section.

The Medium Effect

Definition and Significance

The medium effect is by no means a new concept. Earlier in the literature it has been referred to by various names, such as the "Verteilungskoeffizient" (distribution, or partition coefficient) of Bjerrum and Larsson (12), the "primary medium effect" of B. B. Owen (65), the "activity coefficient referred to water" of Bronsted (16) and the "degenerate activity coefficient" of Grunwald (33). Kolthoff (56), Bruckenstein (56) and Laitinen (60) use the terminology of Bjerrum and Larsson. Since the medium effect is a concept unfamiliar to many, it is best to begin its discussion by pointing out how the medium effect manifests itself in solution chemistry.

As an example, let us consider the electrochemical cell used for the establishment of pH scales, namely, the hydrogen-silver chloride cell,

$$\mathrm{Pt(s);\ H_2(g)/H^+,\ Cl^-/AgCl(s);\ Ag(s)} \qquad (I)$$

In both aqueous and nonaqueous solvents the e.m.f., E, of this cell is given by

$$E = {}_wE^\circ - \frac{RT}{nF} \ln a_H a_{Cl} \qquad (2a)$$

and

$$E = {}_sE^\circ - \frac{RT}{nF} \ln a^*_H a^*_{Cl} \qquad (2b)$$

where ${}_{w}E^{\circ}$ and ${}_{s}E^{\circ}$ are the standard potentials of the above cell referred to the aqueous and nonaqueous standard states, respectively, while the asterisk indicates that the activity $\underline{a}^{*}$ is referred to the infinitely dilute solution in the nonaqueous solvent rather than in water. If we then define the quantities

$$pa_{H} = -\log a_{H} \tag{3a}$$

and

$$pa_{H}^{*} = -\log a_{H}^{*} \tag{3b}$$

equations (2a) and (2b) can be rewritten in terms of concentrations and activity coefficients to express the pa_{H}.

$$pa_{H} = \frac{nF(E - {}_{w}E^{\circ})}{RT \ln 10} + \log m_{Cl} + \log \gamma_{Cl} \tag{4a}$$

and

$$pa_{H}^{*} = \frac{nF(E - {}_{s}E^{\circ})}{RT \ln 10} + \log m_{Cl} + \log {}_{s}\gamma_{Cl} \tag{4b}$$

Here γ_{Cl} and ${}_{s}\gamma_{Cl}$ are the familiar salt-effect, or Debye-Hückel, activity coefficients, which approach unity at infinite dilution in water and in the given nonaqueous solvent, respectively. In equation (2b) and in equation (4b) which follows from it, our choice of the nonaqueous standard state, as manifested by the use of ${}_{s}E^{\circ}$, was arbitrary. If instead of the nonaqueous standard state we had chosen to use the aqueous solvent, i.e., if we had chosen to interpret the e.m.f. using the ${}_{w}E^{\circ}$, equation (4b) would become identical with equation (4a), even though the potential $\underline{E}$ was measured in the nonaqueous solvent.

However, when we study the behavior of the activity coefficient in equation (4a) as a function of chloride concentration in the nonaqueous solvent, we find that this activity coefficient does not behave in the usual manner. That is, as the concentration of chloride approaches zero in the nonaqueous solvent, the activity coefficient γ_{Cl} does not approach unity. Instead, depending on the nonaqueous solvent used, it approaches values which are, as a rule, orders of magnitude greater than unity. The value of γ_{Cl} is found to be the product of the salt-effect activity coefficient, ${}_{s}\gamma_{Cl}$, and of another activity coefficient, ${}_{m}\gamma_{Cl}$, which is termed the medium effect. The medium effect becomes unity only in aqueous solution.

$$\gamma_{Cl} = {}_{s}\gamma_{Cl}\ {}_{m}\gamma_{Cl} \tag{5}$$

From equation (5) we can see that as the composition of the solvent approaches pure water, the activity coefficient is given simply by the salt-effect. Thus, we see that as a result of our choice of the aqueous standard state when working with nonaqueous solvents, the medium effect appears as a manifestation of the unusual behavior of the activity coefficient.

Equation (5) also shows that the medium effect serves as a conversion factor correlating the aqueous and nonaqueous activity scales. It follows from equation (5) that the activity of solute <u>i</u> on the aqueous scale, a_i, is related to its activity on the nonaqueous scale, $a_i^{\star}$, by the medium effect:

$$a_i = a_i^{\star}\ {}_{m}\gamma_i \tag{6}$$

Now that we have seen how the medium effect arises, we can look at its significance, to see what this actually represents in physical terms. What changes occur when we transfer a solute from one solvent to another? We must remove the solute from its solvation sphere in the first solvent, transfer it to the second solvent and then solvate it. We can theoretically treat this process by considering the solute i at finite concentration in a nonaqueous solution. Its free energy of solvation, G_i, can be expressed in two reasonable ways: It can be referred to the nonaqueous standard state

$$G_i = {}_sG_i^\circ + RT \ln a_i^*, \tag{7}$$

where ${}_sG_i^\circ$ is the standard free energy of solvation in the given nonaqueous solvent. On the other hand, we can express the same free energy by referring it to the aqueous standard state. In this case

$$G_i = {}_wG_i^\circ + RT \ln a_i, \tag{8}$$

where ${}_wG_i^\circ$ is the standard free energy of solvation in aqueous solution. Since the free energy of the solute G_i, is the same regardless of our choice of standard state, equations (7) and (8) can be combined resulting in

$${}_sG_i^\circ - {}_wG_i^\circ = RT \ln \frac{a_i}{a_i^*}. \tag{9}$$

This, when combined with equation (6), shows that the medium effect is a measure of the difference between the standard free energies of solvation of the solute _in the two solvents_.

$$\ln {}_m\gamma_i = \frac{{}_sG_i^\circ - {}_wG_i^\circ}{RT} \qquad (10)$$

Medium Effects for Single Ions

We can now show how a knowledge of medium effects for single ions can be used to solve the three interrelated problems outlined earlier. We will consider first the problem of establishing a single scale for pH, or any other ion activity in all solvents.

As was pointed out earlier, the medium effect can be used to relate activities expressed on the nonaqueous scale to those expressed on the aqueous scale, according to equation (6). It follows that the pH on the nonaqueous scale is related to that on the aqueous scale through the logarithm of the medium effect of the hydrogen ion.

$$pa_H = pa_H^{\star} - \log {}_m\gamma_H \qquad (11)$$

Equation (11) is of great practical importance in pH work because it permits measurements of pH in nonaqueous solvents to be expressed on the aqueous pH scale, the pa_H scale. In this way the solution of pH 4.0 in the nonaqueous solvent referred to earlier can be compared with the aqueous solution of pH 4.0 if we know the medium effect for the hydrogen ion in that medium. For example, if the logarithm of the medium effect for the hydrogen ion in ethanol is 1.8, the pa_H of an alcoholic solution of $pa_H^{\star}$ 4.0 will be

$$pa_H = 4.0 - 1.8 = 2.2 \qquad (12)$$

indicating that the alcoholic solution of pa_H^* 4.0 is more acidic than the aqueous solution of pa_H 4.0.

In addition to correlating activity scales, the medium effect correlates standard potential series in different solvents. It has been shown (69) that the change in the solvation energy of an electrode-active ion i upon transfer from water to a nonaqueous solvent is given by the difference in the corresponding standard electrode potentials in the two solvents.

$$E^\circ_{i,SH} - E^\circ_{i,H_2O} = \frac{{}_sG^\circ_i - {}_wG^\circ_i}{nF} \qquad (13a)$$

where the solvation energies, G°_i, refer to the oxidized species in the balanced equation for the galvanic cell. Similarly, for the solvation energy of the reduced species:

$$E^\circ_{i,SH} - E^\circ_{i,H_2O} = \frac{{}_wG^\circ_i - {}_sG^\circ_i}{nF} \qquad (13b)$$

Since the medium effect represents the difference in solvation energy in the two solvents, SH and H_2O (equation 10), it follows that

$${}_wE^\circ_{i,SH} = {}_wE^\circ_{i,H_2O} + \frac{RT}{nF} \ln {}_m\gamma_i \qquad (14a)$$

where ${}_m\gamma_i$ is the medium effect of the oxidized species

and

$${}_wE^\circ_{i,SH} = {}_wE^\circ_{i,H_2O} - \frac{RT}{nF} \ln {}_m\gamma_i \qquad (14b)$$

where ${}_m\gamma_i$ is the medium effect of the reduced species. Here ${}_wE^\circ_{i,SH}$ and ${}_wE^\circ_{i,H_2O}$ are both expressed on the same (invariably aqueous) scale. Thus, knowledge of the medium effect of an ion enables us to express, on the aqueous scale, the standard potential of the electrode reversible to it in a nonaqueous solvent. From equation (14a) we can see that the standard electrode potential of hydrogen in a nonaqueous solvent, when expressed on the common aqueous scale will, as a rule, no longer be equal to zero. Instead, the potential will assume the value

$$ {}_wE^\circ_{H,SH} = 0.00 + \frac{RT}{nF} \ln {}_m\gamma_H \qquad (15) $$

The last of the three interrelated problems - that of estimating liquid-junction potentials at aqueous-nonaqueous interphases - arises when we attempt a comparison of electrochemical measurements in different solvents carried out in cells with liquid junction. For example, consider a galvanic cell composed of two identical half-cells in different media, such as a hydrogen electrode in water and in an ethanolic solution as given in cell (II):

$$ Pt(s);\ H_2(g)/H^+\ (H_2O)/H^+\ (EtOH)/H_2(g);\ Pt(s) \qquad (II) $$

At unit activity of hydrogen ion in both half-cells the e.m.f. of the cell is given by

$$ E_{cell} = {}_wE^\circ_{H,EtOH} - {}_wE^\circ_{H,H_2O} + E_j \qquad (16) $$

Since it follows from equation (14a) that the difference ${}_{w}\overset{*}{E}{}^{\circ}_{H,EtOH} - {}_{w}E^{\circ}_{H,H_2O}$ represents a medium effect term, the measured potential of this cell is then a combination of the medium effect term for the hydrogen ion and the liquid-junction potential at the aqueous-ethanolic boundary.

$$E_{cell} = \frac{RT}{nF} \ln {}_{m}\gamma_{H} + E_{j} \qquad (17)$$

Thus, any attempt to equate the potential of a cell such as (II) to the liquid-junction potential will be in error by a term which includes the medium effect. Equation (17) shows that once the medium effect for the hydrogen ion in ethanol is known, the liquid-junction potential in cell (II) follows from the measured potential of the cell.

Experimental Determination of Medium Effects

Medium effects are most commonly determined from solubility and from e.m.f. measurements on electrochemical cells without liquid junctions.

If we consider a saturated aqueous solution of a solute, i in equilibrium with the solid phase, the free energy of the solute is given by

$$G_{i,H_2O} = {}_{w}G^{\circ}_{i} + RT \ln (a_{i})_{Sat} \qquad (18)$$

Analogously for a nonaqueous solution in solvent SH (using the nonaqueous standard state) the free energy of the same solute is given by

$$G_{i,SH} = {}_{s}G^{\circ}_{i} + RT \ln (a^{*}_{i})_{Sat} \qquad (19)$$

Since, in both the aqueous and the nonaqueous solutions the solute is in equilibrium with the same solid phase

$$G_{i,H_2O} = G_{i,SH} \tag{20}$$

and equations (18) and (19) can be combined resulting in

$$\frac{{}_sG_i^\circ - {}_wG_i^\circ}{RT} = \ln \frac{(a_i)_{Sat}}{(a_i^*)_{Sat}} \tag{21}$$

Then from equation (10)

$${}_m\gamma_i = \frac{(a_i)_{Sat}}{(a_i^*)_{Sat}} \tag{22}$$

For a uni-univalent electrolyte

$$a_i = a_+ a_- = a_\pm^2 \tag{23}$$

and we have

$${}_m\gamma_i = \frac{(a_\pm)^2_{Sat}}{(a_\pm^*)^2_{Sat}} \tag{24}$$

Equation (24) forms the basis for the experimental determination of medium effects of electrolytes from their solubilities.

When the electrolyte is not completely dissociated into ions, as is the case in solvents of low dielectric constant, the degree of dissociation, α, must be known since the mean ionic activity is given by

$$a_\pm = m_s\gamma_\pm \qquad (25)$$

where m_s and $\gamma_\pm$ are the molal solubility and the molal activity coefficient, respectively. Then, equation (22) becomes

$$_m\gamma_i = \frac{(\alpha\ m_s\gamma_\pm)^2_{water}}{(\alpha\ m_s\gamma_\pm)^2_{nonaq}} \qquad (26)$$

Thus, the experimental evaluation of medium effects from solubilities involves a knowledge of three quantities: (1) the solubility, (2) the degree of dissociation and (3) the activity coefficient. Each of the above quantities must be known for both the reference solvent (generally water) and for the given nonaqueous solvent.

The above considerations assume that the free energies of the solute in the two saturated solutions are the same. This assumption is valid only if the solid with which the solute is in equilibrium is identical for both the aqueous and the nonaqueous solvents. Only then the free energy of the solute is the same in both solvents. If a crystal solvate forms in either or in both solvents, the free energies of the solid in the two solvents are different. For the case of hydrate formation, for example

$$_sG_i \neq {}_wG_{i \cdot yH_2O} \qquad (27)$$

In the general case of solvate formation, equations (18) and (19) must include the free energy change accompanying the transfer of solvent, S, from the pure solvent to the solvate:

$$G = x\,RT\,\ln\,(p_S/p_{i.xS}) \tag{28}$$

Here p_S is the vapor pressure of the solvent and $p_{i.xS}$ is the vapor pressure of the system

$$i(\text{solid}) + xS(g) = i\cdot xS(\text{solid}) \tag{29}$$

often referred to as simply the "vapor pressure of the solvate." When this is done, equation (21) will take the form

$$\frac{{}_sG_i^\circ - {}_wG_i^\circ}{RT} = \ln \frac{(a_i)_{Sat}}{(a_i^*)_{Sat}} + \frac{y}{x}\,\ln \frac{p_{H_2O}\;p_{i\cdot xS}}{p_S\;p_{i\cdot yH_2O}} \tag{30}$$

Medium effects for electrolytes can also be determined from the standard potentials of galvanic cells composed of electrodes which respond reversibly to the ions of the electrolyte. Let us consider the determination of the medium effect for HCl. For this we need a cell composed of one electrode reversible to hydrogen ions and one reversible to chloride ions. The familiar cell,

$$\text{Pt(s); } H_2(g)/\ H^+\ Cl^-/\text{AgCl(s); Ag(s)} \tag{I}$$

is suitable for this determination. The potential of this cell measured in the nonaqueous solvent and expressed on the nonaqueous scale is given by

$$E_{cell} = {}_sE^\circ_{H,AgCl} - \frac{RT}{nF}\,\ln\,a_H^* a_{Cl}^* \tag{31}$$

while for the same cell in aqueous solution:

$$E_{cell} = {}_{w}E^{\circ}_{H,AgCl} - \frac{RT}{nF} \ln a_{H}a_{Cl} \qquad (32)$$

At unit activities of HCl in both media, $E_{cell} = E^{\circ}_{cell}$ and we can combine equations (31) and (32) to get:

$$\ln \frac{a_{H}a_{Cl}}{a^{*}_{H}a^{*}_{Cl}} = \frac{nF({}_{w}E^{\circ}_{H,AgCl} - {}_{s}E^{\circ}_{H,AgCl})}{RT} \qquad (33)$$

By definition the left side of equation (33) is the logarithm of the medium effect for HCl.

$$\ln {}_{m}\gamma_{H}\,{}_{m}\gamma_{Cl} = \ln {}_{m}\gamma_{HCl} = \frac{nF({}_{w}E^{\circ}_{H,\,AgCl} - {}_{s}E^{\circ}_{H,AgCl})}{RT} \qquad (34)$$

As equation (34) indicates, the logarithm of the medium effect for HCl is in reality the sum of the logarithms of the medium effects for the hydrogen ion and for the chloride ion

$$\log {}_{m}\gamma_{HCl} = \log {}_{m}\gamma_{H} + \log {}_{m}\gamma_{Cl} \qquad (35)$$

It should be pointed out that the logarithm of the medium effect for any uni-univalent electrolyte is the sum of the logarithms of the medium effects of its constituent ions.
For the general case of an electrolyte A_xB_y

$$\log {}_{m}\gamma_{A_xB_y} = x \log {}_{m}\gamma_{A} + y \log {}_{m}\gamma_{B} \qquad (36)$$

Thus, from the standard potentials of galvanic cells without liquid junctions, the medium effects of complete electrolytes, or the products of ionic medium effects, can be determined by rigorous thermodynamic methods.

Unfortunately, when we consider the determination of medium effects for single ions we find that this cannot be done by exact thermodynamic methods. The combination of medium effects for complete electrolytes is thermodynamically rigorous, but this leaves us with only products of medium effects for ions of opposite charge or ratios of medium effects for ions of like charge.

When we consider the determination of single-ion medium effects directly from standard potentials by rearranging equations (14a) and (14b) corresponding to

$$ {}_wE^\circ_{i,SH} - {}_wE^\circ_{i,H_2O} = \pm \frac{RT}{nF} \ln {}_m\gamma_i \qquad (37)$$

we find that we need the standard potentials of the element both in water and in the nonaqueous solvent expressed on a single scale. Because there are as yet no reliable methods of determining experimentally of of calculating the absolute (single) electrode potentials (69), the aqueous e.m.f. series (${}_wE^\circ_H = 0$) is invariably chosen as the single scale for comparison. However, to know the standard potential of an element in a nonaqueous solution on the aqueous e.m.f. scale in turn requires knowledge of the corresponding medium effect for that element. The determination of single ion medium effects from solubilities is out of the question since obviously it is impossible to distribute a single ion between two phases. A counter-ion is always involved, resulting in the combined medium effect for both ions.

Since the medium effects for single ions are not accessible by rigorous thermodynamics, we must resort to extrathermodynamic methods to provide us with estimates, if not exact values, for the medium effects for single ions. It should be pointed out that once the medium effect for any one single ion is obtained, the medium effect for all other single ions will follow from the medium effect for complete electrolytes according to equation (36). The next section will describe the attempts that have been made to date at the estimation of medium effects for single ions.

Previous Approaches to the Problem

Introduction

Several attempts have been made at establishing single activity and standard potential scales in different solvents. Perhaps the first attempt in this direction was that of Bjerrum and Larsson (12), who utilized concentrated salt bridges in an effort to eliminate the liquid-junction potentials arising at aqueous-nonaqueous interphases. The more recent attempts of Pleskov (69) and Strehlow (55) were based on the use of redox couples comprising large ions which were assumed to have approximately constant solvation energies, which also meant constant standard potentials of electrodes reversible to these ions in different solvents. Grunwald (33) attacked the problem by evaluating medium effects from an empirical analysis of the effects of solvents on the dissociation constants of acids. Izmaylov (43), after several initial approaches, used an extrapolation procedure to obtain the solvation energy of the hydrogen ion and other single ions. Each of the above approaches will be analyzed in detail subsequently.

The Method of Bjerrum and Larsson

Niels Bjerrum and Erik Larsson (12) determined medium effects for single ions in ethyl alcohol and ethyl alcohol-water mixtures from e.m.f. measurements on galvanic cells with liquid junctions. By utilizing concentrated salt bridges, these authors assumed the liquid-junction potentials to be very small and, in fact, zero. For example, the medium effect for the hydrogen ion was determined from measurements on the cell

$$\mathrm{Pt(s);\ H_2(g)/H^+,Cl^-//\ 3.5N\ KCl(aq)/\ HgCl(s);Hg(s)} \qquad \mathrm{(III)}$$

The 3.5 normal KCl aqueous calomel electrode was used as a reference electrode and the hydrogen electrode was used in both the aqueous and the nonaqueous solvents. The medium effect of the hydrogen ion was then calculated from the difference in the standard potentials of cell (III) in the two solvents analogously to equation (34).

$$P(H) = \frac{nF(E^\circ_{III,H_2O} - E^\circ_{III,alcohol})}{RT} \qquad (38)$$

Here P(H) is Bjerrum and Larsson's notation for the logarithm of the medium effect. E°_{III,H_2O}, the standard potential of cell (III) using the aqueous hydrogen electrode is given by $E^\circ_{III,H_2O} = E^\circ_{H,H_2O} - E^\circ_{calomel}$, while $E^\circ_{III,alcohol}$, the standard potential of the same cell using the alcoholic hydrogen electrode is given by $E^\circ_{III,alcohol} = E^\circ_{H,alcohol} - E^\circ_{calomel}$. Since $E^\circ_{calomel}$ is the same for both measurements, the difference in the standard potentials of the cell yields the difference in the standard potential of the hydrogen electrode referred to the aqueous standard state through the aqueous calomel electrode.

In a similar manner, using a silver electrode in silver nitrate solutions and a silver benzoate electrode in solutions of sodium and guanidinium benzoate, the medium effects of silver and benzoate ions were determined.

Aside from the basic assumption that the liquid-junction potential is zero, this treatment is open to additional criticism. The standard potentials were calculated from the measured potentials using the Nernst equation in which the activity coefficients were estimated from the cube root formula of Bjerrum

$$\log f = -k\sqrt[3]{C} \qquad (39)$$

where k was given the value 2.0 in alcohol and 0.2 in water. Equation (39) is no longer accepted as a means of estimating activity coefficients. It is also well known that the electrolytes they used are not completely dissociated in ethyl alcohol and in ethyl alcohol-water mixtures. Bjerrum and Larsson apparently do not take incomplete dissociation into account, for no mention is made of electrolytic conductance measurements, which are necessary to determine degree of dissociation.

If the liquid-junction potentials at the alcohol-saturated aqueous potassium chloride and water-saturated aqueous potassium chloride interphases were truly equal to zero, P(H) calculated via equation (38) would be precisely the medium effect for the hydrogen ion. Since the liquid-junction potential is neither zero, nor is it equal for both measurements so as to cancel out, Bjerrum and Larsson actually calculated the sum of the liquid-junction potential and the logarithm of the medium effect. The E°_{III,H_2O} and $E^{\circ}_{III,alcohol}$ calculated by them each include a liquid-junction potential, so that the difference between the E°'s in equation (38) includes a residual liquid-junction potential in exactly the same manner as does a pH measurement using a glass-saturated calomel electrode pair. In this way

$$P(H) = \log {}_m\gamma_H + E_j \qquad (40)$$

where E_j is the difference between the liquid-junction potential for the dilute aqueous solution and the dilute alcoholic solution against the saturated aqueous potassium chloride solution.

The P(X) values reported by Bjerrum and Larsson are given in Table I. As one can see from the Table, the values of P(X) are reported to only one significant figure. This is indicative of the uncertainty involved in the assumption that the liquid-junction potential is zero.

An important point brought up by Bjerrum and Larsson which is receiving considerable attention at the present time (20,21), is that the over-all medium effect may be considered to be made up of several parts: an electrostatic part, P_e, a neutral part, P_u (the subscript u stands for "unelectrisch"), and a part due to solvation, P_s. The total medium effect, P, was given by

Table I. Single-Ion Medium Effects in Absolute Ethanol at 25°C, According to Bjerrum and Larsson (<u>12</u>).

Ion	$P(X) = \log {}_m\gamma_{ion}$	Ion	$P(X) = \log {}_m\gamma_{ion}$
H^+	2.5	Cl^-	2.5
Li^+	2.8	Br^-	1.8
Na^+	3.5	I^-	1.4
K^+	4.1	ClO_4^-	0.7
Rb^+	3.9	Benzoate	1.3
Cs^+	4.0	<u>o</u>-Nitrobenzoate	1.7
Ag^+	2.1	<u>m</u>-Nitrobenzoate	0.7
NH_4^+	2.7	<u>p</u>-Nitrobenzoate	0.8
$N(CH_3)_4^+$	3.0	Salicylate	1.2
$N(C_2H_5)_4^+$	2.7	Laurate	-2.4
		Myristate	-3.5
		Palmitate	-3.7
		Stearate	-4.0

$$P = P_e + P_u + P_s \tag{41}$$

The electrostatic part was considered to be represented by the Born (13) equation

$$P_e = \frac{e^2}{2rkT \ln 10}\left(\frac{1}{D_2} - \frac{1}{D_1}\right) \tag{42}$$

where k is the Boltzman constant, T is the absolute temperature, D is the dielectric constant of solvents 1 and 2, e is the electron charge and r, the radius of the ion. The neutral part is given by

$$P_u = \frac{A_1 - A_2}{kT} \tag{43}$$

where the term $A_1 - A_2$ is the difference in the free energy of solvation of a neutral molecule of similar structure to the ion. For calculating the neutral term for potassium and chloride ions these authors suggested the solvation-energy difference for argon, since this element has the same electronic structure as potassium and chloride ions. To calculate the neutral part of the medium effect for the benzoate ion, benzoic acid was chosen for the same purpose. The solvation part of the total medium effect, P_s, was determined from the equilibrium constant for the exchange of solvent in the solvation sphere of the ion. In the cases of potassium and chloride ions this term was considered to be small and was neglected.

Once the medium effect for single ions were obtained, the e.m.f. series referred to $E^\circ_H = 0$ in ethyl alcohol could be related to the series referred to $E^\circ_H = 0$ in water and both series expressed on this common aqueous scale. Although Bjerrum and Larsson were not interested in relating standard potentials per se, rather, they wanted to study the nature of the medium effect, their work is important because it represents the first major step forward in the correlation of physical-chemical data obtained in different solvents.

Pleskov's Normal Element Method

Later it was V. A. Pleskov (69) who became interested in correlating standard potential series in different solvents. From Pleskov's point of view, the choice of $E^\circ_H = 0$ in each solvent as a basis for the establishment of standard potential series seemed very unreasonable, for this resulted in a set of totally independent e.m.f. series in each solvent.

Since the standard electrode potential is determined by the magnitude of the change in the free energy associated with the transfer of the ion from the electrode into the solution, this potential jump should depend on the interaction between the ion and the solvent, in other words on the energy of solvation of the ion. Because the hydrogen ion, as Pleskov shows, undergoes the greatest change in solvation energy and, consequently, the greatest change in standard potential upon transfer from one solvent to another, the choice of hydrogen as a reference element for all standard potentials was a very poor one, based only on historical tradition. A much better choice, according to Pleskov, would be to refer all potentials to the potential of such an element the chemical solvation energy of whose ions would be equal in all solvents or would at least undergo only slight change. Such an element Pleskov called the "normal element". The first requirement to be fulfilled by the "normal element" is that the energy of solvation of its ions be small in all solvents, so that differences in the energy of solvation in different solvents would be negligible.

The magnitude of the solvation energy, Pleskov states, is determined essentially by the radius and charge of the ion, its polarizability and tendency toward specific interaction with solvent. Therefore, the ions of the element to be chosen as the "normal element" should meet the following requirements. They should have: (1) large radius; (2) low charge and polarizability; (3) minimal tendency toward specific interaction with solvent as expressed,for example, by the formation of complex ions and complex solvates.

Of the materials at his disposal, Pleskov concluded that the above conditions were best met by the alkali-metal ions of high atomic weight, namely the ions of rubidium and cesium. Both of these elements form univalent cations of large radius (1.49Å for Rb^+ and 1.65Å for Cs^+). Their solvation energy, according to all estimates, is considerably lower than that of any other metal ion. Neither rubidium, nor cesium form any complex ions and their salts, as a rule, do not form crystal solvates.

On this basis, Pleskov assumed that the standard potentials of rubidium and cesium should not change significantly with solvent and chose rubidium as the "normal element" for purposes of comparing electrode potentials in different solvents. Logically, the choice of cesium would have been better founded, but the standard potential of cesium, even in water, was not reliably known at the time. However, it should be pointed out that the potentials of rubidium and cesium practically coincide in all solvents, which makes the choice of one or the other of these metals equally good.

Table II shows the e.m.f. series in several solvents as obtained by Pleskov. Note that the standard potential of rubidium rather than hydrogen is set equal to zero in all of the solvents. The results in Table II are in qualitative agreement with what one would expect from purely chemical considerations. In ammonia and hydrazine, the potential of hydrogen is found to be shifted in the more negative, or less noble,direction from water. This is in agreement with the formation of the stable ions NH_4^+ and $N_2H_5^+$ indicating a decrease in the solvation energy of the proton in these solvents. Also well known is the ability of ammonia and hydrazine to form complex ions and crystal solvates with the heavy metals, such as copper, silver and mercury. The potentials of each of these elements are also found to be shifted in the less noble direction, as expected. In the acidic solvent formic acid, the potential of hydrogen

Table II. Standard Potential Series Obtained by Pleskov (<u>69</u>).

Element	H_2O	CH_3CN	HCOOH	N_2H_4	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^{++}	3.28	2.89	3.31	----	2.36
Hg/Hg^+	3.73	----	3.63	----	----
Hg/Hg^{++}	3.79	3.42	----	----	2.68
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

indicates an increase in the solvation energy of the proton, as compared to water. According to Naumann (62), acetonitrile, the simplest organic derivative of hydrogen cyanide, possesses, as does hydrogen cyanide, a pronounced tendency to form complexes with the heavy metals, such as silver and copper. In agreement with this, the potentials of silver and copper are shifted in the less noble direction.

Pleskov concludes that the strict comparison of electrode potentials in different solvents is impossible until such a time when the development of our concepts of the structure of matter will enable us to carry out a theoretical calculation of the potential difference at the interphases of different solvents. The feasibility of this calculation, he points out, is in principle beyond any doubt. However, until that time the method of the "normal element" enables us to carry out approximate comparisons, the results of which are in good agreement with our knowledge of the solvation of ions.

The Method of Strehlow

Although the results of Pleskov's method are in qualitative agreement with our knowledge of solvation, the assumption that the standard potential of rubidium is the same in all solvents is only approximately correct. According to H. Strehlow (78), to obtain a better approximation it is necessary toestimate as well as possible the small differences between the free energy of solvation of the rubidium ion in water and in the various solvents.

In order to estimate the free energy of solvation of the rubidium ion Strehlow used a modification of the Born equation, proposed by Latimer (59)

$$G = -\frac{Ne^2}{2}\left(1 - \frac{1}{D}\right)\left(\frac{1}{r_+} + \frac{1}{r_-}\right) \tag{44}$$

where r_+ and r_-, the effective radii of cation and anion, are given by

$$r_+ = r_{cryst} + R_+ \tag{45a}$$

$$r_- = r_{cryst} + R_- \tag{45b}$$

The increments R_+ and R_- added to the crystallographic radii account for an effective increase in size due to solvation. The standard potential of rubidium obtained by Strehlow in various solvents is given in Table III, referred to $E^\circ_H = 0$ in water. Strehlow was of the opinion that the traditional reference point, $E^\circ_H = 0$ in water, should be maintained and therefore used this potential, rather than $E^\circ_{Rb} = 0$ in water, as the reference point for the establishment of standard potential series in all solvents. The results in Table III show that the standard potential of rubidium is not constant in all solvents.

Strehlow felt that still another method for estimating free energies of transfer for single ions would support those already proposed. Following the reasoning of Pleskov, Strehlow (55) proposed the use of the ferrocene-ferricinium ion and cobaltocene-cobaltocinium ion redox couples whose

Table III. Standard Potentials of Rubidium in Various Solvents Referred to $E^{\circ}_{H} = 0$ in Water.

	H_2O	CH_3OH	CH_3CN	HCOOH
$E_{Pleskov}$ (<u>69</u>)	-2.92	-2.92	-2.92	-2.92
$E_{Pleskov}$ (Corrected by Strehlow) (<u>55</u>)	-2.92	-2.97	-3.03	-2.98

standard electrode potentials he felt should be independent of solvent. Since the ions involved here are much larger (average radius of about 2.3Å) than rubidium or cesium, these couples would appear to offer an improvement over the couples used by Pleskov.

Table IV shows the standard potential of hydrogen obtained by this method in comparison with Pleskov's method and with Pleskov's method corrected by Strehlow. The Table shows excellent agreement between the ferrocene and cobaltocene methods and fair agreement with the other methods. In spite of this agreement the methods involving ferrocene and cobaltocene suffer two distinct drawbacks. The first drawback is that the standard potentials are determined from polarographic half-wave potentials, severely limiting their accuracy. The second drawback arises from the presence of an uncharged species in the redox couple

$$\mathrm{Ox}^{+} + e^{-} = \mathrm{Red}$$

The assumption is made that the difference in solvation energy for the neutral species in the two solvents is the same as that for the charged species. Since the charged species has a small "Born" solvation energy in each solvent, the differences in solvation energies in different solvents can be assumed to be negligible. However, the assumption that the same is true of the neutral species is open to criticism. The inverse relation between solvation energy and radius of an ion given by the Born equation and its modifi-

Table IV. Standard Potential of Hydrogen Electrode at 25°C Obtained by Various Methods.

	H_2O	CH_3OH	CH_3CN	$HCONH_2$
$E_{Pleskov}$ (69)	0	+0.02	+0.25	---
$E_{Pleskov}$ (Corrected by Strehlow) (55)	0	-0.03	+0.14	---
$E_{Ferrocene}$ (78)	0	-0.01	+0.15	-0.15
$E_{Cobaltocene}$ (78)	0	-0.01	+0.16	-0.14

cations applies only to charged species. There is no theoretical justification in the assumption that the neutral species undergoes little or no change in solvation energy upon transfer from water to a nonaqueous solvent.

Grunwald's Empirical Method

E. Grunwald's approach to the evaluation of medium effects for single ions in ethanol-water mixtures is unique in that it is the only recent method that does not focus on the inverse relation between solvation energy and radius of the ion. The method depends on the effect of solvents on the pK's of acids.

The solvent dependence of the acid dissociation constant is given by Grunwald and Berkowitz (32) as

$$\Delta pK = pK_{HA} - pK^{*}_{HA} = \log \frac{{}_{m}f_{H}\,{}_{m}f_{A}}{{}_{m}f_{HA}} \qquad (46)$$

where pK and pK^{*} are the acid dissociation constants measured in the aqueous and nonaqueous solvent, respectively, and expressed on the corresponding activity scales. The terms ${}_{m}f_{H}$, ${}_{m}f_{A}$ and ${}_{m}f_{HA}$ are the medium effects on the molar activity scale. From plots of ΔpK vs. solvent composition these authors found that for various acids ΔpK increased with increasing ethanol content of the solvent. Since $\log {}_{m}f_{H}$ is a function of solvent only it follows from these observations that $\log {}_{m}f_{A}/{}_{m}f_{HA}$ must be a function of acid structure and possibly of solvent. On the basis of these observations Grunwald and Berkowitz proposed the activity postulate

$$\log \frac{{}_m f_A}{{}_m f_{HA}} = \underline{m}_A Y \tag{47}$$

where $\underline{m}_A$ is a parameter which is characteristic of the acid only while $\underline{Y}$ is a parameter of solvent only and is called the activity function. For uncharged acids, such as carboxylic acids, the notation Y_- was used for the activity function in conformity with the Hammett function H_-, while the notation Y_o was used for positively charged acids such as the ammonium hydrochlorides. From equation (46) and (47) it follows that

$$\Delta pK = \log {}_m f_H + \log \frac{{}_m f_A}{{}_m f_{HA}} = \log {}_m f_H + \underline{m}_A Y \tag{48}$$

Then, from an empirical analysis of ΔpK's, the activity function $\underline{Y}$ and the solvent-independent parameter, $\underline{m}_A$, are determined for acids of two different charge types. We then have values for $\underline{m}_o Y_o$ and $\underline{m}_- Y_-$ from which

$$\log f_o = \Delta pK_o - \underline{m}_o Y_o \tag{49a}$$

and

$$\log f_- = \Delta pK_- - \underline{m}_- Y_- \tag{49b}$$

can be calculated.

Having demonstrated that $\log f_o$ and $\log f_-$ were equal and well approximated by $\log {}_m f_H$ these authors arrived at the medium effect for the proton in several ethanol-water mixtures. Their results are given in Table V.

Table V. Medium Effects for Hydrogen Ion Obtained by Grunwald in Ethanol-Water Mixtures at 25° C (<u>33</u>).

Weight-Percent Ethanol	log $_m f_H$	log $_m \gamma_H$
0	0	0
20	0.008	-0.006
35	0.042	0.017
50	0.251	0.211
65	0.524	0.485
80	1.152	1.077
100	4.707	4.603

Izmaylov's Three Approaches

The largest body of information about medium effects and related single-ion properties associated with the name of one author is undoubtedly that contributed by N. A. Izmaylov and co-workers (3,40-52). In the course of their work, these investigators proposed several approaches to obtain medium effects for single ions by employing extra-thermodynamic assumptions.

Their first approach (41,42) was to divide the medium effect for strong acids equally between the hydrogen ion and the anion

$$\log {}_{m}\gamma_{H} = \log {}_{m}\gamma_{A} = \tfrac{1}{2} \log {}_{m}\gamma_{HA} \qquad (50)$$

This approach was based on the observation that the medium effects for all of the monobasic strong acids studied were approximately the same in a given solvent. The criticism of this approach is that it not only assumes that the solvation energies of the hydrogen ion and the anion are the same in all solvents, but it also assumes that strong-acid anions have the same solvation energies in a given solvent. These assumptions can only be approximately correct at best. If we accept the results of Bjerrum and Larsson in Table I as a qualitative guide for purposes of discussion, we can see that the medium effects and the corresponding solvation energies are not equal for the anions of the strong acids HCl, HBr, HI and $HClO_4$ in ethanol. For HCl, however, Izmaylov's first approach appears to be successful, $\log {}_{m}\gamma_{H}$

is equal to log ${}_m\gamma_{Cl}$ in ethanol, according to Bjerrum and Larsson.

Izmaylov then set out to improve on this approach by taking into account the relative basicities of water and the nonaqueous solvent (43). He considered the medium effect of an acid, HA, to be composed of two terms, a basicity term, ${}_m\gamma_{basic}$, and an electrostatic term, ${}_m\gamma_{el}$, as given in equation (51).

$$\log {}_m\gamma_{HA} = 2 \log {}_m\gamma_{basic} + 2\log {}_m\gamma_{el} \qquad (51)$$

By assuming that the basicity term was due solely to the proton and that the electrostatic term was equally divisible between the proton and the anion, Izmaylov concluded that the medium effect of the proton was given by

$$\log {}_m\gamma_H = 2 \log {}_m\gamma_{basic} + \log {}_m\gamma_{el}. \qquad (52)$$

The basicity term was evaluated from the expression

$$\log {}_m\gamma_{basic} = \tfrac{1}{2} \log K_r + \log \frac{a^*_{H_2O}}{a^*_{SH}} \qquad (53)$$

where K_r, the equilibrium constant for the proton exchange between aqueous and nonaqueous solvents, was obtained from indicator measurements. The activities $a^*_{H_2O}$ and a^*_{SH} are referred to the infinitely dilute solution of water in the solvent SH and to the pure solvent SH, respectively (51).

Having evaluated the basicity term, Izmaylov then obtained the electrostatic term via the equation

$$\log {}_m\gamma_{el} = \tfrac{1}{2} \log {}_m\gamma_{HA} - \log {}_m\gamma_{basic} \tag{54}$$

It is difficult to evaluate the validity of Izmaylov's second approach in the light of our present inadequate knowledge of the intricate structure and solvation properties of alcohol-water mixtures. Criticism has been voiced (23) that the type of indicator and electrometric measurements which lead to the exchange constant, K_r, do not really reflect the differences in basicity of water and alcohol molecules. Moreover, this approach essentially assumes the validity of the electrostatic model of ion solvation, as given by equation (56), modified by the relative basicity term.

A basicity term has also been introduced by Bates and co-workers (66,81) in an attempt to explain differences between experimentally observed solvation energy changes, ΔG, for the transfer of tris(hydroxymethyl)aminomethane from water to 50 wt.-% methanol, and those calculated on the basis of an electrostatic model, ΔG_{el}. The calculation of ΔG_{el} was essentially a modified Born calculation due to Hepler (35). The difference between the observed and calculated ΔG's was given by

$$\Delta G^{\circ} - \Delta G_{el} = \Delta G_b \tag{55}$$

where ΔG_b is the "basicity effect."

Izmaylov's final approach (43,46,47,49,50) was based on the inverse relation between solvation energy and radius of an ion. He considered the equation,

$$G_i = \frac{-Ne^2z^2}{2r_i}\left(1 - \frac{1}{D}\right) - \frac{N\,ze\,\mu\,n}{r_i^2} \tag{56}$$

where n is the solvation number, μ the dipole moment of the solvent, and the other symbols have their usual meaning, an accurate expression of the solvation energy of an ion. This approach involved plotting sums and differences of solvation energies for ions, keeping one ion constant and varying the other, as a function of reciprocal radius of the varying ion. An extrapolation to infinite radius was assumed to yield the value for the solvation energy of the constant ion. This method is described in more detail below.

Sums of solvation energies of single ions are rigorous thermodynamic quantities, they are the solvation energies of complete electrolytes. For a uni-univalent electrolyte:

$$G_{\text{cation}} + G_{\text{anion}} = G_{\text{electrolyte}} \tag{57}$$

Differences of solvation energies of cations or anions can also be obtained by rigorous thermodynamics from the solvation energies of complete electrolytes. For example, the difference in solvation energies of hydrogen and potassium ions can be obtained by

$$G_H - G_K = G_{HCl} - G_{KCl}. \tag{58}$$

From the solvation energies of the halogen acid series HF, HCl, HBr and HI the sums, $G_H + G_X$, where X refers to halogen, were obtained. In a similar manner differences in solvation energies of hydrogen and alkali metal cations, $G_H - G_M$, were obtained for Li^+, Na^+, K^+, Rb^+ and Cs^+ as shown by equation (58). A plot was then made of the sums $G_H + G_X$ as a function of the reciprocal crystallographic radius of the corresponding halide ion. A similar plot of $G_H - G_M$ as a function of reciprocal crystallographic radius of the alkali metal ion was also made. Since the solvation energy of X and M decreases as the radius increases, G_X and G_M become zero at $1/r = 0$. Therefore, by extrapolating the graphs to $1/r = 0$ the solvation energy of the hydrogen ion is obtained. Figure 1 shows the extrapolation used by Izmaylov to obtain the hydration energy of the hydrogen ion. From the hydration energy and the solvation energy in a given solvent, the medium effect for the proton in that solvent can be obtained via equation (11). Table VI shows the medium effects for several ions obtained by Izmaylov.

In principle, Izmaylov's extrapolation procedure may well be the best method to evaluate single-ion properties. However, its application has led to highly uncertain results. This incertainty is demonstrated by lack of internal consistencies in the single-ion medium effects obtained. Since the medium effect for a uni-univalent electrolyte is exactly the sum of the medium effects for its constituent ions, the single-ion medium effects in Table VI should add up to the

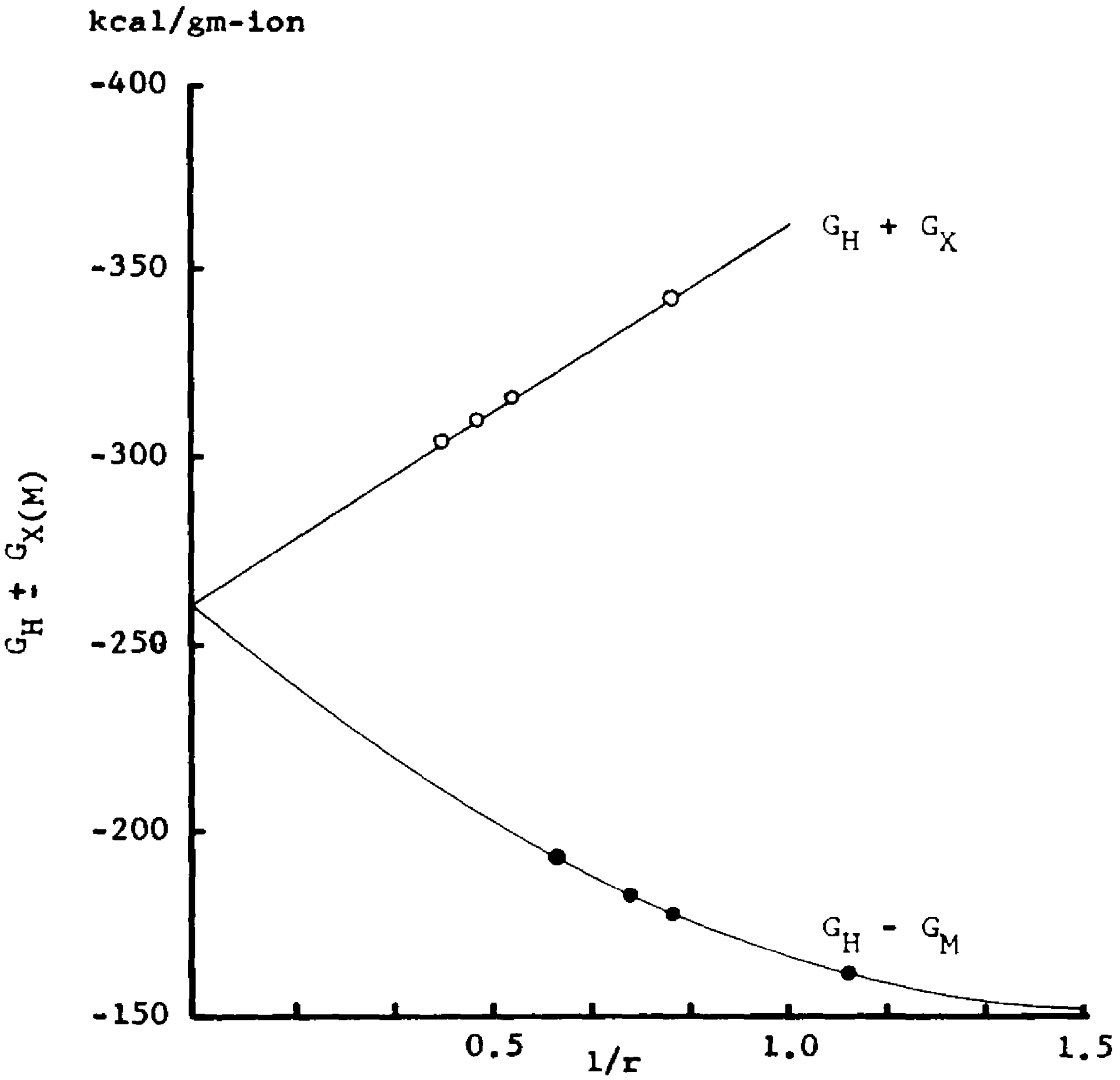

Figure 1. Determination of hydration energy of hydrogen ion according to Izmaylov (48).

Table VI. Selected Single-Ion Medium Effects Obtained by Izmaylov (50).

Ion	$\log {}_m\gamma_i$	
	Methanol	Ethanol
H^+	3.1	3.9
Cl^-	1.0	1.2
K^+	2.0	4.0
Ag^+	3.5	3.7
Rb^+	2.8	4.6

observed medium effects for the complete electrolyte. As Table VII shows the single-ion medium effects obtained are too often inconsistent with the experimentally determined and thermodynamically rigorous values for complete electrolytes.

These internal inconsistencies probably arise as a result of the type of data used to calculate the solvation energies. The calculations combine a large body of thermochemical and spectral data, such as heats of reaction, ionization energies, sublimation energies and dissociation energies, with e.m.f. and solubility values. From them the solvation energies are obtained by means of the Born-Haber cycle. As a result, small errors at the various steps in the cycle could be compounded, with a large error resulting in the solvation energy. In addition, the extrapolations are long, adding to the uncertainty of the results. Izmaylov estimates the accuracy of the extrapolated solvation energies to be ±0.5 kcal/g-ion (<u>50</u>), corresponding to log $_m\gamma$'s accurate to ±0.5 log units.

Medium effects, as opposed to solvation energies, have an additional source of error because they are quite often obtained from small differences between solvation energies. Of course, one can raise objections to Izmaylov's model on which the extrapolation procedure is based (equation 56). The underlying assumption in the extrapolation method is that all components of the solvation energy of ions vary as $1/r^n$. Should there be other components of solvation energy which

Table VII. Comparison of Sums of Izmaylov's Single-Ion Medium Effects With Experimentally Observed Values for Electrolytes in Methanol.

Electrolyte	$\log {}_{m}\gamma_{\text{electrolyte}}$	
	Observed (<u>70</u>)	Calculated (<u>50</u>)
HCl	3.93	4.1
KCl	3.84	3.0
AgCl	2.86	4.5

vary as $\underline{r}^n$ (and such have been mentioned in the literature (<u>50</u>,<u>20</u>)), the energy of the infinitely large ion would approach infinity, and not zero.

<u>Other More Recent Approaches</u>

Aside from the present approach which will be taken up in the next section, there have been no totally new ideas for the estimation of medium effects or the establishment of single e.m.f. series in different solvents. However, the work of Feakins and Watson (<u>21</u>) and of de Ligny and Alfenaar (<u>20</u>) deserve mention.

Feakins and Watson, following the reasoning of Izmaylov, plotted changes in free energy of solvation, ΔG_t, on transfer from one solvent to another against $1/r_x$ for the hydrogen halide series. ΔG_t was the energy of transfer from water to 10 wt.-% or 43.12 wt.-% methanol in water. Assuming that the resulting functions should be linear, these authors proposed the equation

$$\Delta G_t = \Delta G_t^\circ(H^+) + \underline{a}r_a^{-1} \qquad (59a)$$

to describe the plots. Here $\underline{a}$ is a constant given by $Ne^2/2$ from the Born equation and r_a, the radius of the anion. The intercept $\Delta G_t^\circ(H^+)$ gave the free energy of transfer of the proton. The free energies of transfer of the chloride ion were then calculated by difference. A "cation" extrapolation which involved plots of ΔG_t vs. $1/r_x$ for the alkali chlorides was also used to obtain the free energy of transfer of the chloride ion according to the equation

$$\Delta G_t = \Delta G_t^\circ(\mathrm{Cl}^-) - \underline{b}r_c^{-1} \qquad (59b)$$

where r_c is the radius of the cation and the slope $\underline{b}$ is opposite in sign to the slope $\underline{a}$. The average value of $\Delta G_t^\circ(\mathrm{Cl}^-)$ from both extrapolations was then used as a basis for separating ΔG_t's into single-ion values. Although the extrapolations involved here offer no new contribution to the estimation of single-ion medium effects, the work is important because it focuses attention on the Born equation, which they consider to be "useless" as an expression of solvation energy.

Following up the work of Feakins and Watson, de Ligny and Alfenaar express the opinion that the free energy of solvation of an electrolyte is composed of a neutral and an electrical part. This composite nature of the total solvation energy has already been proposed by Bjerrum and Larsson (12) and its significance was discussed in an earlier section of this thesis.

According to de Ligny and Alfenaar,

$$\Delta G = \Delta G_{el} + \Delta G_{neutral}. \qquad (60)$$

In exactly the same manner as proposed by Bjerrum and Larsson, these authors maintain that the electrical part is given by the Born equation

$$\Delta G_{el} = \frac{Ne^2z^2}{2r}\left(\frac{1}{D_2} - \frac{1}{D_1}\right). \qquad (61)$$

They further state that as 1/r approaches zero it is only the ΔG_{el} which approaches zero as well. $\Delta G_{neutral}$ is proportional to surface area (r^2) and, therefore, as 1/r approaches zero, $\Delta G_{neutral}$ approaches infinity. De ligny and Alfenaar conclude that extrapolation of ΔG to $1/r = 0$ is possible only after subtracting $\Delta G_{neutral}$ from the total ΔG of solvation.

As estimates of the $\Delta G_{neutral}$ for ions in a given solvent these authors use the corresponding ΔG values for isoelectronic noble gases. Bjerrum and Larsson (12) also suggested the use of argon to evaluate the neutral part of the solvation-energy changes for potassium and chloride ions. To evaluate the neutral part for the benzoate ion, they chose benzoic acid. In view of the practically identical structures involved, this last example seems very reasonable. However, the use of noble gases for evaluating $\Delta G_{neutral}$ of ions is open to criticism on several grounds. For one thing, the polarizability of the noble gases is much greater than that of an ion. Secondly, as pointed out by Izmaylov (48), the van-der-Waals component of solvation energy, which increases with the surface area, would comprise no more than 1 - 2% of the total solvation energy for small ions. Only when the radius of the ion is greater than 10.0Å, will the "neutral part" play a significant role. A very plausible approach to the subtraction of the "neutral part" from the total solvation energy of an ion was utilized by Grunwald, Baughman and Kohnstam (31), towards the interpretation of solvation-energy changes in the 50% dioxane-water mixtures. They employed tetraphenylmethane as the neutral equivalent of both the tetraphenylphosphonium and the tetraphenylbotare ions.

The Present Approach

The extrathermodynamic method used in this research to evaluate medium effects for single ions is based on the assumption that for a "reference electrolyte" composed of large ions of equal size and solvation, the free energy of transfer from its aqueous to nonaqueous standard state and the corresponding medium effect can be apportioned equally between the anion and the cation:

$$\log {}_m\gamma_{cation} = \log {}_m\gamma_{anion} = \tfrac{1}{2} \log {}_m\gamma_{reference} \qquad (61)$$

Equal apportioning of the total medium effect between anion and cation requires that both of these ions undergo equal changes in solvation energy upon transfer from water to the nonaqueous solvent. In order to fulfill this condition, the ions of the reference electrolyte should be as identical as possible in the properties which determine solvation energy. These properties have been reviewed in the discussion of Pleskov's "normal element" method. To recapitulate, the energy of solvation is determined by the radius and charge of the ion, its polarizability and its tendency toward specific interaction with solvent.

The reference electrolyte must therefore consist of large symmetrical counterions, as identical as possible in size, surface charge density and solvation properties. In contrast to methods based on large-ion redox couples, the present approach does not require that the reference ions experience a negligible change in solvation energy upon transfer from one solvent to another; the requirement is that the energy changes due to solvent be equal for the two ions. The assumption that two very similar ions experience equal energy changes when transferred at infinite dilution from one solvent to another seems more plausible than the assumption that they experience no energy change.

The reference electrolyte chosen for this work is triisoamyl-n-butylammonium tetraphenylborate[1] (TAB(BPh_4)). The same electrolyte was employed earlier for the estimation of medium effects for single ions in methanol and in an isopropanol-toluene mixture (70). This salt has been used by Coplan and Fuoss (18) for the determination of single-ion limiting equivalent conductances in nonaqueous solvents by apportioning the limiting equivalent conductance equally between its ions

$$\lambda_{\circ TAB} = \lambda_{\circ BPh_4} = \tfrac{1}{2}\Lambda_{\circ TAB(BPh_4)} \qquad (62)$$

This assumption was corroborated with transference data in methanol (18) and in water (76) which showed that the ionic limiting equivalent conductances agree to 1%. Later, Cotzee and Cunningham (19) suggested a better electrolyte for

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[1] The name "tetraphenylborate" has been recommended by the I.U.P.A.C. (39). In the past the name"tetraphenylboride" was frequently used.

apportioning limiting equivalent conductances. This electrolyte, tetraisoamylammonium tetraphenylborate, gave single-ion conductances in acetonitrile which agreed to better than 0.1%. However, preliminary work in this laboratory has shown that it would be difficult, if not impossible, to use tetraisoamylammonium tetraisoamylborate as the reference electrolyte for the estimation of medium effects for single ions, as the tetraalkylborate ions decompose in hydroxylic solvents.

Having obtained the medium effects of TAB and BPh_4 ions via equation (61), we can calculate the medium effects for all other single ions from those of complete electrolytes. In this research we are particularly interested in the evaluation of the medium effect for the proton so as to be able to interpret pH data obtained in ethanol and ethanol-water mixtures on a single scale, the aqueous pa_H scale.

The medium effect for the proton could most readily be arrived at by combination of the medium effect for hydrogen tetraphenylborate ($H(BPh_4)$) with that for BPh_4 ion according to the equation

$$\log {}_m\gamma_H = \log {}_m\gamma_{H(BPh_4)} - \log {}_m\gamma_{BPh_4}. \qquad (63)$$

Unfortunately, attempts to isolate solid $H(BPh_4)$ were unsuccessful (70). Alternatively, the medium effect for the proton can be arrived at through the series

$$\log {}_m\gamma_H = \log {}_m\gamma_{HCl} - \log {}_m\gamma_{KCl} + \log {}_m\gamma_{K(BPh_4)} - \log {}_m\gamma_{BPh_4} \qquad (64)$$

This equation shows that evaluation of the medium effect for the proton involves the determination of medium effects for HCl, KCl and potassium tetraphenylborate ($K(BPh_4)$) as well as for the reference electrolyte, $TAB(BPh_4)$. Experimentally, medium effects for $K(BPh_4)$ and $TAB(BPh_4)$ are determined from solubility according to equation (26). Medium effects for KCl are determined from e.m.f. measurements of the cell,

$$K(Hg) \ / \ K^+, \ Cl^- \ / \ AgCl(s); \ Ag(s) \qquad \text{(IV)}$$

while those for HCl are calculated via equation (34) from the available literature values for the standard potentials of cell (I) in ethanol-water mixtures (17,34,67,73,80) and in water (8).

In the solvents of low ethanol content (< 35 wt.-% ethanol) the solubility of the reference electrolyte is too low for accurate determination by the ultraviolet spectrophotometric method used to determine solubilities of tetraphenylborates. In these cases, the medium effect for the reference electrolyte is obtained indirectly by the appropriate combination of medium effects for electrolytes containing the ions of interest.

$$\log {}_m\gamma_{TAB(BPh_4)} = \log {}_m\gamma_{TABPi} + \log {}_m\gamma_{K(BPh_4)} - \log {}_m\gamma_{KPi} \qquad (65)$$

Here, $\log {}_m\gamma_{TABPi}$ and $\log {}_m\gamma_{KPi}$ are the medium effects for triisoamyl-n-butylammonium picrate (TABPi) and for potassium picrate (KPi). Medium effects for the picrates are also determined from solubilities, using visible spectrophotometry as the analytical method. The picrates were chosen for this purpose because they are readily synthesized and have low solubilities so that activity coefficients, if estimated by a suitable extension of the Debye-Hückel equation, would not introduce a serious error.

As shown by equations (26) and (34) the evaluation of medium effects for the above electrolytes involves the experimental determination of solubilities, activity coefficients (salt-effect), degrees of dissociation and standard potentials, throughout the entire range of ethanol-water mixtures. The experimental procedures for these determinations are described in detail in Part II of this thesis.

Part II. Experimental Methods.

Synthesis of Electrolytes and Preparation of Solvents

Introduction

The electrolytes which had to be synthesized for this research were lithium picrate (LiPi), potassium picrate (KPi), potassium tetraphenylborate (K(BPh_4)), triisoamyl-n-butylammonium iodide (TABI), triisoamyl-n-butylammonium picrate (TABPi) and triisoamyl-n-butylammonium tetraphenylborate (TAB(BPh_4)). TABI was used to prepare both TABPi and TAB(BPh_4). The syntheses described here closely parallel those in the literature (18, 58, 71).

Ethanol-water mixtures were prepared from 95% ethanol by adding water. Absolute ethanol was prepared from commercial absolute alcohol by distilling from magnesium ethoxide. The exact composition of the ethanol-water mixtures was determined from density measurements.

Experimental

Reagents: The following reagents were used without further purification as starting materials for the synthesis of the above electrolytes: lithium chloride (Baker Analyzed), potassium chloride (Baker Analyzed), potassium hydroxide (Fisher Certified), sodium tetraphenylborate (Fisher Certified), picric acid (Baker Analyzed), 1-iodobutane (Eastman Kodak White Label) and triisopentylamine (Eastman Kodak Yellow

Label).

U.S.P. 95% ethanol and U.S.P. absolute alcohol (Commercial Solvents Corporation) were used to prepare the ethanol-water mixtures.

Procedure: Lithium picrate was prepared by metathesis of lithium chloride and picric acid in absolute alcohol. Neutralization of lithium hydroxide with picric acid was not feasible because of the low solubility of the hydroxide. Equimolar amounts of lithium chloride and picric acid were combined in ethanol. The resulting solution was evaporated to reduce the volume and then allowed to cool. On cooling crystals separated. These crystals were filtered off, washed with absolute alcohol. The crystals obtained were then dried in a vacuum oven at 80°C for forty-eight hours.

Potassium picrate was prepared in a 1:1 (by volume) methanol-water mixture by neutralization of picric acid with potassium hydroxide. The picric acid was dissolved by heating and then treated with an equimolar solution of potassium hydroxide. On cooling, large needles separated. The needles were washed by decantation, and recrystallized twice from distilled water. Recrystallization from distilled water yielded smaller crystals than from methanol. These small crystals were more suitable for dissolution than the larger crystals, as they required no grinding with the accompanying chance of contamination. The crystals were dried in a vacuum oven at 80°C for twenty-four hours.

$K(BPh_4)$ was prepared by metathesis of sodium tetraphenylborate and potassium chloride. Sodium tetraphenylborate dissolved in distilled water was slowly added to an equimolar amount of potassium chloride in water. The milky precipitate which resulted was filtered by suction and washed with a large quantity of distilled water. This crude product was then recrystallized three times from a 3:1 (by volume) acetone-water mixture. The crystals obtained were dried in a vacuum oven at 80°C for twenty-four hours.

TABI was prepared from triisopentylamine and 1-iodobutane by refluxing in 95% ethanol at 85°C for forty-eight hours. Crude TABI was obtained by pouring the reaction mixture into cold water and then filtering. The crude product was purified by recrystallizing three times from ethyl acetate and drying in a vacuum oven at 50°C for twenty-four hours.

TABPi was also prepared directly by metathesis. Methanolic solutions containing equimolar quantities of TABI and picric acid were first heated separately in a hot water bath to about 50°C and then combined. Water was added slowly to the mixture to the point at which the solution just became cloudy. On cooling, crude TABPi separated. The yield was increased by adding more water after the mixture had cooled. It was necessary to separate the crude product from the reaction mixture as quickly as possible, because the iodide liberated in the reaction could further react to reduce the picrate ion. The crude product was recrystallized by dissolving in methanol and adding water to the hot solution to the point at which the solution just became cloudy. Further heating and a little methanol dissolved the precipitate. On cooling, crystals separated. The salt was then dried in a vacuum oven at 60°C for twenty-four hours.

TAB(BPh_4) was prepared in 1:1 (by volume) methanol-water mixture by metathesis of TABI and sodium tetraphenylborate. Crude TAB(BPh_4) was filtered off and thoroughly washed with distilled water. The crude product was recrystallized three times from 3:1 (by volume) acetone-water mixture and then dried in a vacuum oven at 60°C for twenty-four hours. Elemental analysis of the final product gave: C, 85.89%; H, 10.36%; N, 2.40% as compared to the theoretical: C, 85.54%; H, 10.35%; N, 2.32%.

U.S.P. 95% ethanol was purified by double distillation from a 30-cm vigreux column. Of about five liters taken for each distillation, the first 1.5 liters were rejected and about 2.5 liters, collected. The ethanol collected from the second distillation had a density of 0.8067 gm/ml at 25°C corresponding to 92.3 wt.-% ethanol.

U.S.P. absolute alcohol was used as starting material for the preparation of 100% ethanol. About five liters of absolute alcohol were refluxed over magnesium ethoxide for about twelve hours while passing a slow stream of nitrogen through the charge and then distilled. The first 1.5 liters were rejected and about 2.5 liters, collected. Nitrogen was bubbled through the charge during the distillation. The ethanol prepared had a specific conductance of about 1×10^{-8} mho/cm and a density of about 0.7851 gm/ml at 25°C. The density compares favorably with the value of 0.7850 gm/ml reported by Graham, Kell and Gordon (30) and the value of 0.7851 gm/ml obtained from the data of Osborne, McKelvy and Bearce (64).

Magnesium ethoxide was prepared by refluxing absolute ethanol over magnesium turnings for about three hours. A crystal of iodine was added to start the reaction. The magnesium ethoxide prepared was then washed with absolute ethanol to remove traces of iodine.

The source of water used for the ethanol-water mixtures depended on the use for which the solvent was prepared. In the case of solubility and e.m.f. measurements, ordinary distilled water was satisfactory. For conductance measurements, distilled water had too high a specific conductivity and deionized water had to be used. Deionized water could be obtained with a specific conductance of 3×10^{-7} mho/cm.

Ethanol-water mixtures were prepared by measuring out, either by weight or by volume, approximate amounts of ethanol and water. The density of the resulting mixture at 25°C was determined by weighing 100 ml of a mixture in a calibrated 100-ml volumetric flask. Duplicate determinations were made and the weight was corrected to vacuum. The exact composition of the mixture was then obtained from a large-scale plot of density vs. weight-percent ethanol prepared from literature data (64).

Solubility Studies

Introduction

In this section the determination of the solubilities of potassium picrate (KPi), potassium tetraphenylborate ($K(BPh_4)$), triisoamyl-n-butylammonium picrate (TABPi) and triisoamyl-n-butylammonium tetraphenylborate ($TAB(BPh_4)$) at 25°C, over the range 0-100 wt.-% ethanol, is described. Except for KPi, $K(BPh_4)$ and TABPi in water, and KPi in ethanol (68, 71, 72), these solubilities have not been reported in the literature. Although Fischer (22) did report the solubility of KPi in ethanol-water mixtures at 25°C, the composition of his solvents was stated as volume-percent ethanol, without specifying unambiguously the method of preparing the mixtures. For example, 50 volume-percent ethanol could be prepared either by diluting 50 ml of ethanol to 100 ml with water or by combining 50 ml of ethanol with 50 ml of water. Because the volumes are not additive the latter mixture will have a different composition than the former. Thus, one cannot convert Fischer's volume-percent to weight-percent in order to compare his data for the ethanol-water mixtures with ours.

The concentrations of saturated solutions of picrates and tetraphenylborates were determined by visible and ultraviolet spectrophotometry, respectively. The solubilities reported here will be used in a later section to calculate activity coefficients and then for the calculation of medium effects for the above electrolytes.

Experimental

Reagents: The preparations and purification of KPi, TABPi, $K(BPh_4)$ and $TAB(BPh_4)$ and of the solvents used here have already been described in this thesis. Sodium tetraphenylborate (Fisher Certified 100.0%) was used as received.

Procedure: The solubility of KPi, TABPi, $K(BPh_4)$ and $TAB(BPh_4)$ was determined at intervals of about 10 wt.-% ethanol. The solutions were saturated by shaking with a large excess of solid electrolyte, in water-jacketed flasks, on a Burrel wrist-action shaker. Water was circulated through the flasks from a bath controlled at 25.00 ± .01°C by a Yellow Springs Instrument Co. model 72 proportional temperature controller. The actual temperature of the bath was determined, to ±0.01°C, by a National Bureau of Standards certified thermometer. By analyzing the solutions at weekly intervals the amount of shaking necessary to insure saturation was found. A solution was considered saturated when successive analyses at weekly intervals agreed to about 1%. In all cases this agreement was achieved after two weeks of equilibration. The saturated solutions were analyzed, after stopping the shaker and allowing the suspensions to settle, by diluting aliquots to the proper spectrophotometric range and recording their spectra on a Cary model 14 spectrophotometer.

Results and Discussion

Molar absorptivities of picrate ion were determined over the entire range of ethanol-water mixtures using KPi and TABPi. First, the absorptivities were determined for KPi solutions ranging from pure water to pure ethanol at about 10 wt.-% intervals. From electrolytic conductance studies, to be presented in the next section, KPi was found to be partially associated in ethanol-water mixtures containing more than 75 wt.-% ethanol, while TABPi was found to be associated over the entire range of ethanol-water mixtures. Since the degree of dissociation was different for the two salts in any given ethanol-water mixtures, the question arose, whether or not ion pairing would influence their molar absorptivities. In order to test that possibility, the molar absorptivities of TABPi were also determined throughout the alcohol-water range. The results, shown in Figure 2, indicate that for the broad picrate maximum at about 355 mμ, both KPi and TABPi have the same absorptivity in a given ethanol-water mixture. The molar absorptivities for the picrate ion interpolated at 10 wt.-% intervals from large-scale plots, such as shown in Figure 2, are given in Table VIII for comparison with values available in the literature. The Table shows excellent agreement for aqueous solutions.

Molar absorptivities of the tetraphenylborate ion were determined over the entire range of ethanol-water mixtures using sodium tetraphenylborate. The two characteristic

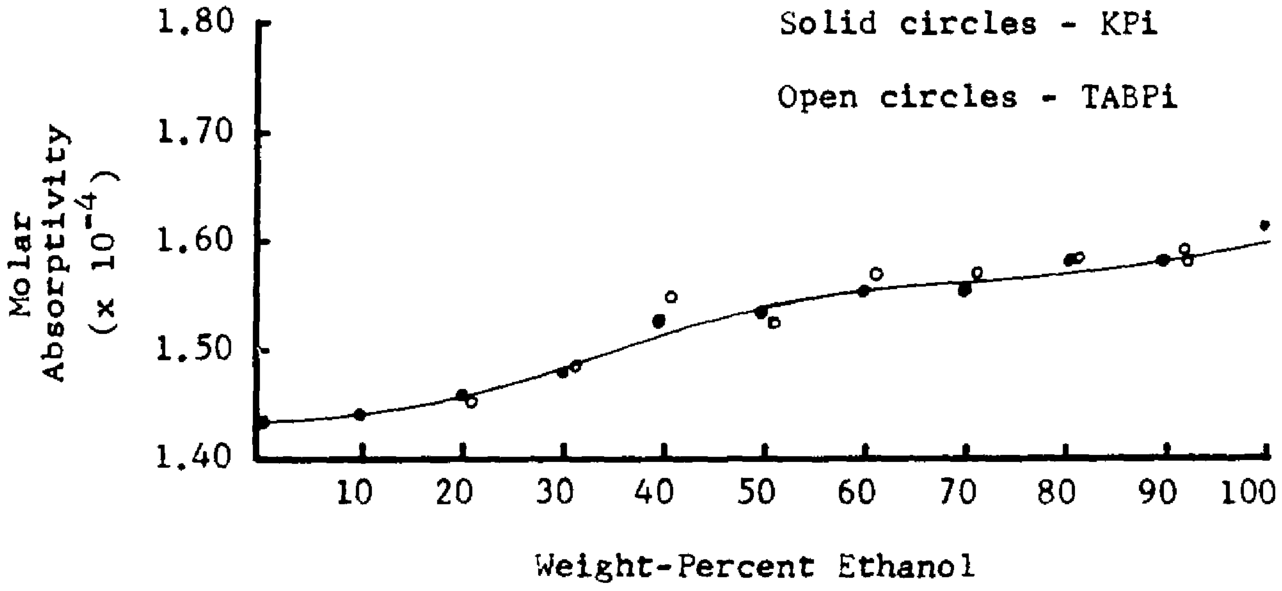

Figure 2. Molar absorptivities of KPi and TABPi in ethanol-water mixtures at 25°C.

Table VIII. Molar Apsorptivities of Picrate and Tetraphenylborate Ions at 25°C.

Solvent wt.-% Ethanol	Molar Absorptivity		
	Picrate (x 10^{-4})	Tetraphenylborate 266 mμ	(x 10^{-3}) 274 mμ
Water	1.43	3.23	1.99
	1.44 (71)	3.25 (71)	2.06 (71)
		3.225 (68)	2.100 (68)
10	1.43	3.21	2.02
20	1.45	3.19	2.05
30	1.48	3.18	2.06
40	1.51	3.16	2.08
50	1.54	3.15	2.08
60	1.55	3.13	2.09
70	1.56	3.11	2.09
80	1.57	3.08	2.09
90	1.58	3.03	2.10
100	1.60	2.97	2.10
Methanol	1.56 (71)	3.00 (71)	2.12 (71)

tetraphenylborate peaks at about 266 and 274 mμ are known to be independent of the associated cation (70). The molar absorptivities for the tetraphenylborate ion at the 266 and 274-mμ maxima, obtained in different solvents by interpolation are included in Table VIII. Excellent agreement with the literature is observed. We also note in the Table that the absorptivity of the tetraphenylborate ion is fairly independent of solvent, as has already been pointed out by Pflaum and Howick (68) for acetonitrile-water mixtures.

Beer's law was found to hold throughout the range of concentrations corresponding to absorbances < 2.0 for both the picrate and the tetraphenylborate ions. Molar absorptivities of picrate and tetraphenylborate ions used in calculations at specific solvent compositions were also obtained by interpolation.

All solutions of the tetraphenylborates were deaerated as a preventive measure against decomposition. Nevertheless they tended to decompose on prolonged shaking. Because of the decomposition, and because of its very low value, the solubility of TAB(BPh_4) could not be determined directly in ethanol-water mixtures below about 35 wt.-% ethanol. K(BPh_4) did not decompose as readily as did TAB(BPh_4), so that its solubility could be determined directly over the entire range of ethanol-water mixtures. Fortunately, this decomposition did not seriously affect the accuracy of our solubility determinations, as its presence was readily detectable from the resulting significant changes in the ultraviolet spectrum of the tetraphenylborate ion. When a sample was found to be decomposed, the determination was repeated. The solubilities obtained in these studies are listed in Table IX at 10 wt.-% intervals. These values were arrived at by interpolation on large-scale plots of solubility vs. solvent composition.

The precision of the spectrophotometric analytical method is estimated to be 0.6%, based on the standard deviation of the analysis of five saturated solutions of KPi in 92.3 wt.-% ethanol. The accuracy of the over-all solubility determination was estimated to be 1.5% for the picrates and 3.0% for the tetraphenylborates, based on duplicate determinations of solubilities of KPi and $K(BPh_4)$ in 92.3 wt.-% and 100% ethanol, respectively.

The solubility curves in Figure 3 exhibit very definite patterns which can be interpreted in terms of solvation properties of the individual ions. The curves for KPi and $K(BPh_4)$ exhibit distinct maxima in the vicinity of 50 wt.-% ethanol, while those for TABPi and $TAB(BPh_4)$ rise monotonically as we proceed to ethanol-rich solvents. This increased solubility in the ethanol-rich solvents corresponds to a lower free-energy state of the corresponding ions in these solvents, as opposed to water. Since the curves for the same cation have the same general shape it is apparently the cation which plays the decisive role in determining the solvation properties of these electrolytes. A detailed discussion of solvation energies will be deferred until Part III of this thesis,

Table IX. Solubilities of Electrolytes in Ethanol-Water Mixtures at 25°C.

Solvent wt.-% Ethanol	Molar Solubility (x 10^3)			
	KPi	TABPi	$K(BPh_4)$	$TAB(BPh_4)$
Water	24.2 (71) 24.1 (74)	0.226 (71)	0.174 (71) 0.178 (68) 0.182 (72)	
10	18.0	0.282	0.220	
20	16.0	0.406	0.342	
30	17.9	0.903	0.670	
40	20.5	2.30	1.45	0.0202
50	22.1	5.25	2.37	0.0603
60	19.1	10.3	2.81	0.134
70	14.2	18.4	2.90	0.293
80	7.64	29.4	2.12	0.53
90	3.23	43.3	1.05	0.87
100	1.04 6.89 (22)	62.7	0.504	1.18

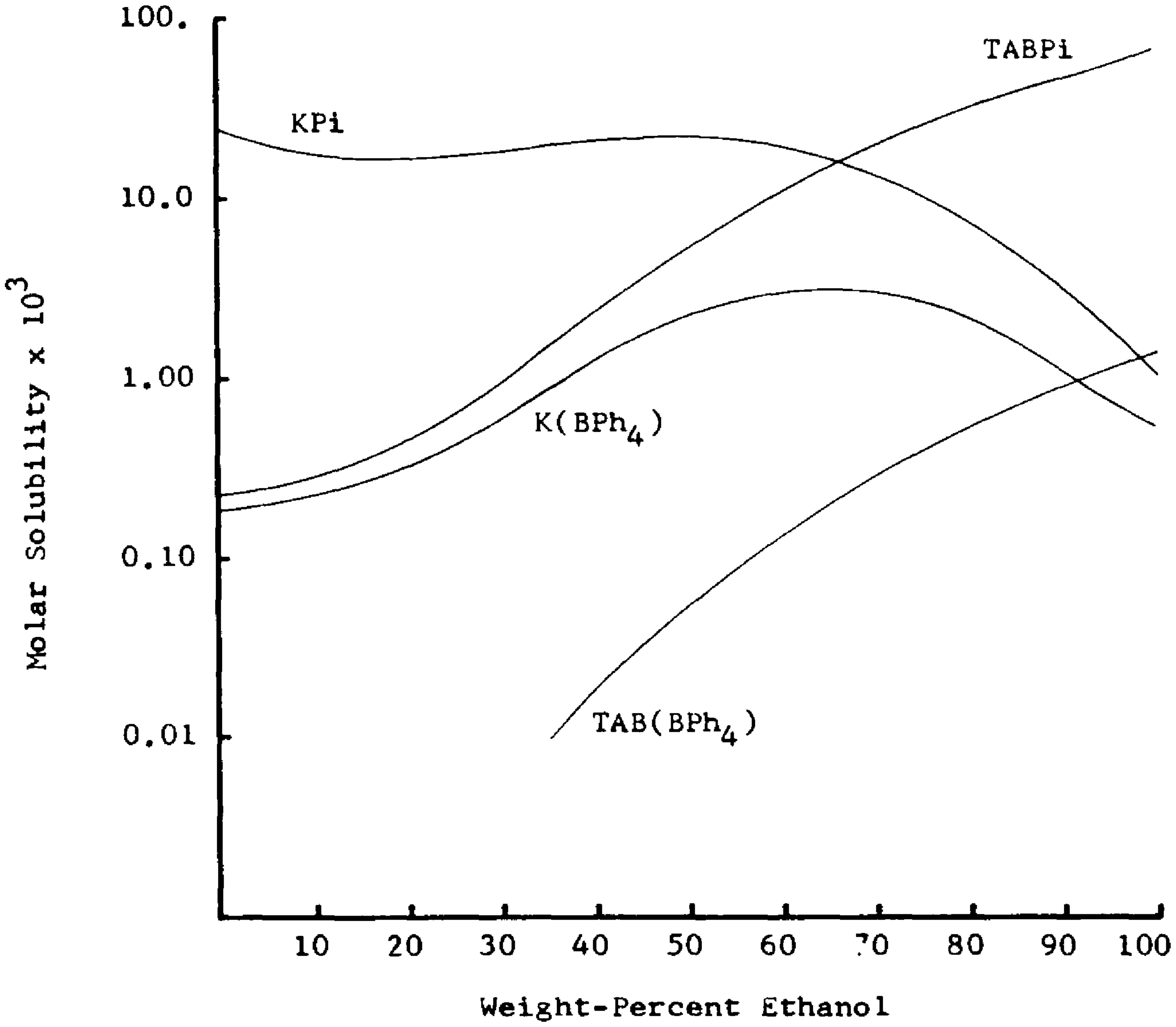

Figure 3. Molar solubilities of picrates and tetraphenylborates in ethanol-water mixtures at 25°C.

after we have evaluated the medium effects for these electrolytes. At that time a quantitative treatment of solvation energies can be presented. Right now we can note the trends which appear in the solubility curves and attempt to interpret them only qualitatively in terms of solvation properties.

The solubility curves for TABPi and TAB(BPh_4) show a marked increase in solubility in ethanol-rich solvents. According to our extrathermodynamic assumption (eq. 61) the solvation properties of TAB^+ and BPh_4^- are identical, so that the increase in solubility of TAB(BPh_4) can be attributed to preferential solvation of both of these ions by ethanol. In water, in view of the extremely low solubility these ions appear to be unsolvated. The increased solubility of TABPi in the ethanol-rich solvent supports this view. The over-all greater solubility of TABPi compared to TAB(BPh_4) can be attributed to the picrate ion. It appears, then, that the picrate ion is solvated both by ethanol and by water, through preferentially by ethanol.

The maxima in the solubility curves for KPi and K(BPh_4) can be definitely attributed to the potassium ion as no such maxima appear in the curves for the other two electrolytes. The curves for KPi and K(BPh_4) have the same general shape in ethanol-rich solvents and in the mid-range of ethanol-water mixtures but differ in the water rich solvents. The solubility of KPi remains fairly high as we go to water-rich solvents while that of K(BPh_4) decreases drastically. The drastic decrease in solubility of K(BPh_4) in water-rich solvents is obviously due to BPh_4^- which, as was pointed out above, is probably unsolvated in these solvents. The solvation behavior of the potassium ion can be visualized by subtracting the influence of BPh_4^- from the total solubility of $K(BPh_4)$. When this is done, the potassium ion appears to be preferentially solvated by water. This view is supported by the high solubility of KPi in the water-rich solvents. We concluded above that the picrate ion is probably solvated by water to some extent. Therefore it reduces the relative solubility of KPi to a lesser extent than BPh_4^- reduces the solubility of $K(BPh_4)$. As a result, we can conclude that potassium is preferentially solvated by water in ethanol-water mixtures.

We can now summarize our tentative conclusions about ion solvation based solely on the solubility of the electrolytes studied. The anions BPh_4^- and Pi^- both appear to be preferentially solvated by the organic solvent. This result is directly contrary to the view held by many authors (20, 21, 23), that anions in alcohol-water mixtures are preferentially solvated by water. However, Grunwald, Baughman and Kohnstam (31) point out that large organic ions with low surface charge density can be expected to be solvated much like the corresponding structure without a net charge. In agreement with the view of these authors the solubility of picric acid (the neutral analog of the picrate ion) is greater in ethanol than in water. The two cations, TAB^+ and K^+, appear to exhibit exactly opposite behavior regarding solvation.

The TAB^+ ion appears preferentially solvated by ethanol. Potassium ion, on the other hand, appears to be preferentially solvated by water. J. P. Hunt (37) is of the opinion that the hydrated potassium ion, which appears to have four water molecules tetrahedrally arranged around the potassium ion, $K(H_2O)_4^+$, fits well into the water structure. According to this view it is not surprising that potassium would be preferentially solvated by water. Thus, the "generally accepted rule" (20,21,23,31) that in alcohol-water mixtures all cations are preferentially solvated by the alcohol does not appear to be followed, at least here in this qualitative treatment which accounts for solvation only by solubility.

Electrolytic Conductance Studies

Introduction

As was pointed out earlier, the calculation of ion-activity products for electrolytes in ethanol-water mixtures where ionic association is appreciable requires knowledge of the degree of dissociation of these electrolytes. The degree of dissociation is most readily obtained from measurements of electrolytic conductance in these solvents.

This section describes studies of the electrolytic conductance of lithium chloride, lithium picrate, potassium picrate (KPi), triisoamyl-n-butylammonium picrate (TABPi), potassium tetraphenylborate ($K(BPh_4)$) and triisoamyl-n-butylammonium tetraphenylborate ($TAB(BPh_4)$) at 25°C over the entire range of ethanol-water mixtures.

The data were analyzed on an IBM 1620 computer using Fortran computer programs either with the aid of the Fuoss-Onsager theory (24,27), or with the aid of the Shedlovsky modification (28,75) of the Ostwald dilution law in order to obtain limiting equivalent conductances, association constants and ion-size parameters.

It should be pointed out that the symbols used in this section conform to the usage by Fuoss and Accascina (24) in their monograph on electrolytic conductance. This was done to make the symbolism for these electrolytic conductance studies consistent with that in the literature, in spite of the fact that the same symbols may be used to express different parameters in other parts of this thesis. In particular, the degree of dissociation is expressed by γ in this section while α is used in other sections. In order to avoid confusion, the results of these conductance studies will be tabulated by name rather than by symbol and, whenever possible, such quantities will be referred to by name rather than by symbol. Only the equations in this section and the computer programs for the conductance calculations will contain the symbols characteristic of the definitive conductance literature.

Experimental

Reagents: Lithium picrate, KPi, TABPi, $K(BPh_4)$ and $TAB(BPh_4)$ and the solvents used in these studies were prepared and purified as described earlier in this thesis. In addition, the above electrolytes were recrystallized once more prior to use and the distillation apparatus for the ethanol was protected from atmospheric carbon dioxide by an ascarite tube. When distilling absolute ethanol, a stream of nitrogen was bubbled through the charge so that the ascarite tube was not necessary. The lithium chloride was prepared for use by double recrystallization of "Baker Analyzed" lithium chloride from distilled water, followed by drying at 110°C for forty-eight hours. The dried product was stored in a desiccator over phosphorous pentoxide. Potassium chloride, used to determine the cell constant, was prepared by double recrystallization of "Baker Analyzed" potassium chloride, first from distilled water, then from absolute ethanol, followed by drying at 110°C for twenty-four hours.

Procedure: The procedure for preparing solutions and making the conductivity measurements was about the same for each of the electrolytes studied. The only electrolyte which required special precautions was lithium chloride, which because of its hygroscopic nature, had to be stored in a desiccator and all its transfers prior to weighing had to be carried out in a dry box (glove bag) over phosphorous pentoxide. Solutions of all the electrolytes were freshly prepared by weighing the components and correcting to weight in vacuo. First a stock solution was prepared by weight, then weighed portions of the stock solution were diluted and the weights (in vacuo) of the resulting solutions obtained. From this data and from the density of the solution (taken to be equal to the density of solvent), the normality of each solution could be calculated.

Before a typical run, the conductance cell was washed with solvent. Prior to filling, the cell was thoroughly rinsed with the solution whose conductance was to be measured. After filling, the cell was tightly sealed by means of a ground-glass cap and immersed in a water bath at 25°C controlled to ±0.003°C by a Yellow Springs Instrument Co. model 72 proportional temperature controller. The absolute temperature of the bath was determined, to ±0.01°C, by means of a National Bureau of Standards certified thermometer. After consecutive conductance readings at 15 minute intervals agreed to 0.1%, the solution in the cell was replenished and readings were again taken at 15 minute intervals until consecutive readings agreed to about 0.05%. This generally required 30 - 40 minutes. Because of exposure of the solutions to the atmosphere and the chance of contamination by carbon dioxide while filling the conductance cell, the conductance of solvent to be used for the solvent correction was measured using a sample of solvent that was treated in much the same manner as the solutions. The measurements were carried out using a Wayne-Kerr model B-221 Universal Bridge and the model Q-221 low impedence adapter. This bridge measured conductance directly and was accurate to 0.1%. The conductance cell contained bright platinum electrodes and had a cell constant of 0.010017 cm^{-1} based on the Jones and Bradshaw aqueous 0.01 demal KCl standard (53).

Results and Discussion

The necessary physical properties of the ethanol-water mixtures used were obtained by interpolation of data available in the literature. The weight-percent ethanol was obtained, as described in an earlier section, from the measured density, d_o, by interpolation of known density data (64). Literature values were interpolated to obtain the viscosity, η, (38) and the dielectric constant, D (2) of each mixture of interest. Table X gives the equivalent conductance, Λ, for the solutions of the electrolytes used. The

Table Xa. Conductance of LiCl in Ethanol-Water Mixtures at 25°C.

10^4c	Λ	$\Delta\Lambda$	10^4c	Λ	$\Delta\Lambda$
92.3 Wt.-% Ethanol			86.6 Wt.-% Ethanol		
$k_o = 2.4 \times 10^{-7}$ mho/cm			$k_o = 2.8 \times 10^{-7}$ mho/cm		
3.638	37.500	-.001	3.970	37.454	-.001
4.638	37.161	-.001	6.927	36.712	+.003
11.006	35.577	+.003	9.855	36.099	-.017
13.864	35.026	-.006	12.011	35.732	-.006
15.723	34.709	-.005	14.825	35.276	-.020
18.249	34.295	-.024	17.015	34.998	+.015
22.735	33.677	-.015	19.832	34.621	+.006
			24.360	34.066	-.018
77.2 Wt.-% Ethanol			68.2 Wt.-% Ethanol		
$k_o = 4.2 \times 10^{-7}$ mho/cm			$k_o = 2.2 \times 10^{-7}$ mho/cm		
7.854	36.807	-.004	11.022	37.101	+.036
15.683	35.756	-.007	15.920	36.561	+.020
18.969	35.412	+.001	19.256	36.295	+.068
23.804	34.940	-.009	23.466	35.877	+.005
26.769	34.686	-.007	26.749	35.650	+.036
31.563	34.301	-.014	32.551	35.212	+.013
39.312	33.738	-.036	41.094	34.686	+.030
57.1 Wt.-% Ethanol			43.5 Wt.-% Ethanol		
$k_o = 3.5 \times 10^{-7}$ mho/cm			$k_o = 3.2 \times 10^{-7}$ mho/cm		
8.460	38.948	0.000	9.158	43.142	0.000
10.447	38.748	+.001	13.146	42.813	0.000
14.392	38.386	-.010	15.820	42.603	-.014
20.905	37.932	+.023	19.874	42.349	0.000
24.902	37.643	-.004	22.435	42.212	+.019
31.128	37.248	-.033	26.317	41.939	-.033
36.781	36.977	-.002	32.514	41.647	-.001
41.008	36.798	+.029			
52.113	36.267	-.007			

Table Xb. Conductance of LiPi in 92.3 Wt.-% Ethanol at 25°C.

10^4C	Λ	$\Delta\Lambda$
$k_o = 0.7 \times 10^{-7}$ mho/cm		
5.689	48.996	+.011
8.002	48.188	-.032
9.631	47.750	+.005
11.606	47.229	+.006
13.584	46.750	+.002
15.481	46.340	+.014
17.676	45.890	+.015
19.587	45.515	+.006

Table Xc. Conductance of KPi in Ethanol-Water Mixtures at 25°C.

10^4c	Λ	$\Delta\Lambda$	10^4c	Λ	$\Delta\Lambda$
100 Wt.-% Ethanol			92.3 Wt.-% Ethanol		
$k_o = 1.0 \times 10^{-7}$ mho/cm			$k_o = 2.4 \times 10^{-7}$ mho/cm		
3.0588	45.191	-.013	3.3101	43.261	+.012
3.3347	44.916	+.007	3.6246	43.053	-.022
3.5146	44.721	-.003	3.8503	42.988	+.036
3.8060	44.441	+.009	4.1068	42.784	-.038
3.9717	44.285	+.014	4.3592	42.696	+.005
4.2874	43.980	+.003	4.7094	42.499	-.021
4.5302	43.738	-.020	4.9381	42.437	+.029
4.7869	43.532	+.001	5.2649	42.263	+.006
5.0864	43.278	+.003	5.5307	42.128	-.009
84.5 Wt.-% Ethanol			79.3 Wt.-% Ethanol		
$k_o = 2.9 \times 10^{-7}$ mho/cm			$k_o = 3.1 \times 10^{-7}$ mho/cm		
2.9212	40.778	-.006	2.3209	39.530	+.035
3.2568	40.636	-.041	2.5822	39.383	-.040
3.6471	40.599	+.045	3.1099	39.261	-.024
3.7690	40.528	+.009	3.5586	39.212	+.036
4.0508	40.460	+.024	3.8446	39.127	+.017
4.3275	40.343	-.016	4.1017	38.989	-.066
4.6527	40.257	-.013	4.3673	39.054	+.059
4.8659	40.202	-.012	5.1269	38.826	-.016
5.1522	40.175	+.037			
5.4256	40.043	-.028			
65.5 Wt.-% Ethanol			62.0 Wt.-% Ethanol		
$k_o = 2.2 \times 10^{-7}$ mho/cm			$k_o = 1.5 \times 10^{-7}$ mho/cm		
3.4508	37.684	+.061	2.596	38.153	+.048
3.7840	37.537	-.031	4.983	37.741	-.004
4.0459	37.538	+.012	7.136	37.474	-.014
4.4129	37.400	-.068	9.550	37.204	-.038
4.7035	37.423	-.003	14.694	36.816	+.012
5.0630	37.381	+.006	16.898	36.605	-.035
5.3644	37.389	+.056	19.200	36.469	-.011
5.6320	37.261	-.035	21.624	36.333	+.011
5.9579	37.187	-.067	24.503	36.176	+.031
6.3569	37.271	+.069			

Table Xd. Conductance of TABPi in Ethanol-Water Mixtures at 25°C.

10^4C	Λ	$\Delta\Lambda$	10^4C	Λ	$\Delta\Lambda$
100 Wt.-% Ethanol			92.3 Wt.-% Ethanol		
$k_o = 1.2 \times 10^{-7}$ mho/cm			$k_o = 1.8 \times 10^{-7}$ mho/cm		
5.956	40.126	+.002	2.317	36.424	-.009
7.848	39.181	-.017	5.740	34.932	+.002
10.180	38.239	+.030	7.108	34.455	-.005
12.049	37.505	-.011	7.943	34.220	+.024
14.140	36.808	-.004	9.346	33.779	-.007
16.095	36.209	-.004	11.677	33.173	-.003
18.158	35.646	+.014	13.668	32.716	+.006
20.463	35.048	+.011	16.118	32.180	-.013
22.514	34.560	+.013	18.691	31.699	-.002
81.8 Wt.-% Ethanol			53.3 Wt.-% Ethanol		
$k_o = 3.2 \times 10^{-7}$ mho/cm			$k_o = 2.0 \times 10^{-7}$ mho/cm		
5.983	30.104	-.001	5.998	22.349	0.000
7.714	29.731	+.014	8.220	22.084	0.000
10.270	29.230	+.014	12.087	21.679	-.004
12.056	28.898	-.007	14.067	21.497	-.001
14.419	28.521	-.008	17.823	21.175	-.001
16.750	28.181	-.009	20.275	20.986	+.003
18.421	27.948	-.018	23.232	20.764	+.001
20.515	27.681	-.021	26.020	20.566	-.001
22.229	27.476	-.021	29.074	20.360	-.003

Table Xe. Conductance of K(BPh_4) in Ethanol-Water Mixtures at 25°C.

10^4C	Λ	$\Delta\Lambda$	10^4C	Λ	$\Delta\Lambda$
100 Wt.-% Ethanol			92.3 Wt.-% Ethanol		
$k_o = 0.8 \times 10^{-7}$ mho/cm			$k_o = 0.7 \times 10^{-7}$ mho/cm		
1.1523	44.956	-.008	1.9438	39.030	-.027
1.3246	44.637	+.021	2.4237	38.890	+.025
1.4951	44.279	-.014	2.6202	38.828	+.037
1.6764	43.964	+.003	2.7873	38.725	-.008
			2.9374	38.683	+.003
			3.1042	38.589	-.036
			3.3022	38.565	+.006
80.1 Wt.-% Ethanol			70.8 Wt.-% Ethanol		
$k_o = 2.0 \times 10^{-7}$ mho/cm			$k_o = 5.1 \times 10^{-7}$ mho/cm		
2.0082	34.755	-.033	4.3500	34.596	-.033
2.5556	34.755	+.031	4.7751	34.654	+.009
2.9813	34.708	+.022	5.2192	34.672	+.010
3.1157	34.670	-.005	5.4491	34.606	-.066
3.2981	34.666	+.004	5.9189	34.798	+.107
3.4754	34.673	+.023	6.2614	34.714	+.010
3.7010	34.594	-.043	6.5940	34.754	+.028
			7.1747	34.691	-.049
			7.5528	34.739	-.016

Table Xf. Conductance of TAB(BPh_4) in Ethanol-Water Mixtures at 25°C.

10^4C	Λ	$\Delta\Lambda$	10^4C	Λ	$\Delta\Lambda$
100 Wt.-% Ethanol			92.3 Wt.-% Ethanol		
$k_o = 1.4 \times 10^{-7}$ mho/cm			$k_o = 1.8 \times 10^{-7}$ mho/cm		
2.9670	35.776	-.036	2.0425	30.683	+.004
3.2637	35.592	0.000	2.2442	30.574	+.005
3.5108	35.421	+.004	2.4098	30.475	-.006
3.7734	35.253	+.015	2.6014	30.384	+.001
4.0337	35.075	+.009	2.9468	30.209	-.006
4.2911	34.944	+.044	3.1818	30.095	-.011
4.5974	34.723	+.008	3.3326	30.037	+.001
4.8476	34.543	-.025	3.5578	29.947	+.011
5.0714	34.440	+.005			
5.4135	34.221	-.024			

10^4C	Λ	$\Delta\Lambda$
80.8 Wt.-% Ethanol		
$k_o = 3.1 \times 10^{-7}$ mho/cm		
2.4138	25.221	-.010
3.0157	25.049	+.015
3.3259	24.981	+.004
3.5042	24.938	+.007
3.7169	24.861	-.017

concentration, C, is given on the molar scale, $\Delta\Lambda$ is the difference between the measured equivalent conductance and that calculated via equation (66), (67) or (68) using the experimentally obtained values for the parameters Λ_0, K_A and J. The specific conductance, k_0, of the solvent measured in this study is also included in the Table.

The data in Table X were analyzed by the two previously mentioned methods. The Fuoss-Onsager equation takes the form

$$\Lambda = \Lambda_0 - SC^{\frac{1}{2}}\gamma^{\frac{1}{2}} + EC\gamma \log C\gamma + JC\gamma - K_A C\gamma f_{\pm}^2\Lambda - F\Lambda_0 C \qquad (66)$$

for associated electrolytes and the form

$$\Lambda = \Lambda_0 - SC^{\frac{1}{2}} + EC \log C + JC - F\Lambda_0 C \qquad (67)$$

for unassociated electrolytes. With the exception of the data for KPi, $K(BPh_4)$ and $TAB(BPh_4)$, in solvents where ionic association was prevalent, all of the conductance data were analyzed by either equation (66) or (67). For reasons which will be pointed out later, the data for KPi, $K(BPh_4)$ and $TAB(BPh_4)$ were analyzed using the Shedlovsky modification of the Ostwald dilution law which takes the form

$$\frac{1}{\Lambda S(z)} = \frac{K_A C\Lambda f_{\pm}^2 S(z)}{\Lambda_0^2} + \frac{1}{\Lambda_0} \qquad (68)$$

Throughout these equations the symbols are the same as those used by Fuoss and Accascina (<u>24</u>). Here, <u>S</u> is the Onsager coefficient, $\alpha\Lambda_0 + \beta$. The constants α and β assume the values $0.8204 \times 10^6/(DT)^{3/2}$ and $82.501/\eta(DT)^{\frac{1}{2}}$, respectively. The constant E is defined by the same variables as S and takes the form

$$E = \frac{6.7747 \times 10^{12}}{D^3T^3} - \frac{0.9977 \times 10^8}{\eta D^2T^2} \tag{69}$$

while J is a function of ion size and is defined below. The Shedlovsky function, S(z), is given by

$$S(z) = (z/2 + [1 + (z/2)^2]^{\frac{1}{2}})^2 \tag{70}$$

where $$z = (S/\Lambda_\circ^{3/2})(C\Lambda)^{\frac{1}{2}} \tag{71}$$

For lithium chloride, the viscosity term, $F\Lambda_\circ C$, was considered negligible because of the small size of the ions involved. The flow times for stock solutions of the remaining electrolytes were found to be practically the same as those of pure solvents. An Ostwald viscometer with a flow-time of about 300sec. was employed. On this basis the viscosity terms were considered to be negligible also for the remaining electrolytes and therefore not included in the calculation.

Solution of equation (66) was achieved by the so-called y - x method described by Fuoss, et. al. (1,24) which is derived as follows:

After eliminating the viscosity term, equation (66) can be rearranged to read:

$$\Lambda + SC^{\frac{1}{2}}\gamma^{\frac{1}{2}} - EC \log C\gamma = JC\gamma - K_A C\gamma f_{\pm}^2\Lambda + \Lambda_\circ \tag{72}$$

If we then define the quantity Λ' by the equation

$$\Lambda' = \Lambda + SC^{\frac{1}{2}}\gamma^{\frac{1}{2}} - EC\gamma \log C\gamma, \tag{73}$$

equation (72) can be rewritten

$$\Lambda' - \Lambda_\circ = JC\gamma - K_A C\gamma f_\pm^2 \Lambda \tag{74}$$

or

$$(\Lambda' - \Lambda_\circ)/C\gamma = J - K_A f_\pm^2 \Lambda \tag{75}$$

Fuoss then defines the quantities

$$\underline{y} = (\Lambda' - \Lambda_\circ)/C\gamma \tag{76}$$

and

$$\underline{x} = f_\pm^2 \Lambda \tag{77}$$

which lead to the linear relationship:

$$\underline{y} = J - K_A\underline{x}. \tag{78}$$

A plot of equation (78) will be linear, yielding $-K_A$ and $\underline{J}$ for the slope and the intercept, respectively. Since we are attempting to evaluate $\Lambda_\circ$ from the conductance data, this quantity in equation (76) is unknown at the start and the calculation of $\underline{y}$ appears impossible. However, the fact that equation (78) should be linear (for the correct value of $\Lambda_\circ$) suggests a solution to the problem. If a trial value for $\Lambda_\circ$ is used to calculate a set of values for $\underline{x}$ and $\underline{y}$, the resulting plot will be linear only if the trial value is the correct one. If the trial value is too small, the resulting $\underline{y}$ - $\underline{x}$ plot turns out to be concave-up, while if the trial value is too large, the resulting $\underline{y}$ - $\underline{x}$ plot is concave-down.

Thus, by calculating and plotting x and y for a series or Λ_0's, the value of Λ_0 which linearizes the y - x plot can be found. Since many trial values may have to be tested before the one which linearizes the y - x plot is found, and especially when many sets of data have to be analyzed, a digital computer is found to be most convenient for these calculations. In this work, Fortran computer programs and an IBM 1620 computer were used to carry out all of the calculations involved.

An actual computation by the y - x method proceeds as follows: As a first approximation, the degree of dissociation is calculated from the equation

$$\gamma_0 = \Lambda/[\Lambda_0 - (S/\Lambda_0^{\frac{1}{2}})(C\Lambda)^{\frac{1}{2}}], \qquad (79)$$

using a reasonable estimate as a preliminary value for Λ_0. Then, from the degree of dissociation, γ_0, we calculate Λ' defined by equation (73). From the values of γ_0 and Λ' so obtained, values of y and x are calculated using trial values for Λ_0 as described above. The activity coefficient, $f_\pm$, used to calculate x is obtained from the Debye-Hückel equation in the form

$$\log f_\pm = \frac{-A\sqrt{C\gamma}}{1 + Ba\sqrt{C\gamma}} \qquad (80)$$

where γ is the degree of dissociation. A reasonable estimate of the ion-size parameter is used in the first approximation. A y - x plot corresponding to each value of Λ_0 is then constructed in order to arrive at the correct value for Λ_0.

From the slope of the plot, K_A is obtained and used in equation (78) along with the values of x and y at each experimental point in order to calculate J-values at each of these points. The average of the J-values so obtained is used to calculate a second-approximation value, for the degree of dissociation, γ, using the E and J terms, which were not included in the first approximation (equation 79).

$$\gamma = \Lambda / [\Lambda_0 - SC^{\frac{1}{2}} \gamma_0^{\frac{1}{2}} + Ec\gamma_0 \log C\gamma_0 + JC\gamma_0] \tag{81}$$

The values for Λ_0 and γ_0 used in equation (81) were obtained from the first approximation. The ion-size parameter is obtained by interpolation of the J-values calculated in the first approximation. Ion sizes so obtained are denoted $\mathring{a}_J$, in contrast to those obtained from K_A, $\mathring{a}_K$, and from Λ_0, $\mathring{a}_\Lambda$. The value of J at 25°C as a function of $\mathring{a}$ is given by

$$J = \sigma_1 \Lambda_0 + \sigma_2 \tag{82}$$

where

$$\sigma_1 = \frac{2.22000 \times 10^5}{D^3} [h(b) + 0.9074 + \ln \frac{2.9127 \times 10^8}{D^{\frac{1}{2}}} \mathring{a}] \tag{83}$$

and

$$\sigma_2 = \frac{761.36}{\eta D^2} + \frac{12.757 \times 10^8}{\eta D} - \frac{974.8}{\eta D^2} [1.0170 + \ln \frac{2.9127 \times 10^8}{D^{\frac{1}{2}}} \mathring{a}] \tag{84}$$

The term h(b) is given by

$$h(b) = (2b^2 + 2b - 1)/b^3 \tag{85}$$

where $$b = 560.37 \times 10^{-8}/\mathring{a}D \qquad (86)$$

The values of $\mathring{a}_J$ calculated in this manner and γ from equation (81) are then used in a second-approximation calculation of x and y, which are again plotted as before. In general, in our calculations, the value of Λ_o obtained in the second approximation agreed with that from the first approximation to within 0.01% so that further approximations were not necessary. If the Λ_o's obtained from the first and the second approximations do not agree, further approximations can be made in the same manner as was the second. Figure 4 shows a typical y - x plot for lithium chloride, illustrating the dependence of linearity on the value of Λ_o.

The choice of the Fuoss-Onsager or of the Shedlovsky method for analysis of conductance data taken in solvents where ionic association was prevalent was determined by the solubility of the electrolyte. For electrolytes with low solubility and correspondingly low conductances, the solvent conductance becomes a large part of the total conductance and variations in the solvent conductance from sample to sample can result in a significant source of error in the equivalent conductance when analyzed by the y - x method. According to Fuoss and Accascina (24), it is futile to attempt to analyze by the y - x method conductance data with precision of 0.1% or less. The sensitivity of the y - x method to the equivalent conductance can be seen when one looks at the expression for y (equation 76). One can see from equation (76) that small errors in Λ', which can

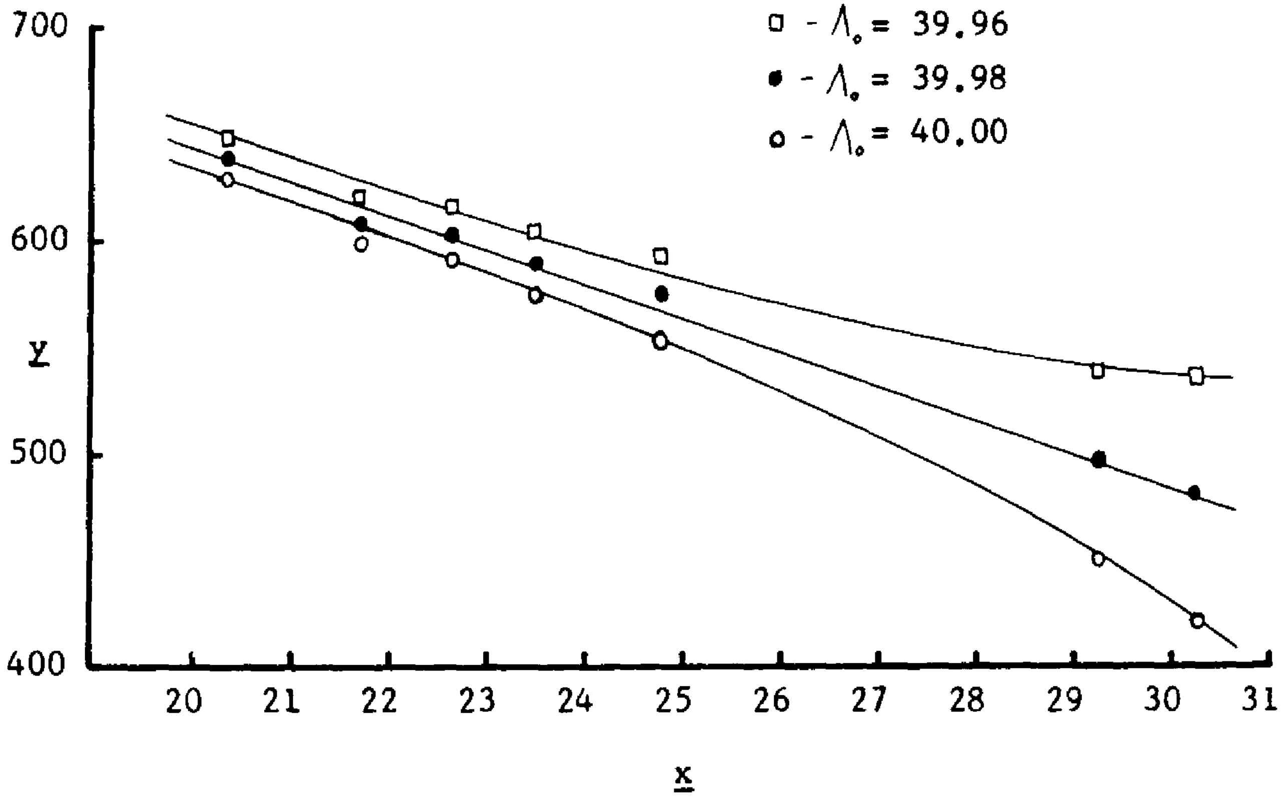

Figure 4. Typical y - x plot for LiCl in 92.3 wt.-% ethanol.

result from inaccuracy in the observed conductance or from an inaccurate knowledge of the constants S and E (which are determined by temperature, viscosity and dielectric constant of the solvent, valence type of the solute and universal constants), can result in a large error in the value of y. As a result, when conductance data for KPi, $K(BPh_4)$ or $TAB(BPh_4)$ were subjected to analysis by the y - x method the points were found to be so badly scattered that it was impossible to determine whether the curve was linear, concave-up or concave-down. Therefore, conductance data for these slightly-soluble electrolytes were analyzed by the Shedlovsky modification of the Ostwald dilution law, which takes the form given in equation (68).

According to the Shedlovsky equation, a plot of $1/\Lambda S(z)$ vs. $C\Lambda f_{\pm}^{2}S(z)$ will be linear with the intercept equal to $1/\Lambda_\circ$ and the slope, $K_A/\Lambda_\circ^{2}$, evaluating the association constant. A Fortran computer program was made up to carry out all the calculations and perform a least-squares computation of $\Lambda_\circ$ and K_A.

For analysis of the data for nonassociated electrolytes, assuming the viscosity term to be negligible, equation (67) is rearranged to the linear form

$$\Lambda' = \Lambda_\circ + JC \tag{87}$$

where

$$\Lambda' = \Lambda + SC^{\frac{1}{2}} - EC \log C \tag{88}$$

Then, from a plot of Λ' vs. C the slope and the intercept are used to evaluate J and $\Lambda_\circ$, respectively. The ion-size parameter is then obtained as in the $\underline{y} - \underline{x}$ method by interpolation. Since $\underline{S}$ and $\underline{E}$ are functions of Λ_0, the actual calculation involves successive approximations of Λ_0 to arrive at its correct value. Again, a Fortran computer program was made up to carry out all the calculations and to perform a least-squares computation in order to eliminate the need for graphical procedures. Table XI summarizes the results of the conductance studies for these electrolytes. Association constants, used later, for calculations at a given solvent composition were obtained by interpolation or extrapolation on a plot of log K_A vs. 1/D such as shown in Figure 5.

That the association constants, or the degrees of dissociation, obtained by the Fuoss and by the Shedlovsky methods of analysis are comparable can be seen by examining the expressions for the degree of dissociation as given by each method. The degree of dissociation obtained from the Fuoss-Onsager theory is given by

$$\gamma = \Lambda/[\Lambda_0 - SC^{\frac{1}{2}}\gamma^{\frac{1}{2}} + EC\gamma \log C\gamma + JC\gamma] \qquad (89)$$

while in the Shedlovsky method it is given by

$$\gamma = \frac{\Lambda}{\Lambda_0} S(z) \qquad (90)$$

In both of these equations, the degree of dissociation is given essentially by the Arrhenius approximation, $\gamma = \Lambda/\Lambda_0$, which is valid for ideal solutions, i.e. at high dilution, where the ions can be assumed to behave as point charges.

Table XI. Conductance Parameters and Constants Obtained at 25°C.

Solvent wt.-% Ethanol	Λ_o	å	K_A	J
Lithium Chloride				
43.5	44.70 ± .02	2.10 ± .16	2.5 ± .2	99.6
57.1	40.66 ± .02	2.47 ± .10	3.1 ± .2	167.4
68.2	39.50 ± .04	2.34 ± .22	4.8 ± .8	231.8
77.2	39.25 ± .02	3.31 ± .04	7.6 ± .3	447.3
86.6	39.65 ± .01	3.35 ± .05	10.5 ± .3	682.9
92.3	39.98 ± .01	3.73 ± .03	15.7 ± .3	954.8
100 (<u>54</u>)	39.94	4.4	27	---
Lithium Pictate				
92.3	52.78 ± .02	3.94 ± .05	18.9 ± .5	1190.4
Potassium Picrate				
62.0	39.00 ± .04	1.98	---	123.7
65.5	38.87 ± .05	2.92	---	250.1
79.3	40.79 ± .04	---	13 ± 4	---
84.5	42.60 ± .03	---	27 ± 2	---
92.3	46.41 ± .03	---	98 ± 2	---
100	50.58 ± .01	---	281 ± 1	---
Triisoamyl-n-butylammonium Picrate				
53.3	23.66 ± .002	0.62 ± .08	20.4 ± .1	12.6
81.8	32.66 ± .02	4.83 ± .09	43.9 ± .6	608.1
92.3	38.67 ± .01	5.23 ± .09	70.7 ± .7	1175.8
100	45.70 ± .02	3.73 ± .04	99.7 ± .6	1484.4
Potassium Tetraphenylborate				
70.8	34.46 ± .05	4.52	---	394.9
80.1	35.63 ± .04	21.0	---	2086.0
92.3	40.68 ± .03	---	17 ± 3	---
100	48.49 ± .02	---	460 ± 3	---

Table XI. (continued)

Solvent wt.-% Ethanol	Λ_0	$\mathring{a}$	K_A	J
	Triisoamyl-n-butylammonium Tetraphenylborate			
80.8	26.54 ± .01	---	47 ± 2	---
92.3	32.64 ± .01	---	106 ± 2	---
100	39.58 ± .02	---	192 ± 2	---

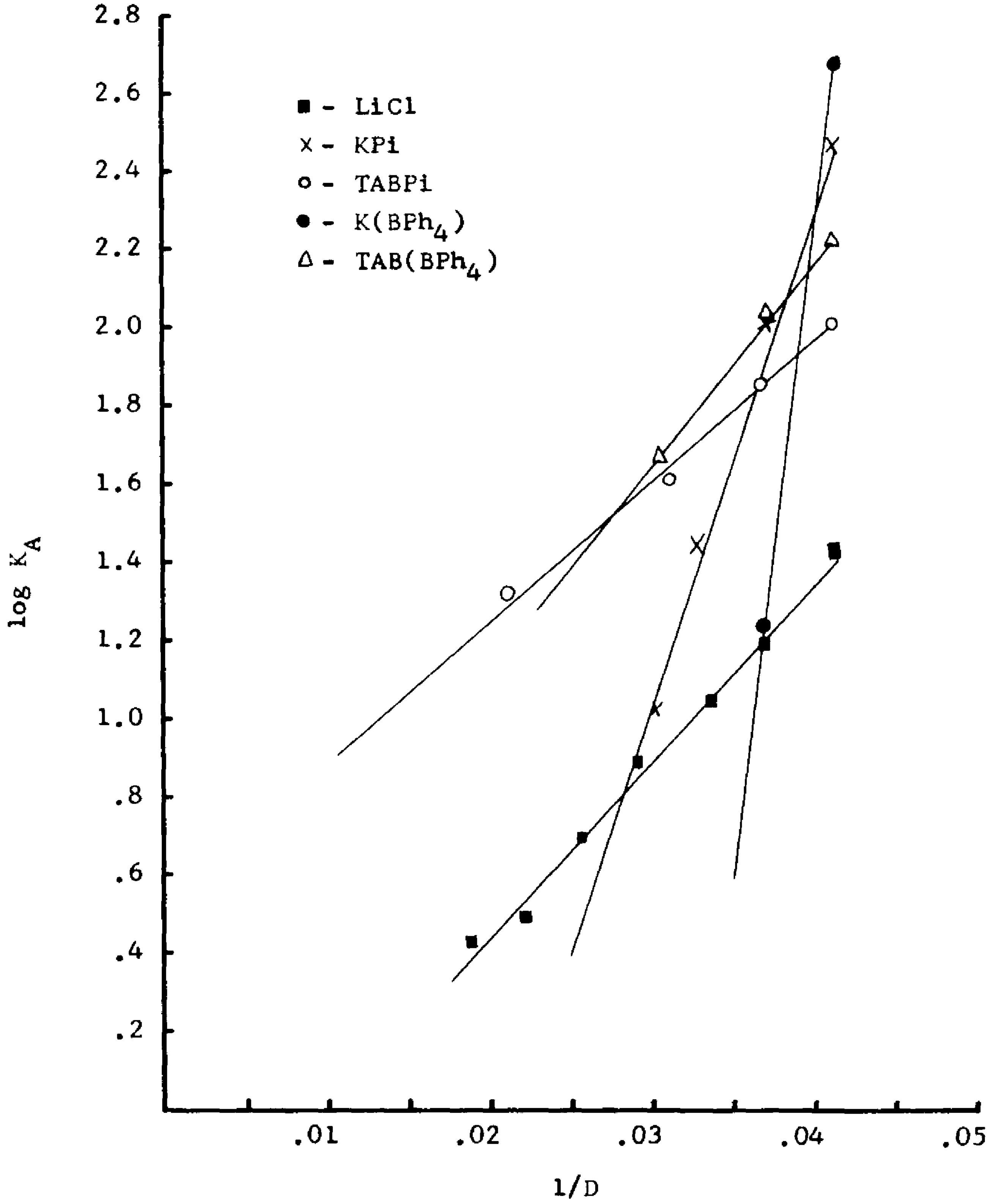

Figure 5. Log K$_A$ vs. 1/D plot for the electrolytes studied.

The modifications account for nonideal behavior in more concentrated solutions. The Fuoss-Onsager equation is derived on the basis of a model whereby an ion is assumed to be a charged sphere, rather than a point charge and the $\underline{S}$, $\underline{E}$ and $\underline{J}$ terms are introduced to take into account the nonideal behavior as we go to higher concentrations. Similarly, the S(z) term was introduced by Shedlovsky to account for nonideal behavior at higher concentrations. That the S(z) term does not account for this effect as completely as the terms in the Fuoss-Onsager equation is unimportant for this discussion. The point to be made is that at low concentrations (the Shedlovsky method was used only for the more insoluble electrolytes), the correction terms in both equations become increasingly less important and in the concentration range used for KPi, $K(BPh_4)$ and $TAB(BPh_4)$ the degree of dissociation is described equally well by either equation (89) or (90).

TABPi was analyzed by both the Fuoss-Onsager and the Shedlovsky procedures and it is instructive to compare the results obtained by the two methods. Figure 6 shows the variation of K_A, as obtained by both methods, with solvent composition. This plot has approximately the same shape as the log K_A vs. 1/D plot because the dielectric constant of ethanol-water mixtures varies almost linearly with weight-percent ethanol. The association constants obtained by the Fuoss-Onsager theory vary almost linearly with the weight-percent ethanol, while those obtained by the Shedlovsky

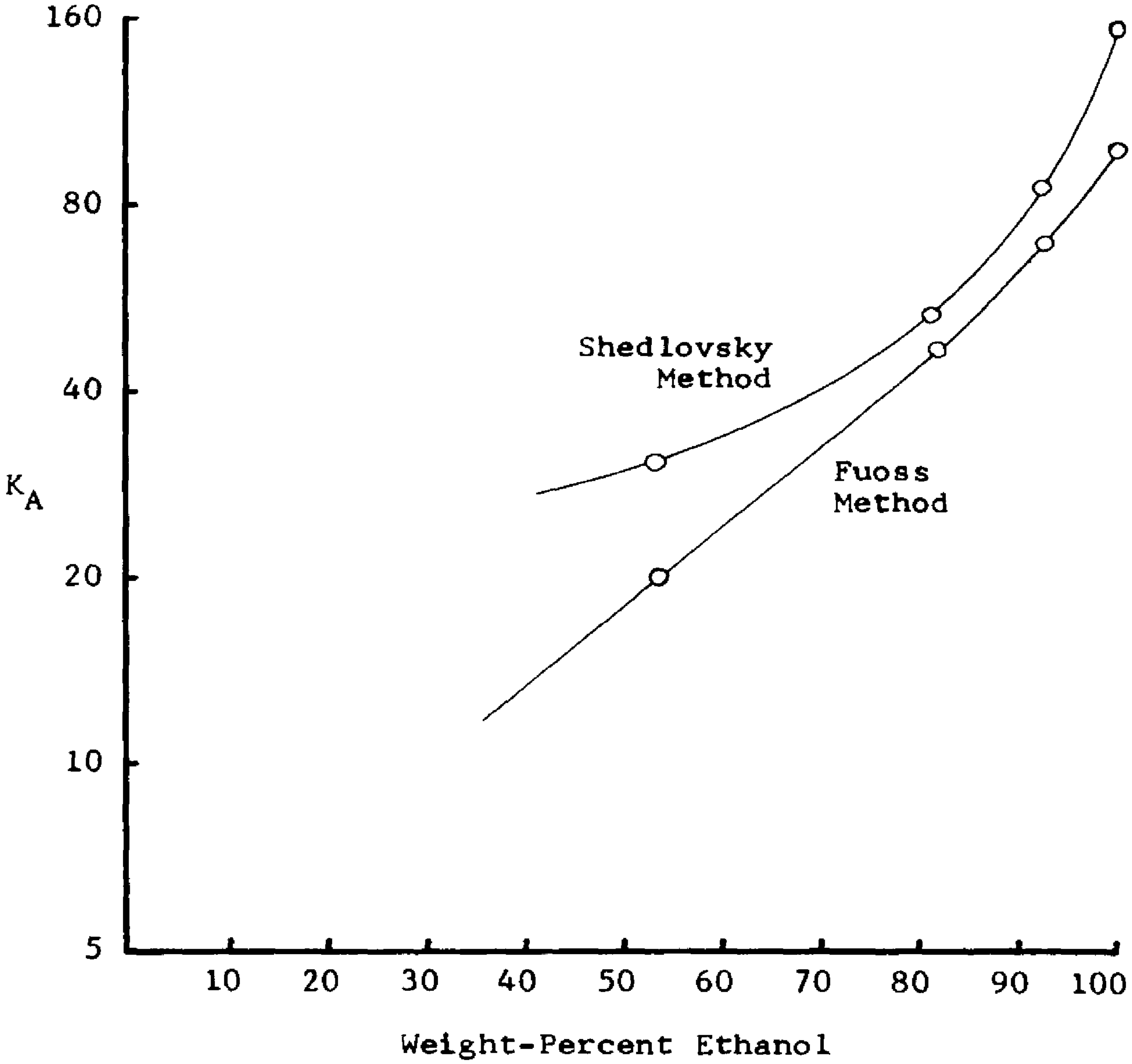

Figure 6. Comparison of association constants obtained by the Fuoss and by the Shedlovsky methods.

method appear to approach a limiting value in solvents with low ethanol content (high dielectric constant). This is unreasonable because in methanol TABPi has $K_A \approx 10$ (18) and in these solvents of low ethanol content, where the dielectric constant is still higher than in methanol, we expect a greater degree of dissociation, in fact, we can expect TABPi to be completely dissociated. This anomaly can be explained by the failure of the S(z) function to describe adequately the degree of dissociation at the concentrations used in these measurements. A comparison of degrees of dissociation obtained by the two methods is given in Table XII.

This Table illustrates what was said above regarding the degree of dissociation for the more insoluble electrolytes, KPi, $K(BPh_4)$ and $TAB(BPh_4)$, namely that at low concentrations the degree of dissociation is described equally well by both the Fuoss-Onsager and the Shedlovsky equations. As can be seen from the Table, the degree of dissociation at low concentrations obtained by both methods is in good agreement, while at higher concentrations the agreement is not as good.

Table XII. Degree of Dissociation of TABPi in 81.8 Weight-Percent Ethanol as Obtained by the Fuoss and by the Shedlovsky Method.

Concentration x 10^4	Degree of Dissociation (Fuoss)	Degree of Dissociation (Shedlovsky)	Percent Difference
5.983	0.980	0.976	0.40
7.714	0.976	0.971	0.41
10.270	0.968	0.963	0.50
12.056	0.963	0.957	0.62
14.419	0.957	0.951	0.68
16.750	0.952	0.945	0.74
18.421	0.948	0.941	0.77
20.515	0.944	0.937	0.79
22.229	0.941	0.933	0.81

Determination of Activity Coefficients

Introduction

Once the molar solubilities and the ionic association constants of our electrolytes of interest were known, the only step remaining before a calculation of their solubility (ion-activity) products was a determination of their activity coefficients. The activity coefficients for KPi, TABPi, $K(BPh_4)$ and $TAB(BPh_4)$ over the range 0 - 100 wt.-% ethanol were determined by the solubility method of Brønsted and La Mer (16). The method is based on the variation exhibited by the activity coefficient of a saturated solution when the ionic strength of the solution is increased by addition of an inert "solvent salt."

Experimental

Reagents: The electrolytes and solvents used in this section were prepared in the same manner as described in Part II. In addition, "Baker Analyzed" lithium chloride was used as a solvent salt without further purification, after drying in a vacuum oven at 110°C for forty-eight hours.

Apparatus and Procedure: The apparatus and procedure used for saturating the solutions was the same as used for the determination of solubilities. The only difference in the procedure was the addition of LiCl solvent salt to vary the ionic strength. The amount of LiCl added depended on the solubility of the electrolyte under study. Generally, the concentration of solvent salt was varied from about 2 to 200 times the solubility of the electrolyte.

Results and Discussion

The experimental determination of activity coefficients from solubility is based on the dependence of the activity coefficient of a saturated solution on its ionic strength. The dependence of the activity coefficient on the ionic strength, μ, is seen in the limiting form of the Debye-Hückel equation

$$\log f_{\pm} = -A\sqrt{\mu} \tag{94}$$

where $f_{\pm}$ is the mean ionic activity coefficient on the molar concentration scale and A is a function of the temperature and the dielectric constant of the solvent. The activity of a saturated solution is given by

$$a_{\pm}^{2} = (\alpha C f_{\pm})^{2} \tag{95}$$

where α is the degree of dissociation and C is the solubility expressed on the molar scale.

Equation (94) shows that as the ionic strength increases, the activity coefficient decreases. Since the activity of a saturated solution is constant, independent of ionic strength, a decrease in the activity coefficient will result in an increase in C so that the equality in equation (95) can be maintained.

We can write expressions similar to equation (95) for saturated solutions of an electrolyte in pure solvent,

$$a^2_{\pm,o} = (\alpha_o C_o)^2 f^2_{\pm,o} \tag{96}$$

and in the presence of a solvent salt, at ionic strength, $\underline{\mu}$.

$$a^2_{\pm,\mu} = (\alpha_\mu C_\mu)^2 f^2_{\pm,\mu} \tag{97}$$

Since $a^2_\pm$ is independent of ionic strength we can equate the two expressions. After taking common logarithms and rearranging we obtain the expression

$$\log \frac{\alpha_\mu C_\mu}{\alpha_o C_o} = \log f_{\pm,o} - \log f_{\pm,\mu} \tag{98}$$

in which $\log f_{\pm,\mu}$ can be replaced by its value from the Debye-Hückel limiting law. The resulting equation,

$$\log \frac{\alpha_\mu C_\mu}{\alpha_o C_o} = \log f_{\pm,o} + A\sqrt{\mu}, \tag{99}$$

is linear in square root of ionic strength. A plot of $\log \frac{\alpha_\mu C_\mu}{\alpha_o C_o}$ vs. $\sqrt{\mu}$ will result in a straight line the slope of which is the Debye-Hückel "$\underline{A}$" and the intercept, the logarithm of the mean ionic activity coefficient of a saturated solution of the electrolyte. Such a plot will be linear with the appropriate slope and intercept, only if the Debye-Hückel limiting law is valid for the electrolyte under study (i.e. if the solubility is low enough for the Debye-Hückel limiting law to hold). If the limiting law is not valid the plot may deviate from linearity at higher ionic strengths and the slope will not correspond to the Debye-Hückel limiting law. However, at low ionic strencth the plot may approach linearity. If this occurs the slope of the linear portion will correspond to the Debye-Hückel "A".

An alternative to equation (99) can be obtained by rearranging it to the linear form,

$$\log\ (\alpha_\mu C_\mu) = A\sqrt{\mu} + \log\ (\alpha_o C_o f_{\pm,o}) \tag{100}$$

In this case the intercept, $\log\ (\alpha_o C_o f_{\pm,o})$, directly evaluates the mean activity of the electrolyte in its saturated solution, while the slope again determines the Debye-Hückel "A". In contrast to equation (99) analysis by equation (100) does not require knowledge of the solubility in pure solvent.

Calculation of the ionic strength in the solvents of low dielectric constant was complicated by the possibility of association between the ions of the electrolyte and those of the solvent salt. For example, in the study of KPi using LiCl as the solvent salt, we have to consider not only the formation of the K^+Pi^- and Li^+Cl^- ion pairs, but the formation of the K^+Cl^- and Li^+Pi^- ion pairs as well. In a rigorous treatment, the following four equilibria and the corresponding association constants would have to be taken into account.

$$K^+ + Pi^- = K^+Pi^-, \qquad K_{KPi} = \frac{(K^+Pi^-)}{(K^+)(Pi^-)} \tag{101}$$

$$Li^+ + Cl^- = Li^+Cl^-, \qquad K_{LiCl} = \frac{(Li^+Cl^-)}{(Li^+)(Cl^-)} \qquad (102)$$

$$K^+ + Cl^- = K^+Cl^-, \qquad K_{KCl} = \frac{(K^+Cl^-)}{(K^+)(Cl^-)} \qquad (103)$$

$$Li^+ + Pi^- = Li^+Pi^-, \qquad K_{LiPi} = \frac{(Li^+Pi^-)}{(Li^+)(Pi^-)} \qquad (104)$$

The first two association constants refer to the electrolyte and the solvent salt, respectively, while the second two result from association between counterions from the two different salts. Similarly, in the determination of the activity coefficient of TABPi, we would have to account for the possibile association of Li^+Pi^- and TAB^+Cl^-, in the case of $K(BPh_4)$ for the association of K^+Cl^- and $Li^+BPh_4^-$, while for $TAB(BPh_4)$, for the formation of $Li^+BPh_4^-$ and TAB^+Cl^- ion pairs. In all cases, except for KCl, there was good reason to assume the interfering ion pairs to be completely dissociated. Only for KCl did the association constants available in the literature indicate appreciable association in ethanol-rich solvents. Our own conductance measurements on LiPi in 92.3 wt.-% ethanol revealed LiPi to be almost completely dissociated in this solvent ($K_A = 19$) so that the assumption of complete dissociation beyond 92.3 wt.-% ethanol would introduce no serious error. Both $Li(BPh_4)$ and TABBr have been reported to be completely dissociated in methanol (<u>58</u>,<u>76</u>) so that the assumption of complete dissociation of $Li(BPh_4)$ and of TABCl in ethanol-water mixtures seemed reasonable.

In this research, the results of the solubility determinations were analyzed with the aid of equation (100) in order to obtain activity coefficients for the electrolytes of interest. The activity coefficients obtained are listed in Table XIII and shown in Figure 7 for comparison with those obtained via equation (94). Figure 7 shows that only for KPi and $K(BPh_4)$ at solubilities below about $10^{-3}M$ was the limiting law valid. Thus, activity coefficients for $K(BPh_4)$ in H_2O, 10, 20 and 30 wt.-% ethanol, where the solubility was less than $10^{-3}M$, were obtained via the Debye-Hückel limiting law. Since the solubility of TABPi in water is well below $10^{-3}M$, the limiting law was assumed to hold in this solvent. This assumption permitted interpolation of activity coefficients for TABPi in ethanol-water mixtures containing less than 38.4 wt.-% ethanol (the lowest experimental point for TABPi). Table XIV lists the activity coefficients for all the electrolytes of interest at 10 wt.-% intervals.

Table XIII. Experimental Mean Molar Activity Coefficients for KPi, TABPi, $K(BPh_4)$ and $TAB(BPh_4)$ in Ethanol-Water Mixtures at 25°C.

Solvent wt.-% Ethanol	Mean Molar Activity Coefficient
KPi	
0.0	0.946
20.6	0.899
37.3	0.855
51.0	0.851
58.8	0.800
68.3	0.729
92.3	0.760
100	0.809
TABPi	
38.4	0.970
53.6	0.904
67.3	0.803
100	0.486
$K(BPh_4)$	
38.4	0.936
60.6	0.870
78.1	0.840
100	0.893
$TAB(BPh_4)$	
60.6	0.975
78.1	0.968
100	0.895

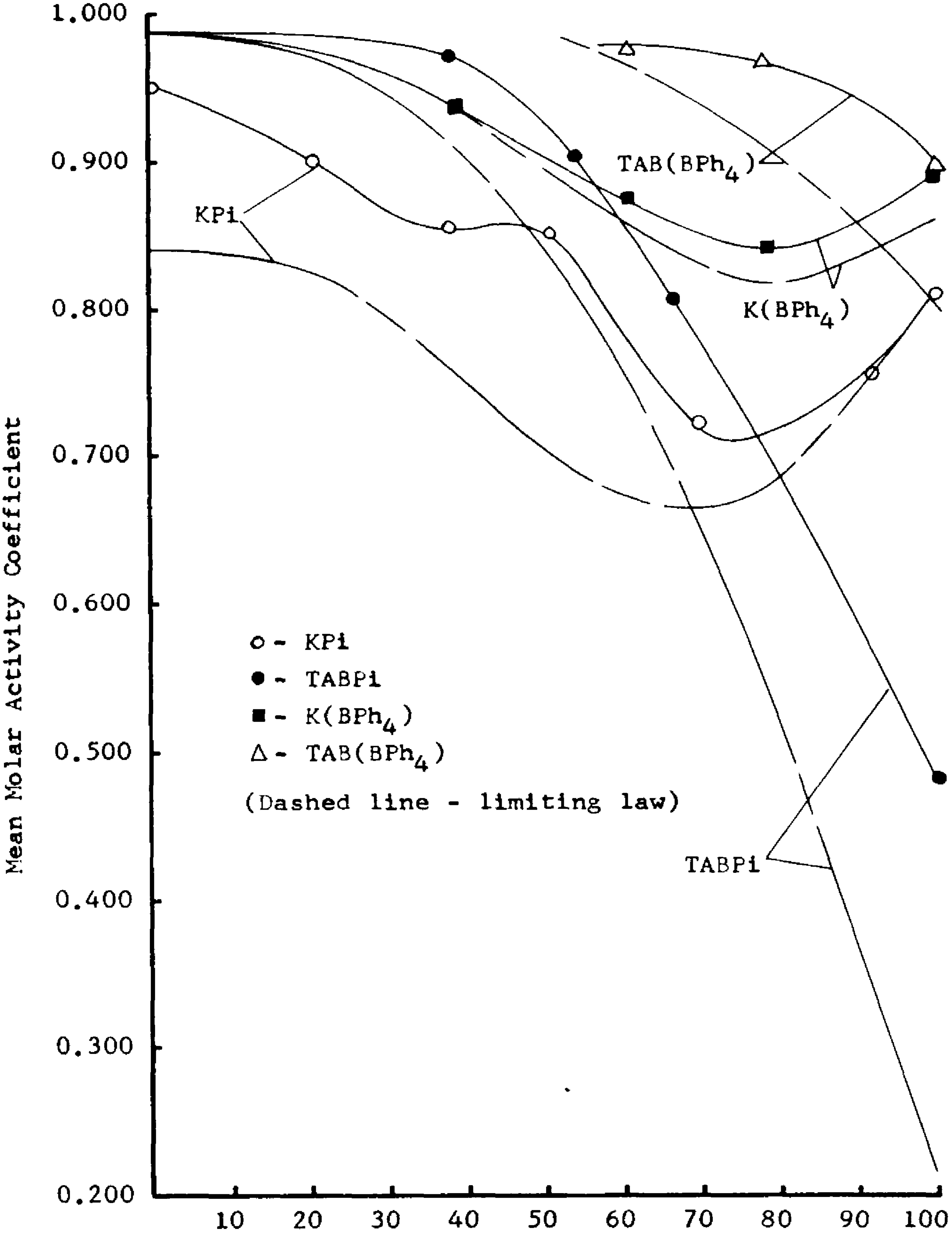

Figure 7. Comparison of activity coefficients obtained experimentally with those obtained via the Debye-Hückel limiting law.

Table XIV. Mean Molar Activity Coefficients for KPi, TABPi, $K(BPh_4)$ and $TAB(BPh_4)$ in Ethanol-Water Mixtures at 25°C Obtained by Interpolation.

Solvent wt.-% Ethanol	KPi	TABPi	$K(BPh_4)$	$TAB(BPh_4)$
0.0	0.946	0.983	0.982	--
10.0	0.931	0.983	0.978	--
20.0	0.903	0.983	0.972	--
30.0	0.868	0.982	0.958	--
40.0	0.856	0.986	0.932	--
50.0	0.852	0.926	0.901	--
60.0	0.785	0.863	0.872	0.976
70.0	0.712	0.780	0.844	0.973
80.0	0.713	0.680	0.841	0.963
90.0	0.749	0.585	0.861	0.941
100	0.809	0.486	0.893	0.895

Potentiometry Studies

Introduction

The medium effect for an electrolyte, as was pointed out in Part I, is obtainable from the standard potentials of a galvanic cell composed of electrodes reversible to the ions of the electrolyte in both aqueous and nonaqueous solutions. In this section we deal with the potentiometry necessary to arrive at the medium effects for KCl in ethanol and in ethanol-water mixtures covering the entire range of solvent composition.

The galvanic cell necessary for the determination of the medium effect for KCl is composed of one electrode reversible to potassium ions and the other electrode reversible to chloride ions. The familiar silver-silver chloride electrode serves as an excellent electrode for chloride ions, while for an electrode reversible to potassium ions we must resort to a dilute potassium amalgam. Pure metallic potassium could not be used in the alcohol-water solvents. The use, limitations and reliability of potassium-amalgam electrodes in aqueous solutions have been thoroughly studied by Armbruster and Crenshaw (4), who conclude that, within certain limitations, reliable and reproducible electromotive-force measurements can be made using either dropping, or stationary potassium-amalgam electrodes. The limitations are that amalgams must be no more dilute than 0.01 gm K/gm Hg and that for electrolyte concentrations less than 0.1N one should use the dropping rather than the stationary type of electrode.

In view of the above considerations and because of the fact that KCl has a solubility below 0.1N in alcohol-rich solvents, e.m.f. measurements on cell (IV) were carried out over the entire range of ethanol-water mixtures using a dropping amalgam electrode with a composition of about 0.02 wt.-% potassium.

$$K(Hg) \; / \; K^+, \; Cl^- \; / \; AgCl(s); \; Ag(s) \qquad (IV)$$

From these measurements the standard potential of cell (IV) is obtainable over the entire range of ethanol-water mixtures. By combining the standard potential of the above cell with the appropriate literature data, the standard potential of the potassium electrode in ethanol water mixtures can be obtained as well. To date, the standard potential of the potassium electrode in ethanol-water mixtures has not been reported in the literature. Izmaylov (45) reports the the standard potential of the potassium electrode to be -2.847 volts in ethanol.

Experimental

Reagents: The purification of the KCl and of solvents used in these measurements have been described in Part II of this thesis. Fisher Certified KOH was used without further purification. Hydrochloric acid used in the preparation of the silver chloride electrodes was purified by double distillation, collecting the middle fractions. Baker-Adamson reagent-grade HCl was diluted to the approximate composition of the HCl-H_2O azeotrope (about 6N) and then distilled. Silver oxide was prepared from analyzed grades of silver nitrate and potassium hydroxide, which were used without further purification. About 40 gm of KOH dissolved in 200 ml of distilled water were added dropwise to a vigorously stirred solution of silver nitrate (169 gm $AgNO_3$ in 1500 ml of distilled water). The silver oxide was washed forty times with distilled water. Each washing used about one liter of water. Bethlehem instrument-grade mercury was used without further purification. This mercury is "continuous vacuum triple distilled" and guaranteed to contain less than one part in ten million residue on evaporation of 2000 gm. Matheson hydrogen has was passed through a "Deoxo" gas purifier (vanadium pentoxide catalyst) to remove oxygen, then through a trap of Linde 5A molecular sieves to remove water.

Preparation of Silver Chloride Electrodes: Silver chloride electrodes of the thermal-electrolytic type were prepared by the procedure described by R. G. Bates (7). The base of each electrode consisted of a helix of number 26 platinum wire, about 7 mm long and about 2 mm in diameter, sealed into a length of 3 mm O. D. softglass tubing. The bases were cleaned in warm 6M nitric acid. A paste of well-washed silver oxide, in water, was then applied to each base and they were placed in an oven at about 450°C to reduce the silver oxide. After about 10 minutes of heating, the silver oxide was completely reduced as indicated by the white deposit of silver.

The silver bases were each electrolyzed in double-distilled 1M HCl at a current of about 10 ma for 45 minutes. A U-shaped tube was used for the electrolysis cell. A platinum wire served as the cathode (negative electrode), while the silver base served as anode (positive electrode). Electrical connection between the electrode and the electrolysis circuit was made by means of a few drops of mercury at the bottom of the glass tube. The electrodes prepared in this manner had a grey to brown color, regardless of whether the electrolysis was carried out in the light or in the dark.

After electrolysis the completed electrodes were placed in 0.05M HCl for about one day and their potentials were intercompared. Out of fourteen electrodes prepared, the potentials were found to agree with one another to better than 0.05 mv. The electrodes were then stored in distilled water.

Preparation of Potassium Amalgam: Potassium amalgam containing approximately 0.02% potassium by weight, was prepared by electrolysis of 1N KOH. The electrolysis was carried out in a vessel which functioned as a separatory funnel, so that the amalgam could be drawn off from the KOH solution. Mercury served as the cathode and a platinum wire as the anode. Nitrogen was bubbled through the mercury during the electrolysis in order to stir the amalgam. After the electrolysis was run for the required period of time, the amalgam was drawn out from the bottom of the electrolysis cell into an evacuated vessel for storage. All further transfers of the amalgam were carried out under an atmosphere of dry hydrogen.

The E.M.F. Cell: The dropping amalgam electrode is shown in Figure 8. In use, the amalgam, contained in the reservoir, was dropped from a 1-cm length of polarographic capillary at a rate which varied from about one drop per second to about one drop every five seconds. This capillary was fastened to the electrode assembly by means of a teflon tubing connector, so as to facilitate replacement if it became clogged during a run. The spent amalgam dropped through the solution, into the trap at the bottom of the electrode compartment, where it was isolated from the bulk of solution in the cell. Isolation of the spent amalgam was necessary to prevent reaction with solvent, which would lead to increased potassium-ion concentration in the solution. The reference-electrode compartment was separated from the amalgam compartment by a sintered glass disk. This was done to prevent the hydrogen used for deaeration of the solutions, from reaching the silver chloride electrodes. Hydrogen was used because it was the most readily available gas from which oxygen could be easily removed. Electrical contact with the amalgam was made by a platinum wire sealed into the neck of the electrode assembly.

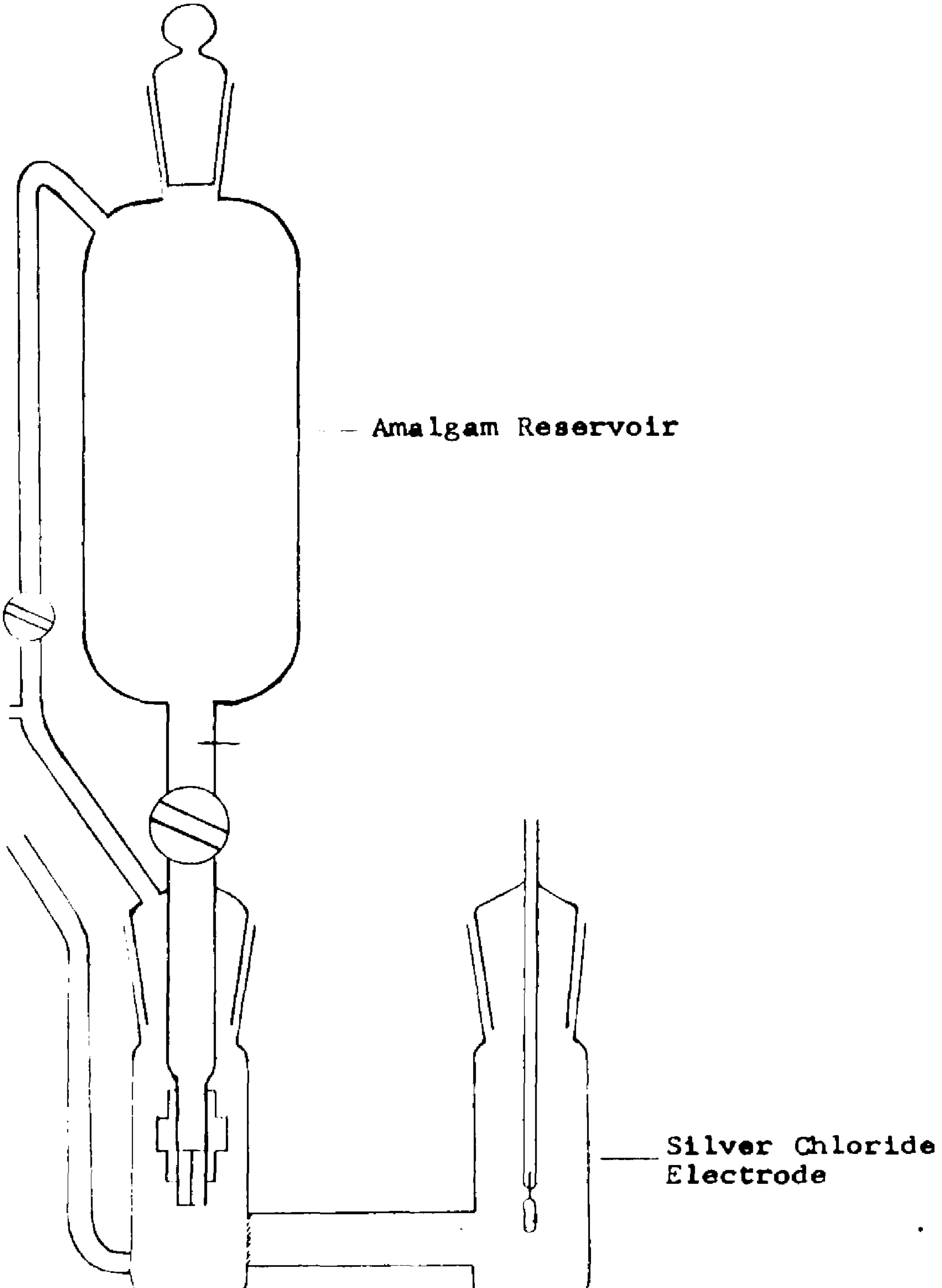

Figure 8. Cell used for potentiometric measurements.

Procedure: The 0.02% potassium amalgam was transferred to the dropping electrode assembly under an atmosphere of dry hydrogen. The solution was placed in both electrode compartments and the cell assembled. The assembled cell was placed in a water bath at 25°C, controlled to better than ±0.01°C by a Yellow Springs Instrument Co. model 72 proportional temperature controller. The actual temperature of the bath was verified by means of a certified National Bureau of Standards thermometer. Each silver-chloride electrode used was stored overnight in the KCl solution in which it was to be used for e.m.f. measurements. The hydrogen used for deaerarion was first passed through a presaturation tower containing the pure solvent.

The solutions were prepared by volumetric dilution of a stock solution. Stock solutions in all the solvents except pure ethanol were prepared by dissolving weighed portions of KCl. In absolute ethanol a saturated solution was used for the stock solution. This stock solution was analyzed for chloride gravimetrically by precipitation as silver chloride.

The potential of cell (IV) was measured when the amalgam drops were fully formed. Readings at about ten-minute intervals were taken after the cell had been in the water bath for about 15 minutes. When consecutive readings agreed to about 0.2 mv, the reading was taken as final. Generally, only 3 or 4 readings were necessary to obtain the above agreement. In a few cases readings were continued for an additional half hour after accepting a final reading based on the above criteria. In all of these cases the readings remained practically unchanged.

The measurements were carried out using an Electro Scientific Instruments model 330 Potentiometric DC Voltmeter. This instrument has an accuracy of 10 ppm of the reading. A certified Eppley Laboratories standard cell was used to check the standard cell in the instrument.

Analysis of the amalgam to determine its exact composition was accomplished by decomposing the amalgam in an excess of hot standard 0.1N H_2SO_4 and back-titrating with standard 0.1N NaOH.

Results and Discussion

The potential, E_{IV}, of cell (IV) at 25°C is given by the equation

$$E_{IV} = E^{\circ}_{IV} + 0.05916 \log a_{K(Hg)} - 0.05916 \log a_K a_{Cl} \qquad (105)$$

where $E^{\circ}_{IV} = {}_{s}E^{\circ}_{AgCl} - {}_{s}E^{\circ}_{K(Hg)}$ and $a_{K(Hg)}$ is the activity of potassium in the amalgam. Generally, the term involving $a_{K(Hg)}$ is included with E°_{IV} resulting in the equation,

$$E_{IV} = E^{\circ'} - 0.05916 \log a_K a_{Cl}. \qquad (106)$$

After accounting for incomplete dissociation and expressing the activities in terms of concentrations and activity coefficients we get

$$E_{IV} = E^{\circ\prime} - 0.1183 \log \alpha C_{KCl} - 0.1183 \log f_{\pm} \qquad (107)$$

where α is the degree of dissociation and $f_{\pm}$ is the mean molar ionic activity coefficient of KCl. The degree of dissociation is obtainable from the conductance data of Hawes and Kay (<u>36</u>), who give association constants, K_A, for KCl over the range of ethanol-water mixtures where ionic association is present. The degree of dissociation is given by the equation

$$\alpha = \frac{-1 + (1 + 4K_A Cf_{\pm}^2)^{\frac{1}{2}}}{2K_A Cf_{\pm}^2} \qquad (108)$$

The activity coefficient, $f_{\pm}$, used to calculate α, is obtained via the extended Debye-Hückel equation

$$\log f_{\pm} = \frac{-A\sqrt{\mu}}{1 + B\mathring{a}\sqrt{\mu}} \qquad (109)$$

in which the ion-size parameter for a given solvent is obtained by interpolation of the values of $\mathring{a}_J$ given by Hawes and Kay (<u>36</u>). For purposes of extrapolating $E^{\circ\prime}$, the Debye-Hückel limiting law is used to express the activity coefficient in equation (107). Equation (107) is then rearranged to the form

$$E' = E^{\circ\prime} + 0.1183A\sqrt{\mu} \qquad (110)$$

where $$E' = E_{IV} + 0.1183 \log \alpha C_{KCl}. \qquad (111)$$

Then from a plot of E' vs. $\sqrt{\mu}$, the standard potential $E^{\circ\prime}$ is obtained by extrapolation to zero ionic strength.

It should be emphasized that the $E^{\circ\prime}$ obtained by such an extrapolation is not the true standard potential of the cell as it includes a term involving the activity of potassium in the amalgam. This activity will be different for different concentrations of potassium resulting in a different value for $E^{\circ\prime}$. The true standard potential of cell (IV) is obtained by subtracting from $E^{\circ\prime}$ the term involving the activity of potassium in the amalgam

$$E^{\circ}_{IV} = E^{\circ\prime} - 0.05916 \log a_{K(Hg)} \qquad (112)$$

It is the standard potential obtained via equation (112) which is used to calculate medium effects. If the same amalgam were used to determine $E^{\circ\prime}$ for both the aqueous and nonaqueous solvents, the term $0.05916 \log a_{K(Hg)}$ would be the same in both cases and $E^{\circ\prime}$ alone would suffice for the calculation of medium effects. A table of activities of potassium in amalgams as a function of mole fraction of potassium is given by Armbruster and Crenshaw (4). From this table we interpolate values of $a_{K(Hg)}$ for our amalgams. Table XVI lists the values of $E^{\circ\prime}$, $a_{K(Hg)}$ and E°_{IV} obtained in this study. The standard potentials on the molal scale were obtained from the molar E° and the density of the solvent via the equation

$$E^{\circ}_{molal} = E^{\circ}_{molar} - \frac{2RT}{nF} \ln d_{\circ} \qquad (113)$$

The value of E° listed for cell (IV) in water is the average

Table XV. Standard Potential of Cell (IV) in Water at 25°C.

Amalgam wt.-% K	$a_{K(Hg)}$	$E^{\circ\prime}$ (molar)	E° (molar)
0.0234	0.001779	2.030(5)	2.193(2)
0.0242	0.001377	2.023(6)	2.192(9)
0.0372	0.002206	2.036(8)	2.193(9)
0.0152	0.000821	2.010(8)	2.193(4)
0.0299	0.002116	2.033(8)	2.192(0)
0.0206	0.001139	2.023(0)	2.197(1)

Table XVI. Standard Potential of Cell (IV) in Ethanol-Water Mixtures at 25°C.

Solvent wt.-% Ethanol	Amalgam wt.-% K	$a_{K(Hg)}$	$E^{\circ\prime}$	Standard Potential	
			(molar)	(molar)	(molal)
Water	Average value from Table XV			2.1931	2.193(2)
15.0	0.0234	0.001779	2.0008	2.1635	2.164(9)
20.8	0.0242	0.001377	1.9859	2.1552	2.157(0)
40.0	0.0372	0.002206	1.9491	2.1062	2.109(8)
60.2	0.0152	0.000821	1.8667	2.0493	2.055(5)
77.7	0.0299	0.002116	1.8287	1.9869	1.995(6)
92.5	0.0299	0.002116	1.7173	1.8755	1.886(6)
100	0.0206	0.001139	1.6420	1.8161	1.828(5)

of five determinations, the results of which are summarized in Table XV.

The true standard potential of the potassium electrode in any solvent is arrived at by adding the standard potentials of the following cells:

$$K(Hg)\ /\ K^+,\ I^-(\text{ethylamine})\ /\ K(s) \qquad (V)$$

$$Ag(s);\ AgCl(s)\ /\ K^+,\ Cl^-(\text{solvent SH})\ /\ K(Hg) \qquad (VI)$$

$$Pt(s);\ H_2(g)\ /\ H^+, Cl^-(\text{solvent SH})\ /\ AgCl;\ Ag(s) \qquad (VII)$$

The sum of the standard potentials of cells (V), (VI) and (VII) gives the standard potential, ${}_sE^\circ_K$, of the potassium electrode in the solvent SH (vs. ${}_sE^\circ_H = 0$ in the same solvent).

$${}_sE^\circ_K = E^\circ_V + E^\circ_{VI} + E^\circ_{VII} \qquad (114)$$

Lewis and Keyes (61) measured the potential of cell (V) using an amalgam containing 0.2216% potassium by weight. Since the potential of a cell of this type is independent of concentration of electrolyte and independent of solvent (provided the solvent does not react with the potassium), the standard potential of this cell is given by

$$E^\circ_V = E - 0.05916 \log a_{K(Hg)} \qquad (115)$$

where $a_{K(Hg)}$ is the activity of potassium in the amalgam. From the table of Armbruster and Crenshaw (4) we interpolate the value of $a_{K(Hg)} = 0.02412$ for the Lewis and Keyes 0.2216% amalgam (mole fraction of potassium = 0.011267). The measured potential of cell (V) is -1.0478 volts (corrected to the new international voltage standard). Substituting the above values for $\underline{E}$ and $a_{K(Hg)}$ into equation (115) gives $E^{\circ}_{V} = -0.9521$ volts.

Since cell (VI) is actually the reverse of cell (IV), the true standard potential of cell (VI) is $-E^{\circ}_{IV}$. E°_{IV} is listed in the last column of Table XVI.

The standard potential of cell (VII) is obtained in this study by interpolation of the available literature values of E° for cell (I). Table XVII summarizes the standard potentials of the potassium electrode obtained in this study and compares them with those available in the literature.

Table XVII. Molal Standard Potentials of Potassium Electrode in Ethanol-Water Mixtures at 25°C.

Solvent wt.-% Ethanol	Standard Potential, ${}_{s}E^{\circ}_{K}$		Reference
	This Study	Other Workers	
0.0	-2.923	-2.9234	(4)
		-2.926	(15)
15.0	-2.907		
20.8	-2.908		
40.0	-2.867		
60.2	-2.837		
77.7	-2.808		
92.5	-2.768		
100	-2.862	-2.847	(45)

Part III. Interpretation and Application of Over-All Results.

Medium Effects for Electrolytes

Now, using the results of Part II and literature data, we have all the information necessary to arrive at medium effects for the electrolytes of interest: KPi, TABPi, $K(BPh_4)$, $TAB(BPh_4)$, KCl and HCl. Tables XVIII and XIX summarize this information and give the logarithms of the medium effects obtained in ethanol-water mixtures.

For KPi, TABPi and $K(BPh_4)$, medium effects on the molal activity scale were obtained by calculating first the mean molar activity, $\alpha C_s f_\pm$, and then converting it to mean molal activity by dividing the former by the density of solvent. The molar solubility, C_s, the degree of dissociation, α, and the mean molar activity coefficient, $f_\pm$, in a given solvent were obtained by interpolation of the results of Part II. The degree of dissociation was obtained from interpolated association constants via equation (108). Molal solubility products (ion-activity products) were then calculated in each solvent and medium effects on the molal activity scale were obtained via equation (26). The logarithm of the medium effect for $TAB(BPh_4)$ over the range of ethanol-water mixtures was obtained via equation (65) since, as was pointed out earlier, we could not determine its solubility in water and in the water-rich solvents. Medium effects for KCl and HCl were calculated from the standard potentials of cells (IV)

Table XVIIIa. Logarithm of Medium Effects for KPi in Ethanol-Water Mixtures at 25°C.

Solvent wt.-% Ethanol	Molar Solubility x 10^3	Mean Molar Activity Coefficient	Degree of Dissociation	log ${}_m\gamma_{KPi}$
0.0	24.2	0.946	1.000	0.000
10.0	18.0	0.931	1.000	0.256
20.0	16.0	0.930	1.000	0.373
30.0	17.9	0.868	1.000	0.295
40.0	20.5	0.856	1.000	0.173
50.0	22.1	0.852	1.000	0.090
60.0	19.1	0.785	1.000	0.266
70.0	14.2	0.712	0.972	0.609
80.0	7.64	0.713	0.953	1.139
90.0	3.23	0.749	0.913	1.854
100	1.04	0.809	0.859	2.794

Table XVIIIb. Logarithm of Medium Effects for TABPi in Ethanol-Water Mixtures at 25°C.

Solvent wt.-% Ethanol	Molar Solubility $\times 10^3$	Mean Molar Activity Coefficient	Degree of Dissociation	$\log {}_m\gamma_{TABPi}$
0.0	0.226	0.983	0.998	0.000
10.0	0.282	0.983	0.997	-0.206
20.0	0.406	0.983	0.996	-0.534
30.0	0.903	0.982	0.989	-1.236
40.0	2.30	0.968	0.968	-2.035
50.0	5.25	0.926	0.930	-2.699
60.0	10.3	0.863	0.870	-3.187
70.0	18.4	0.780	0.794	-3.547
80.0	29.4	0.680	0.712	-3.766
90.0	43.3	0.585	0.629	-3.890
100	62.7	0.486	0.551	-3.967

Table XVIIIc. Logarithm of Medium Effects for $K(BPh_4)$ in Ethanol-Water Mixtures at 25°C.

Solvent wt.-% Ethanol	Molar Solubility x 10^3	Mean Molar Activity Coefficient	Degree of Dissociation	log ${}_{m}\gamma K(BPh_4)$
0.0	0.174	0.982	1.000	0.000
10.0	0.220	0.978	1.000	-0.215
20.0	0.342	0.972	1.000	-0.605
30.0	0.670	0.958	1.000	-1.191
40.0	1.45	0.932	1.000	-1.854
50.0	2.37	0.901	1.000	-2.273
60.0	2.81	0.872	1.000	-2.415
70.0	2.90	0.844	1.000	-2.437
80.0	2.12	0.841	1.000	-2.187
90.0	1.05	0.861	0.995	-1.620
100	0.504	0.893	0.862	-0.920

Table XVIIId. Logarithm of Medium Effect for TAB(BPh_4) in Ethanol-Water Mixtures at 25° C.

Solvent wt.-% Ethanol	log $_m\gamma$ TAB(BPh_4)
0.0	0.000
10.0	-0.677
20.0	-1.511
30.0	-2.722
40.0	-4.062
50.0	-5.062
60.0	-5.868
70.0	-6.593
80.0	-7.091
90.0	-7.364
100	-7.681

Table XIXa. Logarithm of Medium Effects for KCl in Ethanol-Water Mixtures at 25°C.

Solvent wt.-% Ethanol	$E^{\circ\prime}_{\mathrm{cell(IV)},H_2O}$	$E^{\circ\prime}_{\mathrm{cell(IV),nonaq.}}$	$\log {}_m\gamma_{KCl}$
	(molal scale)		
0.0	--	--	0.00
10.0	--	--	0.30
15.0	2.0306	2.0022	0.480 *
20.8	2.0237	1.9877	0.608 *
30.0	--	--	1.05
40.0	2.0369	1.9527	1.423 *
50.0	--	--	1.86
60.2	2.0109	1.8729	2.333 *
70.0	--	--	2.87
77.7	2.0339	1.8374	3.313 *
80.0	--	--	3.61
90.0	--	--	4.79
92.5	2.0339	1.7284	5.164 *
100	2.0231	1.6544	6.232 *

* obtained experimentally (all others obtained by interpolation)

Table XIXb. Logarithm of Medium Effects for HCl in Ethanol-Water Mixtures at 25°C.

Solvent wt.-% Ethanol	$E^\circ_{cell(I)}$ (molal scale)	Reference	log $_m\gamma_{HCl}$
0.0	0.22234	(8)	0.000
10.0	0.21467	(67)	0.130
20.0	0.20757	(67)	0.2479
30.0	0.20033	(34)	0.3721
40.0	0.19454	(34)	0.4699
46.0	0.1928	(17)	0.499
50.0	0.18588	(34)	0.6151
60.0	0.175	(73)	0.79
70.0	----	--	1.12 *
71.9	0.1554	(17)	1.13
80.0	0.129	(73)	1.57
88.5	0.1053	(17)	1.978
90.0	----	--	2.15 *
94.3	0.066	(73)	2.64
98.0	0.0215	(17)	3.394
100	-0.08138	(80)	5.1340

* obtained by interpolation.

and (I), respectively, using an equation analogous to equation (34).

In the case of KCl, medium effects were determined from the $E^{\circ\prime}$ for cell (IV), as the same amalgam was used for measurements in both aqueous and nonaqueous solutions. In this manner we avoid any uncertainties in determining the activity of potassium in the amalgam by interpolation from the table of Armbruster and Crenshaw (4). The standard potential of cell (I) in ethanol-water mixtures covering the entire range were available in the literature (8,17,34, 67,73,80). Figure 9 shows the logarithms of the medium effects for all the electrolytes studied.

At this point we can note that the medium-effect curves for KPi, $K(BPh_4)$, TABPi, $TAB(BPh_4)$ exhibit the same general trends as do the solubility curves in Figure 3. Therefore, the same conclusions regarding solvation properties of the individual ions which were arrived at in Part II are corroborated here. Introduction of the degree of dissociation and activity coefficient did not change the qualitative picture of solvation of the individual ions. It is difficult, on the basis of medium effects for complete electrolytes alone, to predict the solvation properties of the chloride and hydrogen ions.

Qualitatively then, the assumption used by previous workers (52,78), that the difference in solvation energy in two solvents can be evaluated from solubility ratios as well as from activity product ratios, is well founded in the light of the present studies.

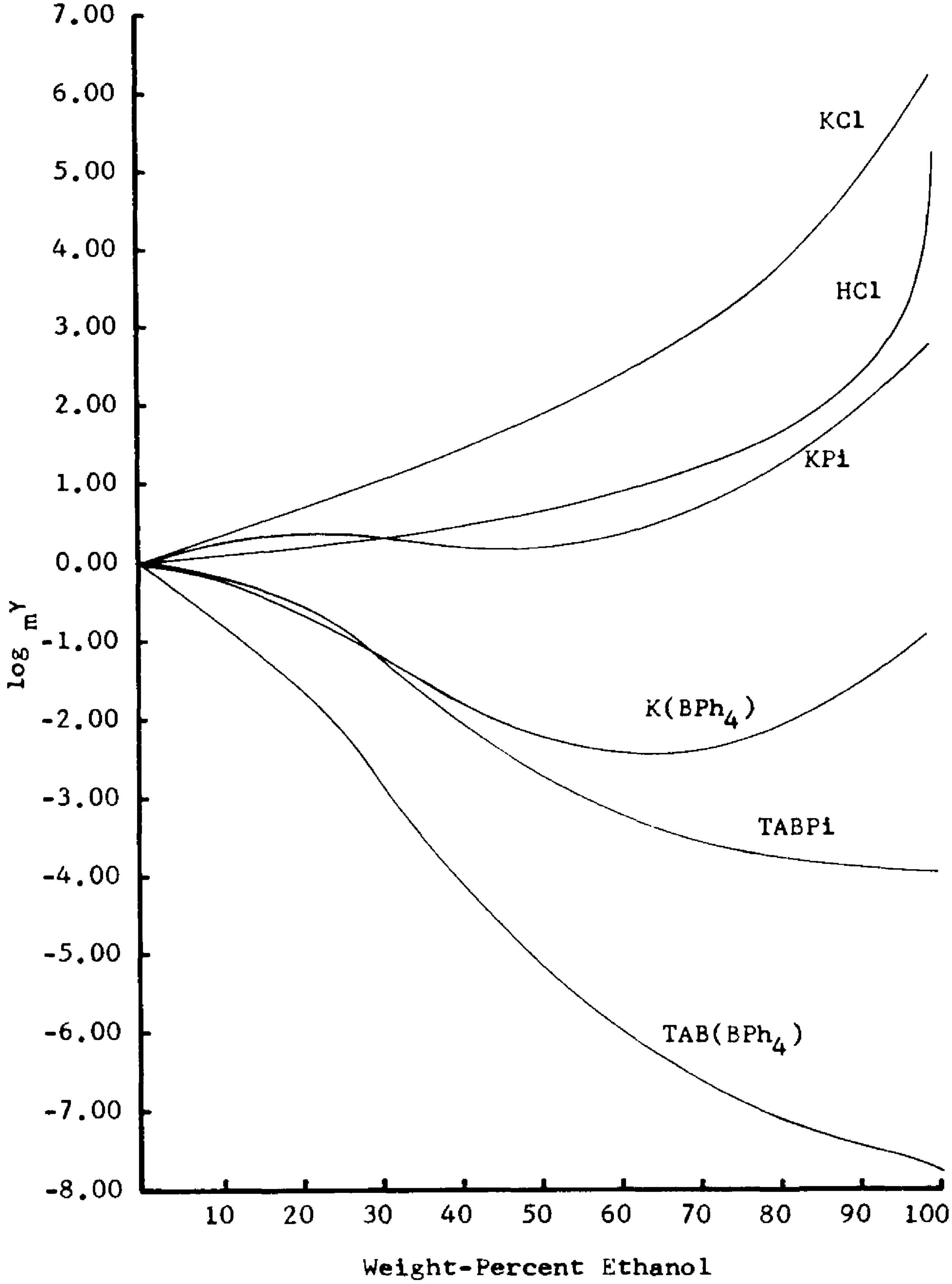

Figure 9. Logarithm of medium effects for electrolytes studied in ethanol-water mixtures at 25°C.

An interesting calculation which can be carried out once the medium effect for an electrolyte in a given solvent is known, is the calculation of its activity product in water using the measured activity product in the given nonaqueous solvent (71). In this research, as was pointed out earlier, the solubility of $TAB(BPh_4)$ was unaccessible in solvents containing less than about 35 wt.-% ethanol because of its low value. However, the medium effects for $TAB(BPh_4)$ in all ethanol-water mixtures could be arrived at by combination of the medium effects for KPi, TABPi and $K(BPh_4)$ via equation (65). As a result we have both medium effects and solubility products in the nonaqueous solvents. From this data we can calculate solubility products for $TAB(BPh_4)$ in water as follows:

$$K^{water}_{sp,TAB(BPh_4)} = {}_{m}\gamma_{TAB(BPh_4)}\, K^{nonaq.}_{sp,TAB(BPh_4)} \qquad (116)$$

Table XX shows the results of this calculation. The average value of 2.00×10^{-14} resulting for the ion-activity product is in fair agreement with the value of 1.18×10^{-14} obtained by Popovych and Friedman (71) by the same indirect procedure, using methanol as the nonaqueous solvent. It should be noted, however, that the activity coefficients for the methanolic solutions of electrolytes were estimated by the above authors from the Debye-Hückel equation, while in the present research they were determined experimentally.

Table XX. Molal Solubility Product for TAB(BPh_4) in Water at 25°C Obtained via Equation (116).

Solvent wt.-% Ethanol	Solubility Product in Nonaqueous Solvent	Medium Effect $_m\gamma_{TAB(BPh_4)}$	Solubility Product in H_2O
60.6	2.07×10^{-8}	1.15×10^{-6}	2.38×10^{-14}
78.1	1.85×10^{-7}	9.55×10^{-8}	1.77×10^{-14}
100	8.84×10^{-7}	2.08×10^{-8}	1.84×10^{-14}
		Average value	2.00×10^{-14}

Medium Effects for Single Ions

The single-ion medium effects for the TAB^+ and BPh_4^- ions can now be arrived at by employing our extrathermodynamic assumption (equation 61), namely that the medium effects for these two ions are equal. The medium effect for either one of these reference ions then provides us with the key to medium effects for all other single ions.

In this research the medium effects for the remaining ions of interest were obtained as follows:

$$\log {}_m\gamma_K = \log {}_m\gamma_{K(BPh_4)} - \log {}_m\gamma_{BPh_4} \tag{117a}$$

$$\log {}_m\gamma_{Pi} = \log {}_m\gamma_{KPi} - \log {}_m\gamma_K \tag{117b}$$

$$\log {}_m\gamma_{Cl} = \log {}_m\gamma_{KCl} - \log {}_m\gamma_K \tag{117c}$$

and

$$\log {}_m\gamma_H = \log {}_m\gamma_{HCl} - \log {}_m\gamma_{Cl} \tag{117d}$$

The results obtained at 10 wt.-% intervals are listed in Table XXI and shown in Figure 10. Figure 10 reveals the quantitative picture of solvation energies of the individual ions. The behavior of the K^+, TAB^+ and BPh_4^- ions appears to be much the same as predicted from solubility and from medium effects for complete electrolytes. The picrate ion, on the other hand, does not experience a very large change

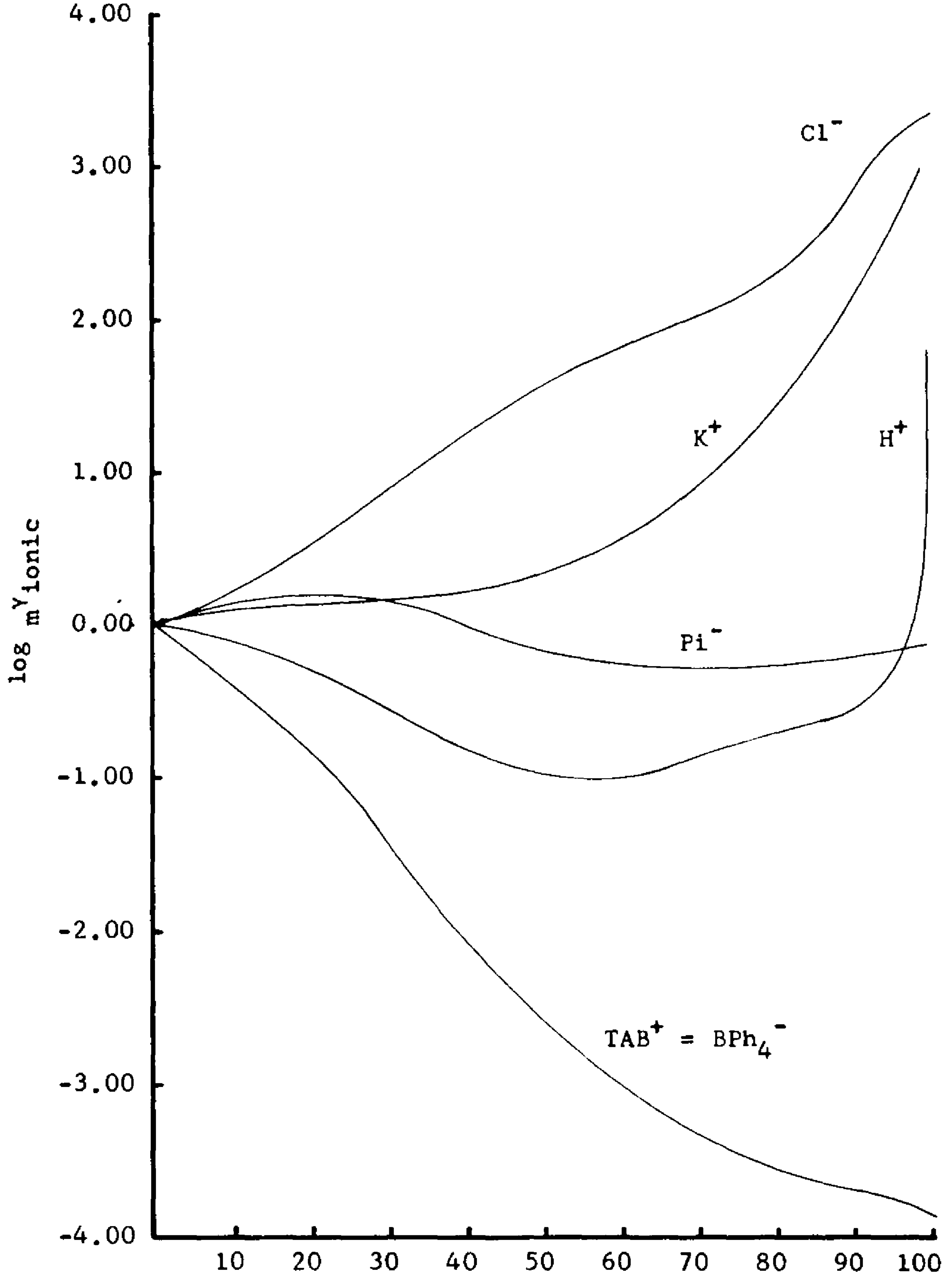

Figure 10. Logarithm of medium effects for single ions in ethanol-water mixtures at 25°C.

Table XXI. Logarithm of Medium Effects for Single Ions in Ethanol-Water Mixtures at 25°C.

Solvent wt.-% Ethanol	log $_{m}\gamma$				
	TAB^+, BPh_4^-	K^+	Pi^-	Cl^-	H^+
0.0	0.000	0.000	0.000	0.000	0.000
10.0	-0.338	0.123	0.133	0.18	-0.05
20.0	-0.755	0.150	0.223	0.53	-0.28
30.0	-1.361	0.170	0.125	0.88	-0.51
40.0	-2.031	0.177	-0.004	1.246	-0.78
50.0	-2.531	0.258	-0.168	1.60	-0.98
60.0	-2.934	0.519	-0.253	1.79	-1.00
70.0	-3.297	0.860	-0.251	2.01	-0.89
80.0	-3.546	1.359	-0.220	2.25	-0.68
90.0	-3.682	2.062	-0.208	2.73	-0.58
100	-3.840	2.920	-0.126	3.312	+1.822

in solvation energy on transfer from water to any of the ethanol-water mixtures. On addition of ethanol to water, the solvation energy of the Pi^- ion at first increases (positive medium effect), reaching a maximum at about 20 wt.-% ethanol (~8 mole-%). At about 40 wt.-% ethanol (~21 mole-%) the solvation energy is the same as in water ($\log {}_m\gamma_{Pi} = 0$). Beyond 40 wt.-% ethanol the solvation energy decreases to a minimum at about 65 wt.-% ethanol (40 mole-%) and then again increases, as we go to 100% ethanol, to almost the same value as in water. A comparison of single-ion medium effects obtained by various authors, in ethanol, is given in Table XXII.

In order to place in proper perspective our analysis of the medium effects for single ions estimated in the present study, it may be useful to recapitulate briefly the up-to-date status of the literature on this subject. As we have seen in the preceeding section, the logarithms of medium effects, $\log {}_m\gamma$, for electrolytes composed of simple inorganic ions (e.g., KCl, HCl) are positive in ethanol and ethanol-water mixtures. The same is known to be true for other alcohols and alcohol-water mixtures (43). A positive value of $\log {}_m\gamma$ indicates that the electrolyte as a whole exists in a preferred (lower) energy state in water as compared to the nonaqueous medium. Medium effects for complete electrolytes are calculated directly from experimental data (equations 26, 34) and, of course, do not involve any extra-thermodynamic assumptions.

Table XXII. Comparison of Logarithm of Ionic Medium Effects Obtained by Different Authors in Ethanol at 25°C.

Ion	log $_m\gamma$		
	This Study	Izmaylov (50)	Bjerrum and Larsson (12)
H^+	1.822	3.9	2.5
K^+	2.920	4.0	4.1
Cl^-	3.312	1.2	2.5
Br^-	2.452	1.2	1.8
Pi^-	-0.126	-	-
TAB^+, BPh_4^-	-3.840	-	-

Such assumptions, however, must be introduced whenever we raise the question of how to apportion the observed medium effect of an electrolyte between its ionic constituents. We need medium effects for single ions to provide solutions to the three interrelated problems to which this thesis is largely devoted (cf. page 1). The different approaches to the estimation of medium effects for single ions have led to considerable discrepancies in the results, especially in the case of alcohol-water mixtures. A polarization of opinion has developed in this field on the basis of two drastically different sets of numerical values for the log $_m\gamma$'s estimated by different methods.

Thus, according to Izmaylov and Aleksandrov (51), the logarithm of the medium effect for the hydrogen ion is positive throughout the ethanol-water (Table XXIII) and the methanol-water (Table XIV) ranges. For ethanol-water mixtures the above estimates were corroborated to a fair degree via an independent method by Gutbezahl and Grunwald (33) (Table V and XXIII). Although none of the above sources focused on the behavior of potassium and chloride ions in alcohol-water media, it is a simple matter to show (equation 117c, d) that their approaches lead to positive values of the log $_m\gamma$'s for these two ions as well. Consequently, the independent methods of Izmaylov and Grunwald arrive at the same conclusion, namely that all three ions considered here - potassium, hydrogen and chloride - make positive contributions to the over-all medium effects of their correspond-

Table XXIII. Comparison of Logarithm of Medium Effects for the Hydrogen Ion in Ethanol-Water Mixtures Estimated by Different Methods.

Solvent wt.-% Ethanol	log $_m\gamma_H$ estimated by			-H for 1 M HCl calc. by Braude and Stern (14)
	Gutbezahl and Grunwald (33)	Izmaylov and Aleksandrov (51)	This Study	
0.0	0.000	0.00	0.00	+0.33
10.0	---	0.09	-0.05	--
16.3	---	--	-0.18	-0.03
20.0	-0.006	0.17	-0.28	--
25.8	---	--	-0.43	-0.53
30.0	---	--	-0.51	--
35.0	0.017	--	-0.65	--
40.0	---	0.33	-0.78	--
50.0	0.211	0.42	-0.98	--
54.4	---	--	-1.00	-0.85
60.0	---	0.60	-1.00	--
65.0	0.485	--	-0.97	-0.94
70.0	---	0.80	-0.89	--
72.0	---	0.87	-0.83	--
75.9	---	--	-0.77	-0.94
80.0	1.077	1.10	-0.68	--
87.8	---	--	-0.64	-0.74
88.5	---	1.50	-0.63	--
90.0	---	2.10	-0.58	--
93.5	---	1.86	-0.50	--
95.8	---	2.14	-0.33	--
98.0	---	2.45	-0.08	--
100	4.603	4.2, 4.1	+1.822	+0.39

Table XXIV. Comparison of Logarithms of Medium Effects for the Hydrogen Ion in Methanol-Water Mixtures Estimated by Different Methods.

Solvent wt.-% Methanol	log ${}_{m}\gamma_{H}$ estimated by		
	Izmaylov and Aleksandrov (51)	Feakins and Watson (21) *	De Ligny and Alfenaar (20) *
0.0	0.00	0.000	0.000
10.0	--	-0.319	-0.188
20.0	0.14	--	--
30.0	0.22	--	--
40.0	0.32	--	--
43.12	--	-1.61	--
43.17	--	--	-1.02
50.0	0.43	--	--
60.0	0.52	-2.42	--
70.0	0.74	--	--
80.0	0.95	--	--
88.0	--	--	-1.98
90.0	1.45	-4.18	--
100	3.21	-1.83	-0.88

* Calculated from the ΔG's given in the originals.

ing electrolytes, HCl and KCl in alcohol-water media.

A sharply dissenting conclusion was reached on this point by both Feakins and Watson (21) and de Ligny and Alfenaar (20). Their independent extrathermodynamic approaches to the estimation of medium effects for single ions in methanol-water mixtures (discussed in Part I of this thesis) yielded negative values for the log $_m\gamma$'s of hydrogen and alkali-metal cations. Accordingly, they obtained large positive values for the log $_m\gamma$'s of halide ions to account for the observed positive logarithms of medium effects for the complete electrolytes. They concluded that cations exist in lower free-energy states in methamol-water mixtures than in water. Conversely, the transfer of halides from water to methanol-water media is energetically disfavored. A similar conclusion was reached by Grunwald, Baughman and Kohnstam (31) in their study of free-energy changes limited to approximately 50-50 dioxane-water mixtures.

None of the above authors reported any work in ethanol-water mixtures, but Braude and Stern (14) in studying the Hammett acidity function H for HCl solutions in mixtures of ethanol, dioxane and acetone with water, observed minima in the acidity function roughly around the 50 mole-% composition with respect to the nonaqueous solvent (72 wt.-% for ethanol) for each of the mixtures. The conclusion of Braude and Stern was that water is more basic in mixtures with other solvents than it is in the pure liquid state. This increase in the effective proton affinity of the water molecules is believed to be brought about by a destruction of water structure, which exposes a larger number of basic sites on the water molecules for bonding with protons. (Calculations by Paabo, Bates and Robinson (66) point to the existence of a basicity maximum at about 60 wt.-% (46 mole-%) of methanol in water.) After about 80 mole-% (91 wt.-% for ethanol), the acidity functions in each of the solvent mixtures rise steeply towards their values in the pure nonaqueous media, presumably due to replacement of hydronium ions with the corresponding nonaqueous oxonium ions.

By way of review, Bates and Robinson (10) summarize the present status of knowledge by stating that in aqueous mixtures containing less than 80 wt.-% methanol, the proton exists in a lower energy state than in the aqueous solvent. On the other hand, Feakins and Watson (21) and de Ligny and Alfenaar (20) extend this conclusion all the way up to 100% methanol. This amounts to saying that methanol is more basic than water, which is in direct contradiction to general opinion. Nevertheless, this dissenting opinion received strong support in the recent review by Franks and Ives (23). It should be noted, however, that even in the last two studies the free energy of the proton passes through a minimum at about 90 wt.-% methanol, followed by a sharp upward swing in the region of pure methanol.

Our results for the medium effects of the hydrogen ion in ethanol-water mixtures are compared with the literature values in Table XXIII. The Hammett acidity function H in the last column is related to log ${}_{m}\gamma_{H}$ as follows. In any solution characterized by the acidity function $\underline{H}$, the negative logarithm of hydrogen-ion activity on the aqueous scale, pa_{H}, is given by

$$pa_{H} = H + \log \frac{{}_{s}\gamma_{B}}{{}_{s}\gamma_{BH^{+}}} + \log \frac{{}_{m}\gamma_{B}}{{}_{m}\gamma_{BH^{+}}} \tag{118}$$

but

$$pa_{H} = pm_{H} - \log {}_{s}\gamma_{H} - \log {}_{m}\gamma_{H} \tag{119}$$

where m_{H} is the molality of hydrogen ions in solution and the subscripts $\underline{B}$ and BH^{+} refer to the basic and the acidic forms of the Hammett indicator, respectively. For a solution with an analytical concentration of HCl equal to m_{HCl} and a degree of dissociation α, we obtain:

$$\log {}_{m}\gamma_{H} = -H - \log m_{HCl} - \log \alpha - \log {}_{s}\gamma_{H} + \log \frac{{}_{s}\gamma_{BH^{+}}}{{}_{s}\gamma_{B}} + \log \frac{{}_{m}\gamma_{BH^{+}}}{{}_{m}\gamma_{B}}. \tag{120}$$

Since in the last column of Table XXIII the HCl is 1 molar, we introduce densities of solvents $\underline{d}_{o}$ to convert to molality; finally obtaining:

$$\log {}_{m}\gamma_{H} = -H - \log d_{o} - \log \alpha - \log {}_{s}\gamma_{H} + \log \frac{{}_{s}\gamma_{BH^{+}}}{{}_{s}\gamma_{B}} + \log \frac{{}_{m}\gamma_{BH^{+}}}{{}_{m}\gamma_{B}} \tag{121}$$

If we now apply the rough approximation inherent in the use of the Hammett acidity function, that the last two activity-coefficient ratios in the above equation deviate little from unity, then the function -H will differ from log $_m\gamma_H$ in each medium mainly by the degree of dissociation and the salt-effect activity coefficient of the hydrogen ion. The density correction is, of course, highest for pure ethanol, where log $d_\circ$ = -0.1. Using Izmaylov's activity coefficient for 1M HCl in ethanol (<u>44</u>), $\gamma_{\pm,HCl} = 0.177$ as an estimate of $_s\gamma_H$, we can calculate from the data of Braude and Stern (<u>14</u>), that for pure ethanol, log $_m\gamma_H$ should be more positive than -H by about 0.9 log units, yielding a value of +1.3, as compared to our value of +1.8 (the last two terms in equation (121) are disregarded in this calculation). In general we would expect the combination of log $d_\circ$, log α and log $_s\gamma_H$ to move -H increasingly negative relative to log $_m\gamma_H$, which is indeed observed. Thus, it appears that at least semiquantitatively, the acidity function reported by Braude and Stern reflects the same variation of solvent proton affinity as do our own estimates of log $_m\gamma_H$'s.

Because Feakins and Watson and de Ligny and Alfenaar reported on work in methanol-water mixtures only, we can compare the present results with theirs only in a qualitative manner, by assuming that findings in ethanol-water mixtures by a given method would parallel those for methanol-water mixtures. Indeed, Izmaylov's medium effects, log $_m\gamma_H$, are positive throughout the methanol-water range (as they are throughout the ethanol-water range) and as such disagree sharply with the results of the previous two studies (Table XXIV). If parallels can be drawn between the ethanol-water and the methanol-water systems, then the results of this study disagree with those of Feakins and Watson and of de Ligny and Alfenaar in two respects. In contrast to their results, we find that 1) the logarithm of the medium effect for the potassium ion is positive throughout the entire ethanol-water range and rises exponentially with increasing ethanol content. 2) While negative log $_m\gamma$'s are obtained by us for the proton below 98 wt.-% ethanol, log $_m\gamma_H$ rises steeply to positive values between 98 and 100 wt.-% ethanol. Thus, the proton exhibits its expected unique dependence on the basicity of solvent and does not behave as just another cation. The medium effect for the proton is sensitive to the solvent basicity maximum, while those of the other ions are not.

Being negative up to 98 wt.-% ethanol, the values of log $_m\gamma_H$ estimated in this study disagree, of course, with the results of Izmaylov and Grunwald (Table XXIII). It is noteworthy, however, that the results of Izmaylov, as well as ours, exhibit the same steep rise of 1.8 log units between 98 and 100 wt.-% ethanol. This region probably reflects the complete conversion of H_3O^+ to $C_2H_5OH_2^+$ which, on the basis of conductometric and other independent data, is known to occur by 90 mole-% ROH (<u>23</u>) (96 wt.-% ethanol).

We can compare the single-ion medium effects for potassium and chloride ions obtained in this study with their "theoretical" values calculated by a modified Born equation. We used a modification of the Born equation introduced by Stokes (77), which accounts for the increase in the size of the ion because of hydration as well as for the dielectric saturation in the vicinity of the ion. The results of this calculation are tabulated in Table XXV and shown in Figure 11 for comparison with our experimental values. The calculated medium effects for the potassium ion are in fairly good agreement with experiment. It must be remembered that in using the Stokes calculation one assumes solvation by water only for all of the ethanol-water mixtures. As a result, the increasing discrepancy between calculated and experimental curves for potassium at high ethanol contents is probably due to increasing solvation by ethanol.

The simple electrostatic picture predicted from the modified Born equation is followed rather poorly by the chloride ion and is completely inapplicable to the large organic ions (TAB^+, Pi^-, BPh_4^-) and to the proton. As mentioned earlier, the medium effect for the proton is a function not only of the dielectric properties of the solvent, but of the latter's proton affinity (basicity) as well. For the large organic ions, on the other hand, the "neutral" (non-electrostatic) part of the solvation energy probably plays a major role, as compared to the electrostatic (Born equation) component. An experimental elucidation of this "neutral" component of the solvation-energy changes for the above ions is a subject for further study.

Table XXV. Comparison of Experimentally Obtained Medium Effects for Potassium and Chloride Ions with Their Theoretical Value.

Solvent wt.-% Ethanol	log $_m\gamma_K$		log $_m\gamma_{Cl}$	
	Experimental	Theoretical	Experimental	Theoretical
0.0	0.000	0.0000	0.00	0.0000
10.0	0.123	0.0578	0.18	0.0634
20.0	0.150	0.128	0.53	0.143
30.0	0.170	0.215	0.88	0.240
40.0	0.177	0.326	1.25	0.362
50.0	0.258	0.461	1.60	0.512
60.0	0.519	0.620	1.79	0.688
70.0	0.860	0.818	2.01	0.908
80.0	1.359	1.07	2.25	1.19
90.0	2.062	1.38	2.73	1.53
100	2.920	--	3.31	--

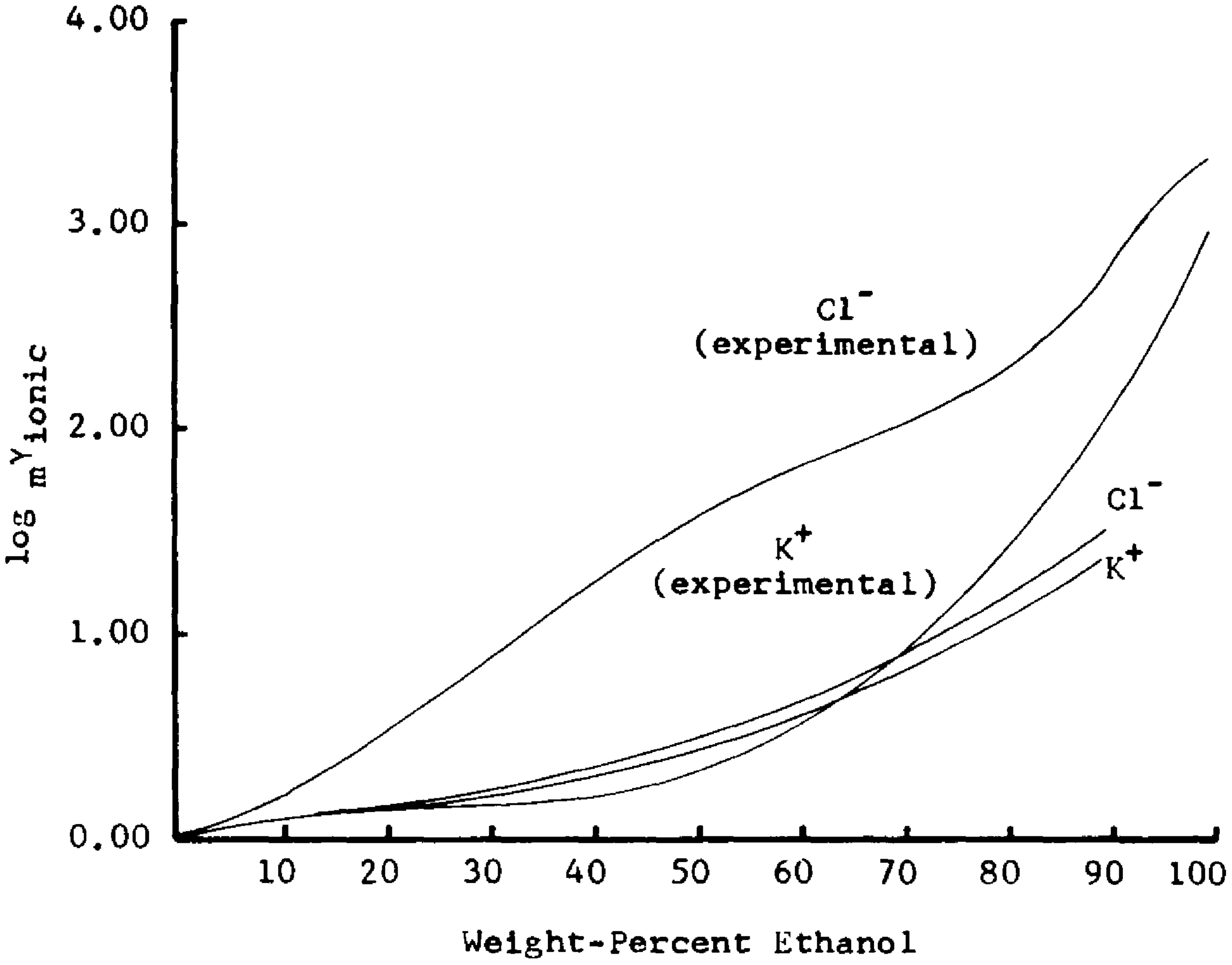

Figure 11. Comparison of experimentally obtained medium effects for potassium and chloride ions with their theoretical value.

Interpretation of pH Scales and Estimation of Liquid-Junction Potentials

In any amphiprotic solvent we can derive values for pa_H^* from the e.m.f. of cell (I) via equation (4b), provided we know the value of the standard potential of the cell, ${}_sE^\circ$, in the same solvent.

$$\text{Pt(s); } H_2\text{(g)/ } H^+\text{, } Cl^-\text{/ AgCl(s); Ag(s)} \qquad \text{(I)}$$

$$pa_H^* = \frac{nF(E - {}_sE^\circ)}{RT \ln 10} + \log m_{Cl} + \log {}_s\gamma_{Cl} \qquad (4b)$$

Equation (4b) has been used to establish pH reference standards in water and in nonaqueous solvents (5).

Since the pa_H^* scale is different for each solvent, a direct comparison of pa_H^* data taken in different media is not possible. If we could express these data on a common scale, a direct comparison could be made. The aqueous pa_H scale is the most logical choice for this common scale, as pH reference standards have been established only in a limited number of nonaqueous solvents. The relation between pa_H and pa_H^*, as was pointed out in Part I, is given by equation (11)

$$pa_H = pa_H^* - \log {}_m\gamma_H \qquad (11)$$

Now that we have medium effects for the hydrogen ion over the entire range of ethanol-water mixtures, we can use them in equation (11) to express pa_H^* data obtained in ethanol-water solvents on the aqueous pa_H scale. Bates, et. al. (9, 11) report pa_H^*'s for solutions of HCl-NaCl, acetic acid-sodium acetate-NaCl and triethanolammonium chloride-triethanolamine in ethanol-water solvents. These pa_H^* values recalculated to the aqueous pa_H scale with the aid of our values of log ${}_m\gamma_H$ are shown in Table XXVI and in Figure 12. As log ${}_m\gamma_H$ is negative for all of these solvents except 98 to 100 wt.-% ethanol, their solutions are shown to be less acidic when expressed on the common aqueous scale, i. e., less acidic than aqueous solutions of the same nominal pH. On the other hand, solutions of a given pa_H^* in pure ethanol will have a pa_H lower by 1.84 units. In terms of proton activity, a solution of pa_H^* 1 in pure ethanol is then about 70 times more acidic than a solution of pa_H 1 in water.

The length of a pa_H^* scale in an amphiprotic solvent having an autoprotolysis constant K_s is arbitrarily taken to extend from zero to log K_s, which for ethanol is -19.1 (57). Using equation (11), we can express the pa_H^* scale in ethanol on a single pa_H scale, referred to the aqueous standard state. In ethanol, the pa_H scale will extend from -1.8 to 17.3 pa_H units.

Most practical pH measurements are made in e.m.f. cells with liquid junctions, such as cell (VIII), using electrodes standardized against aqueous pH standards. The

Table XXVI. pH of Solutions in Ethanol-Water Mixtures (9, 11) Expressed on the Aqueous Scale at 25°C.

Solvent wt.-% Ethanol	m_1	pa_H^*	pa_H
HCl (m_1), NaCl (m_2); $m_2 = 4m_1$			
0.0	0.002006	2.753	2.75
16.2	0.002058	2.739	2.92
33.2	0.002116	2.769	3.38
52.0	0.002210	2.787	3.79
73.4	0.002338	2.881	3.70
85.4	0.002422	3.012	3.64
100	0.002548	5.081	3.26
Acetic acid (m_1), Sodium acetate (m_2), NaCl (m_3) $m_2 = 0.5m_1$; $m_3 = 0.25m_1$			
0.0	0.0201	4.408	4.41
16.2	0.0206	4.644	4.82
33.2	0.0212	4.992	5.60
52.0	0.0221	5.400	6.40
73.4	0.0234	6.065	6.89
85.4	0.0242	6.652	7.28
100	0.0255	9.950	8.13
Triethanolammonium chloride (m_1), Triethanolamine (m_2) $m_2 = 0.5m_1$			
0.0	0.00401	7.501	7.50
16.2	0.00412	7.367	7.55
33.2	0.00423	7.176	7.79
52.0	0.00442	6.923	7.92
73.4	0.00468	6.745	7.57
85.4	0.00484	6.743	7.37
100	0.00510	9.048	7.23

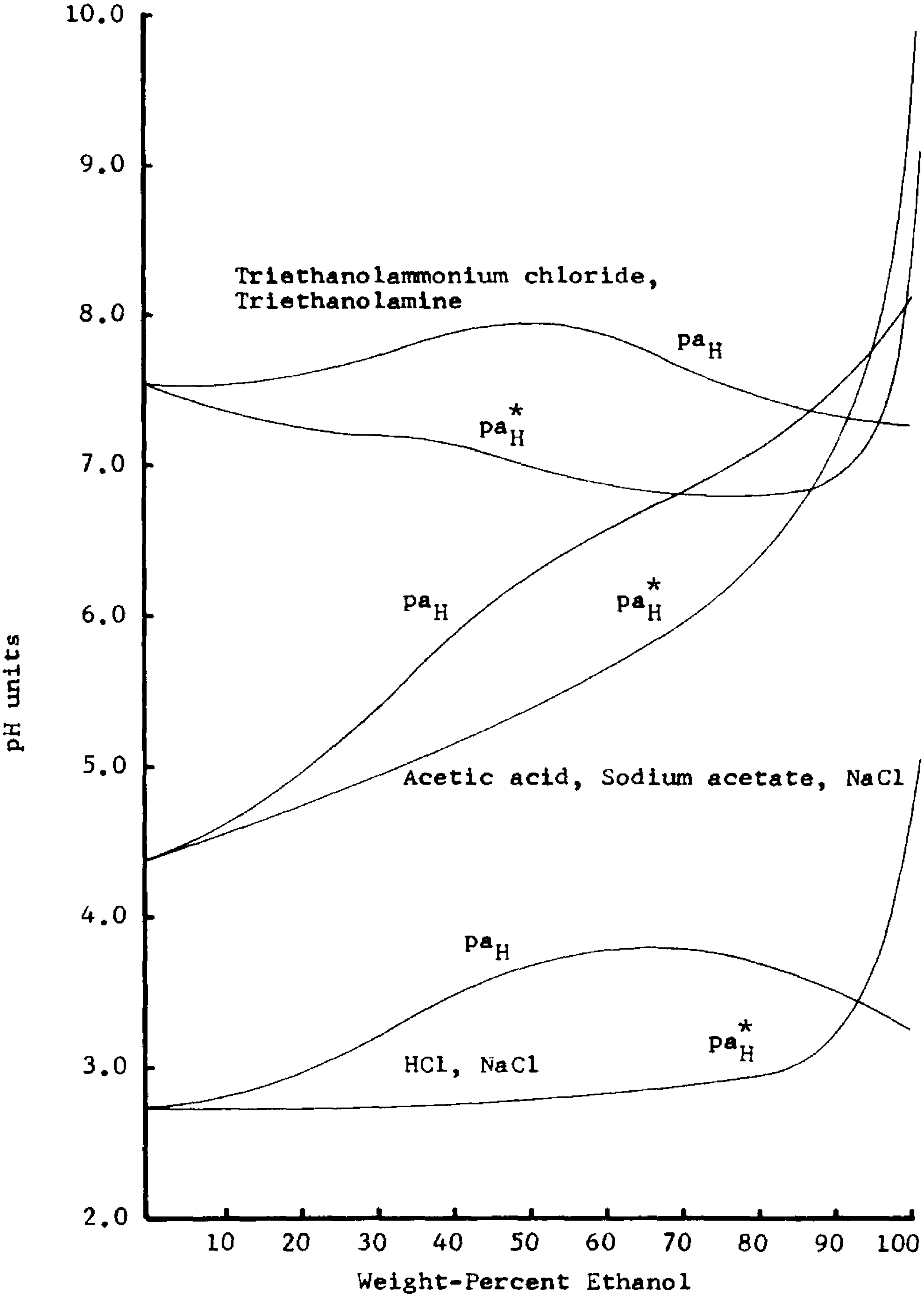

Figure 12. Comparison of pa_H^* with pa_H for solutions in Table XXVI.

$$Pt(s); H_2(g)/ \text{ conc. } KCl(aq); \text{ reference electrode} \quad (VIII)$$

resulting "operational pH" readings in any solvent deviate from pa_H by the difference between the liquid-junction potentials in the aqueous standard and in the test solutions, E_j:

$$pH - pa_H = \frac{E_j}{RT(\ln 10)/nF} \qquad (122)$$

When we combine equations (11) and (122) we see that the relationship between pH and pa_H^* involves both a medium effect term and a liquid-junction potential term.

$$pH - pa_H^* = \frac{E_j}{RT(\ln 10)/nF} - \log {}_m\gamma_H = \bar{E}_j - \log {}_m\gamma_H \qquad (123)$$

The right side of equation (123) has been designated by the symbol, $\underline{\delta}$, by Bates, Paabo and Robinson (9), who give values for $\underline{\delta}$ in ethanol-water solvents.

$$\delta = \bar{E}_j - \log {}_m\gamma_H \qquad (124)$$

From these values of $\underline{\delta}$ and our values for the medium effect of the hydrogen ion we can calculate the liquid-junction potentials at the aqueous-nonaqueous interphases.

The results given in Table XXVII show the division of $\underline{\delta}$ into its component parts, $\bar{E}_j$ and $\log {}_m\gamma_H$. This division permits us to see how the pH meter reading for electrodes standardized with an aqueous buffer, differs from the true

Table XXVII. Liquid-Junction Potentials at Aqueous-Nonaqueous Interphases at 25°C.

Solvent wt.-% Ethanol	$\underline{\delta}$ ($\underline{9}$)	$\log {}_m\gamma_H$	Liquid-Junction Potential pH units	mv.
0.0	0.000	0.00	0.00	0
16.2	+0.003	-0.18	-0.18	-11
33.2	+0.086	-0.61	-0.52	-31
52.0	+0.221	-1.00	-0.78	-46
73.4	+0.196	-0.82	-0.62	-37
85.4	-0.032	-0.63	-0.66	-39
100	-2.91	+1.82	-1.09	-64

pa_H^* when used for measurements in a nonaqueous solvent. As Table XXVII shows, negative values for $\bar{E}_j$ (expressed in pH units) are obtained which are of comparable magnitude to $\log {}_m\gamma_H$. Thus, with the exception of 100% ethanol, the terms on the right side of equation (124) tend to cancel, resulting in the observed small values for $\underline{\delta}$. In the case of 100% ethanol exactly the reverse occurs. The $\log {}_m\gamma_H$ term is positive so that when subtracted from $\bar{E}_j$ the large value observed for $\underline{\delta}$ results, i. e., both $\bar{E}_j$ and $\log {}_m\gamma_H$ cause deviation of pa_H^* from pH in the same direction.

The values for $\bar{E}_j$ found in this research do not, in general, agree with those reported by Gutbezahl and Grunwald (33). These authors report positive values for $\bar{E}_j$ for ethanol-water mixtures containing more than about 20 wt.-% ethanol. These values increase in a regular manner up to 2.35 pH units as we go from 20 to 100 wt.-% ethanol. In this study, values for $\bar{E}_j$ are negative throughout the range of ethanol-water mixtures. They decrease from zero in water to a minimum at about 50 wt.-% ethanol, rising somewhat as we go to 70 wt.-% ethanol and then again dropping as we go to 100% ethanol.

Correlation of E.M.F. Series

It has been shown in Part I (equation 10), that with the aid of the medium effect for the electrode-active ion, $\log {}_m\gamma_i$, the standard potential of an electrode measured in a nonaqueous solvent, SH, can be expressed on the single aqueous scale (i. e., referred to the single reference point of ${}_wE^\circ_{H,H_2O} = 0$):

$$ {}_wE^\circ_{i,SH} = {}_wE^\circ_{i,H_2O} + \frac{RT}{nF} \ln {}_m\gamma_i \qquad (14a) $$

for cation-active electrodes and

$$ {}_wE^\circ_{i,SH} = {}_wE^\circ_{i,H_2O} - \frac{RT}{nF} \ln {}_m\gamma_i \qquad (14b) $$

for anion-active electrodes.

In this research we have evaluated medium effects for the hydrogen and potassium ions in ethanol-water mixtures with which we can express the standard potential of the hydrogen and potassium electrodes on the aqueous e.m.f. scale (referred to ${}_wE^\circ_{H,H_2O} = 0$) via equation (14a). The results of this calculation are shown in Table XXVIII.

Once we know the standard potential of the hydrogen electrode in the nonaqueous solvent, SH, referred to the common aqueous standard state, ${}_wE^\circ_{H,H_2O} = 0$, we know the

Table XXVIII. Standard Potentials of Hydrogen and Potassium Electrodes in Ethanol-Water Mixtures at 25°C.

Solvent wt.-% Ethanol	${}_wE^\circ_{H,SH}$	${}_sE^\circ_{K,SH}$ *	${}_wE^\circ_{K,SH}$
0.0	0.000	-2.923	-2.923
10.0	-0.003	-2.913	-2.916
20.0	-0.017	-2.900	-2.913
30.0	-0.030	-2.885	-2.913
40.0	-0.046	-2.870	-2.913
50.0	-0.058	-2.854	-2.908
60.0	-0.059	-2.838	-2.892
70.0	-0.053	-2.821	-2.872
80.0	-0.040	-2.803	-2.843
90.0	-0.034	-2.777	-2.801
100	+0.108	-2.862	-2.750

* obtained by graphical interpolation of experimental values.

position of the ${}_{s}E^{\bullet}_{i,SH}$ series relative to the ${}_{w}E^{\circ}_{i,SH}$ series. Thus, correlation of all e.m.f. series follows from the equation,

$$ {}_{w}E^{\circ}_{i,SH} = {}_{s}E^{\circ}_{i,SH} + {}_{w}E^{\circ}_{H,SH} \qquad (125) $$

where ${}_{w}E^{\circ}_{H,SH}$ and ${}_{w}E^{\bullet}_{i,SH}$ are the standard potentials of the hydrogen electrode and the electrode reversible to ion i, respectively, measured in the solvent SH and referred to the aqueous standard state, while ${}_{s}E^{\bullet}_{i,SH}$ is the standard potential measured in the solvent SH, referred to the nonaqueous standard state (${}_{s}E^{\bullet}_{H,SH} = 0$).

The striking feature of the standard hydrogen-electrode potentials referred to the single aqueous standard state is the fact that up to about 90 wt.-% ethanol they do not differ much from the aqueous value of zero volts and do not vary much among themselves. Thus, contrary to general opinion and to our own expectations, the standard hydrogen electrode turned out to be a fairly constant reference electrode, at least for ethanol-water mixtures.

The standard potassium electrode becomes continuously more positive with increasing ethanol content, i. e., the higher solvation energy of the electrode-active ion in the nonaqueous solvent is causing the ion to be more readily reduced, i. e., the electrode becomes more "noble." In Table XXIX we have compiled values of ${}_{s}E^{\circ}_{i,SH}$ for several electrodes in absolute ethanol available in the literature and expressed these values referred to ${}_{w}E^{\circ}_{H,H_2O} = 0$. For

100% ethanol (Table XXIX) we observe a shift towards more positive potentials (relative to the aqueous value) for all of the electrodes considered, including the hydrogen electrode.

Table XXIX. Comparison of Molal Standard Potentials in Ethanol at 25°C on Aqueous and Nonaqueous Scales.

Electrode	${}_{s}E^{\circ}_{i,SH}$ (referred to ${}_{s}E^{\circ}_{H,SH} = 0$)	${}_{w}E^{\circ}_{i,SH}$ (referred to ${}_{w}E^{\circ}_{H,H_2O} = 0$)
Li/Li^+	-3.042 (79)	-2.934
K/K^+	-2.862	-2.750
Na/Na^+	-2.657 (79)	-2.549
Tl/Tl^+	-0.38 (79)	-0.27
Ag/AgBr	-0.1816 (63)	-0.074
Ag/AgCl	-0.08138 (80)	+0.027
H_2/H^+	0.000	+0.108

Summary

The work reported here has offered one possible solution to the three interrelated problems outlined at the beginning of this thesis: the correlation of ion-activity scales and e.m.f. series in different solvents and the evaluation of liquid-junction potentials at aqueous-nonaqueous interphases. This solution to the three problems depends on a new method for the estimation of medium effects for single ions. In the new method, the medium effect of a "reference electrolyte" triisoamyl-n-butylammonium tetraphenylborate (TAB(BPh_4)) is apportioned equally between those of its ions. Medium effects for other ions of interest were then obtained from those of the following electrolytes: potassium picrate (KPi), triisoamyl-n-butylammonium picrate (TABPi), potassium tetraphenylborate (K(BPh_4)), KCl and HCl. As a result, we have evaluated medium effects for the H^+, K^+, Cl^-, Pi^-, TAB^+, and BPh_4^- ions.

The medium effects for the large organic ions, except for picrate, behaved in the expected manner. Their logarithms were negative, indicating that these ions were preferentially solvated by the alcoholic rather than the aqueous solvent. Picrate ion did not have a very large medium effect in any of the alcohol-water mixtures. The medium effect for the chloride ion was also found to exhibit the expected behavior; anions

prefer solvation by water. The experimentally obtained medium effect of the potassium ion was found to agree quite well with its theoretical value calculated from a modification of the Born equation. The logarithms of the medium effect for the proton was negative up to about 98 wt.-% ethanol, after which it became positive, indicating a lower-energy state in the aqueous solvent relative to pure ethanol.

Medium effects for complete electrolytes obtained by taking into account activity coefficients, and degrees of dissociation were found to agree qualitatively with those obtained on the basis of solubility alone. The solubility of $TAB(BPh_4)$ in water was calculated from the medium effect of $TAB(BPh_4)$ in several ethanol-water m ixtures and from its solubility in these solvents.

The single-ion medium effects obtained were then applied to the interpretation of pH scales in ethanol-water mixtures, the estimation of liquid-junction potentials at aqueous-nonaqueous interphases, and the correlation of e.m.f. series in ethanol-water mixtures.

As log ${}_m\gamma_H$ is negative for all ethanol-water solvents, except for 98 to 100 wt.-% ethanol, solutions of a given pa_H^* in these solvents are shown to be less acidic when expressed on the common aqueous pa_H scale. In pure ethanol the reverse was found. In terms of proton activity, a solution of pa_H^* 1 in pure ethanol is about 70 times more acidic than a solution of pa_H 1 in water. The difference between pa_H^* value was found to be small for ethanol-water mixtures because the liquid-junction error and the medium effect term cancelled to an extent. In pure ethanol the reverse was found. The medium effect term reinforced the liquid-junction error, resulting in a large deviation of pH from pa_H^* (2.91 pH units). The range of the pa_H scale in ethanol was found to extend from -1.8 to 17.3 pa_H units.

The standard hydrogen electrode potential referred to the single aqueous standard state was found not to differ much from the aqueous value of zero volts, revealing the hydrogen electrode to be a fairly constant reference electrode in ethanol-water mixtures. The potassium electrode was found to become more noble (potassium is more readily reduced) as the solvent composition changes from water to absolute ethanol. When referred to the aqueous standard hydrogen electrode, all of the standard electrodes considered here exhibit a shift toward more positive potentials in absolute ethanol.

In addition to offering a solution to the three interrelated problems, this research has supplied a wealth of physical-chemical data on the electrolytes studied over the the entire range of ethanol-water mixtures. Solubilities of KPi, TABPi and $K(BPh_4)$ have been measured over the entire range. For $TAB(BPh_4)$ the solubilities were measured from about 40 to 100 wt.-% ethanol. The electrolytic conductance of the above electrolytes as well as of lithium picrate and lithium chloride in ethanol-water mixtures was measured and values for their association constants, limiting equivalent conductances and ion-size parameters in these mixtures were reported. Activity coefficients for KPi, TABPi and $K(BPh_4)$ were determined over the entire range of ethanol-water mixtures and the range of validity of the Debye-Hückel limiting law was pointed out. For $TAB(BPh_4)$ activity coefficients have been determined over the range 60 to 100 wt.-% ethanol. The standard potential of the potassium electrode over the entire range of ethanol-water mixtures is reported here for the first time.

Appendix A. Physical Properties of Ethanol-Water Mixtures at 25°C.

Table XXX. Density of Ethanol-Water Mixtures at 25°C (64).

Solvent wt.-% Ethanol	Density (gm/ml)
0.000	0.997077
4.907	0.988317
9.984	0.980461
19.122	0.967648
22.918	0.962133
30.086	0.950529
39.988	0.931507
49.961	0.909937
59.976	0.887051
70.012	0.863380
80.036	0.839031
90.037	0.813516
99.913	0.785337

Table XXXI. Dielectric Constant of Ethanol-Water Mixtures at 25°C (2).

Solvent wt.-% Ethanol	Dielectric Constant
0	78.5
10	72.8
20	67.0
30	61.1
40	55.0
50	49.0
60	43.4
70	38.0
80	32.8
90	28.1
100	24.3

Table XXXII. Viscosity of Ethanol-Water Mixtures at 25°C (38).

Solvent wt.-% Ethanol	Viscosity (millipoise)
10	13.28
20	18.08
30	22.03
40	23.74
45	23.87
50	23.68
60	22.32
70	20.25
80	17.38
90	14.22
100	11.01

Appendix B. Fortran Computer Program Listings.

```
C      CONDUCTANCE CALCULATION *SHEDLOVSKY METHOD*
C
C      SWITCH 1 OFF - THEORETICAL DEBYE-HUCKEL A USED IN CALCULATION
C      SWITCH 1 ON - TYPE IN DEBYE-HUCKEL A
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      QZ = ESTIMATE OF LAMBDA ZERO  ETA = VISCOSITY IN POISE
C      Q = EQUIVALENT CONDUCTANCE  CONC = 1000CONC
C
       DIMENSION Q(50),CONC(50),Z(50),PROD(50),GAMMA(50),FSQRD(50),X(50)
       DIMENSION Y(50),SZ(50),CALKA(50),CALQZ(50),CALY(50),DELQ(50)
     1 PUNCH 1001
  1001 FORMAT(43H CONDUCTANCE CALCULATION, SHEDLOVSKY METHOD//)
     2 READ 1002
  1002 FORMAT(55H
       PUNCH 1002
     3 READ 1003,MAXCY,TOL
  1003 FORMAT(I5,5X,F10.0)
     4 READ 1004,N,QZ,D,T,ETA
  1004 FORMAT(I5,5X,4F10.0)
       DO 6 J=1,N
     5 READ 1005,CONC(J),Q(J)
  1005 FORMAT(2F10.0)
     6 CONC(J) = 0.0001*CONC(J)
     7 PUNCH 1007,MAXCY,TOL,QZ
  1007 FORMAT(/7HMAXCY =I4,8H   TOL =F7.4,23H  INITIAL LAMBDA ZERO =F6.2
     8 PUNCH 1008,D,T,ETA
  1008 FORMAT(14HDIELEC CONST =F6.2,9H   TEMP =F7.2,11H   VISCOS =F8.5/)
     9 PUNCH 1009
  1009 FORMAT(55HCONCENTRATION     LAMBDA    1/LAMBDA X S(Z)    C F S(Z)
       NPROB=0
       NDONE=0
       NCYC=0
       SQRDT = SQRT(D*T)
       IF (SENSE SWITCH 1)11,10
    10 A = 1.8246E+06/(SQRDT**3)
       GO TO 12
    11 ACCEPT 1011,A
  1011 FORMAT(F10.0)
    12 ALPHA=0.8204E+06/(SQRDT**3)
       BETA=82.501/(SQRDT*ETA)
    15 S = (ALPHA*QZ)+BETA
       CONST=((1./QZ)**1.5)*S
    20 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
   61 XLPLU=1./CEPT
      DIFF=ABS(XLPLU-QZ)
      IF(TOL*XLPLU-DIFF)65,69,69
   65 QZ=XLPLU
      NCYC=NCYC+1
   67 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
      SIGKA=SQRT(SUMKA/(G-1.))
      SIGQZ=SQRT(SUMQZ/(G-1.))
      DO68 J=1,N
   68 PUNCH 1068,CONC(J),Q(J),Y(J),X(J)
 1068 FORMAT(F12.5,4X,F8.3,5X,F12.5,4X,F11.4)
   72 PUNCH 1072
 1072 FORMAT(//51H   ACTIVITY COEFF.  DEGREE OF DISSOC.  DELTA LAMBDA)
      DO 73 J=1,N
   73 PUNCH 1073,FSQRD(J),GAMMA(J),DELQ(J)
 1073 FORMAT(3X,F10.4,F18.4,F17.4)
   70 PUNCH1070,XLPLU,XK
 1070 FORMAT(/10X,14HLAMBDA ZERO = F8.3,5X,5HKA = F10.4)
   78 PUNCH 1078,SIGQZ,SIGKA
 1078 FORMAT(10X,15HSTANDARD DEV. =F8.4,4X,15HSTANDARD DEV. =F8.4)
   71 PUNCH 1071,WP,XKD
 1071 FORMAT(10X,16HWALDEN PRODUCT =F7.4,4X,5HKD = F11.4)
      GO TO 100
   89 NPROB=NDONE+1
   90 PUNCH1090,NPROB,NCYC
 1090 FORMAT(I5,5X,I5,5X,30H             ITERATION DIVERGING//)
  100 NDONE =NDONE +1
      PAUSE
      GO TO 1
      END
```

```
C     CONDUCTANCE CALCULATION - FUOSS-ONSAGER NONASSOC. ELECTROLYTE CALC
C     VALUES OF CONSTANTS FROM FUOSS AND ACCASCINA, ELECTROLYTIC COND.
C     VISCOSITY TERM NEGLECTED
C
      DIMENSION C(10),Q(10),X(10),Y(10),CALQZ(10),CALQP(10),DELQ(10)
      DIMENSION QP(10)
    1 PUNCH 1001
 1001 FORMAT(38HNONASSOCIATED ELECTROLYTE CALCULATION/)
    2 READ 1002
 1002 FORMAT(55H                                                       )
      PUNCH 1002
    3 READ 1003,MAXCY,TOL
 1003 FORMAT(I5,5X,F10.0)
    4 READ 1004,N,QZ,D,T,ETA
 1004 FORMAT(I5,5X,4F10.0)
      DO 6 I=1,N
      READ 1006,C(I),Q(I)
 1006 FORMAT(2F10.0)
    6 C(I)=C(I)*1.E-04
    7 PUNCH 1007,MAXCY,TOL,QZ
 1007 FORMAT(/7HMAXCY =I4,8H   TOL =F7.4,23H  INITIAL LAMBDA ZERO =F6.2
    8 PUNCH 1008,D,T,ETA
 1008 FORMAT(14HDIELEC CONST =F6.2,9H   TEMP =F7.2,11H   VISCOS =F8.5/)
      E1=6.7747E+12/((D**3)*(T**3))
      E2=0.9977E+08/(ETA*(D**2)*(T**2))
      SQRDT=SQRT(D*T)
      ALPHA=0.8204E+06/(SQRDT**3)
      BETA=82.501/(ETA*SQRDT)
   15 E=(E1*QZ)-E2
      S=(ALPHA*QZ)+BETA
      DO30 I=1,N
      QP(I)=Q(I)+S*SQRT(C(I))-(E*C(I)*LOG(C(I)))/2.30258
      Y(I)=QP(I)
   30 X(I)=C(I)
      SUMY=0.
      SUMX=0.
      SUMXY=0.
      SUMXX=0.
      DO 40 I=1,N
      SUMY=SUMY+Y(I)
      SUMX=SUMX+X(I)
      SUMXX=SUMXX+X(I)**2
   40 SUMXY=SUMXY+Y(I)*X(I)
      G=N
      DENOM=SUMX**2-G*SUMXX
      SLOPE=(SUMX*SUMY-G*SUMXY)/DENOM
      CEPT=(SUMX*SUMXY-SUMY*SUMXX)/DENOM
      XQZ=CEPT
      DIFF=ABS(XQZ-QZ)
      IF(TOL*XQZ-DIFF) 65,69,69
   65 QZ=XQZ
      NCYC=NCYC+1
      IF(MAXCY-NCYC) 189,189,15
   69 H=SLOPE
```

```
      WP=ETA*QZ
      AZ=20.
  115 AZ=AZ*1.E-08
      B=16.708E-04/(D*T*AZ)
      XLOG=LOG(0.50294E+10*AZ/SQRT(D*T))
      S1=5.8844E+12/((D*T)**3)
      S11=((2.*(B**2))+(2.*B)-1.)/B**3
      SIG1=S1*(S11+0.9074+XLOG)
      S2=0.67683E+08/(ETA*((D*T)**2))
      S22=0.38035E+12*AZ/(ETA*D*T)
      S222=0.8666E+08/(ETA*((D*T)**2))
      SIG2=S2+S22-(S222*(1.017+XLOG))
      XJ=(SIG1*QZ)+SIG2
      AZ=AZ*1.E+08
      IF(XJ-H) 118,118,117
  117 SXJ=XJ
      SAZ=AZ
      AZ=AZ-(AZ*.1)
      GO TO 115
  118 AZ=(SAZ-AZ)*(H-XJ)/(SXJ-XJ)+AZ
      SUMQZ=0.
      DO 180 I=1,N
      CALQZ(I)=QP(I)+H*C(I)
      CALQP(I)=SLOPE*C(I)+CEPT
      DELQ(I)=Q(I)-CALQP(I)+S*SQRT(C(I))-(E*C(I)*LOG(C(I)))/2.30258
      DQZSQ=(CALQZ(I)-QZ)**2
  180 SUMQZ=SUMQZ+DQZSQ
      SIGQZ=SQRT(SUMQZ/(G-1.))
  160 PUNCH 1160
 1160 FORMAT(55HCONCENTRATION    LAMBDA    LAMBDA PRIME    DELTA LAMBDA
      DO 168 I=1,N
  168 PUNCH 1168,C(I),Q(I),QP(I),DELQ(I)
 1168 FORMAT(E12.5,3X,F8.3,6X,F8.3,F15.4)
  170 PUNCH 1170,QZ,SIGQZ
 1170 FORMAT(/12HLAMBDA ZERO=F8.3,5X,14HSTANDARD DEV.=F8.4)
  172 PUNCH 1172,H,AZ
 1172 FORMAT(5HJ(A)=F10.4,10X,9HION SIZE=E11.3)
      GO TO 190
  189 TYPE 1189
 1189 FORMAT(/19HITERATION DIVERGING)
  190 TYPE 1190
 1190 FORMAT(/18HSTART NEXT PROBLEM)
      PAUSE
      GO TO 1
      END
```

```
C     FIRST APPROXIMATION OF X AND Y FOR DETERMINATION OF ASSOC. CONST.
C
C     VALUES OF CONSTANTS FROM FUOSS AND ACCASCINA, ELECTROLYTIC COND.
C     QZERO=TRIAL VALUES FOR LAMBDA ZERO
      DIMENSION C(10),Q(10),G(10),CG(10),SQRCG(10),SCG(10),ECLCG(10)
      DIMENSION QP(10),Y(10),FSQRD(10),X(10)
      TYPE 1000
 1000 FORMAT(25H ADJUST PAPER,PRESS START/)
      PAUSE
    1 READ 1001
 1001 FORMAT(55H                                                       )
      PRINT 1001
    2 READ 1002,AZ
 1002 FORMAT(F10.0)
      AZ=AZ*1.0E-08
    3 READ 1003,N,QZ,D,T,ETA
 1003 FORMAT(I5,4F10.0)
      SQRDT=SQRT(D*T)
      ALPHA=0.8204E+06/(SQRDT**3)
      BETA=82.501/(ETA*SQRDT)
      S=(ALPHA*QZ)+BETA
      E1=6.7747E+12/((D**3)*(T**3))
      E2=0.9977E+08/(ETA*(D**2)*(T**2))
      E=(E1*QZ)-E2
      A=3.6494E+06/(SQRDT**3)
      B=0.50294E+10/SQRDT
    4 PRINT 1004,N,D
 1004 FORMAT(//4H N =I3,27H                   DIELECT.CONST=F8.4,9H  LAMBDA )
    5 PRINT 1005,QZ
 1005 FORMAT(5HZERO=F8.3/)
    6 PRINT 1006,T,ETA
 1006 FORMAT(6H TEMP=F7.2,17H       VISCOSITY=F8.5,12H      ALPHA=)
    7 PRINT 1007,ALPHA
 1007 FORMAT(E12.5/)
    8 PRINT 1008,BETA,S,E1
 1008 FORMAT(6H BETA=E12.5,5H  S =E12.5,13H         E1 =E12.5/)
    9 PRINT 1009,E2,E,AZ
 1009 FORMAT(5H E2 =E12.5,6H   E =E12.5,18H         ION SIZE=E9.2//)
      DO 12 I=1,N
   12 READ 1012,C(I),Q(I)
 1012 FORMAT(2F10.0)
   18 READ 1018,QZERO
 1018 FORMAT(F10.0)
   19 PRINT 1019,QZERO
 1019 FORMAT(29H TRIAL VALUE FOR LAMBDA ZERO=F10.3//)
   10 PRINT 1010
 1010 FORMAT(6X,1HC,5X,26HSCG1/2    ECGLOGCG    QPRIME,6X,1HY,9X,1HX,7X)
   11 PRINT 1011
 1011 FORMAT(6HLAMBDA/)
      DO 13 I=1,N
      C(I)=C(I)*1.0E-04
      G(I)=Q(I)/(QZ-(S*(SQRT((C(I)*Q(I))/QZ))))
      CG(I)=C(I)*G(I)
      SQRCG(I)=SQRT(CG(I))
```

```
      SCG(I)=S*SQRCG(I)
      ECLCG(I)=E*CG(I)*((LOG(CG(I)))/2.303)
      QP(I)=Q(I)+SCG(I)-ECLCG(I)
      Y(I)=(QP(I)-QZERO)/CG(I)
      FSQRD(I)=EXP((-2.303*A*SQRCG(I))/(1.+(B*AZ*SQRCG(I))))
      X(I)=FSQRD(I)*Q(I)
      C(I)=C(I)*1.0E+04
   13 PRINT 1013,C(I),SCG(I),ECLCG(I),QP(I),Y(I),X(I),Q(I)
 1013 FORMAT(2F9.3,2F10.3,F10.1,2F10.3/)
   14 PRINT 1014
 1014 FORMAT(///)
      GO TO 18
      END
```

```
C     SECOND APPROXIMATION FOR X AND Y
C
C     VALUES OF CONSTANTS FROM FUOSS AND ACCASCINA, ELECTROLYTIC COND.
C     QZ=LAMBDA ZERO FROM FIRST APPROXIMATION
C     QZERO=TRIAL VALUES FOR LAMBDA ZERO
C     AZ=ION SIZE FROM FIRST APPROXIMATION
      DIMENSION C(10),Q(10),G(10),CG(10),SQRCG(10),SCG(10),ECLCG(10)
      DIMENSION QP(10),Y(10),FSQRD(10),X(10)
      TYPE 1000
 1000 FORMAT(25H ADJUST PAPER,PRESS START/)
      PAUSE
      PRINT 100
  100 FORMAT(55HSECOND APPROXIMATION OF X AND Y FOR DETERMINATION OF AS
      PRINT 101
  101 FORMAT(10HSOC.CONST.//)
    1 READ 1001
 1001 FORMAT(55H
      PRINT 1001
    2 READ 1002,AZ,XJ
 1002 FORMAT(2F10.0)
      AZ=AZ*1.0E-08
    3 READ 1003,N,QZ,D,T,ETA
 1003 FORMAT(I5,4F10.0)
      SQRDT=SQRT(D*T)
      ALPHA=0.8204E+06/(SQRDT**3)
      BETA=82.501/(ETA*SQRDT)
      S=(ALPHA*QZ)+BETA
      F1=6.7747E+12/((D**3)*(T**3))
      F2=0.9977E+08/(ETA*(D**2)*(T**2))
      F=(F1*QZ)-F2
      A=3.6494E+06/(SQRDT**3)
      B=0.50294E+10/SQRDT
    4 PRINT 1004,N,D
 1004 FORMAT(//4H N =I3,27H             DIELECT.CONST=F8.4,9H  LAMBDA )
    5 PRINT 1005,QZ
 1005 FORMAT(5HZERO=F8.3/)
    6 PRINT 1006,T,ETA
 1006 FORMAT(6H TEMP=F7.2,17H       VISCOSITY=F8.5,12H      ALPHA=)
    7 P-INT 1007,ALPHA
 1007 FORMAT(F12.5/)
    8 PRINT 1008,BETA,S,F1
 1008 FORMAT(6H BETA=F12.5,5H  S =F12.5,13H           F1 =F12.5/)
    9 PRINT 1009,F2,F,AZ
 1009 FORMAT(5H F2 =F12.5,6H   F =F12.5,18H          ION SIZE=E9.2//)
      DO 12 I=1,N
   12 READ 1012,C(I),Q(I)
 1012 FORMAT(2F10.0)
   18 READ 1018,QZERO
 1018 FORMAT(F10.0)
   19 PRINT 1019,QZERO
 1019 FORMAT(29H TRIAL VALUE FOR LAMBDA ZERO=F10.3//)
   10 PRINT 1010
 1010 FORMAT(6X,1HC,5X,26HSCG1/2   ECGLOGCG   QPRIME,6X,1HY,9X,1HX,7X)
   11 PRINT 1011
```

```
1011 FORMAT(6HLAMBDA/)
     DO 13 I=1,N
     C(I)=C(I)*1.0E-04
     G(I)=Q(I)/(QZ-(S*(SQRT((C(I)*Q(I))/QZ))))
     CG(I)=C(I)*G(I)
     SQRCG(I)=SQRT(CG(I))
     SCG(I)=S*SQRCG(I)
     ECLCG(I)=E*CG(I)*((LOG(CG(I)))/2.303)
     G(I)=Q(I)/(QZ    -SCG(I)+ECLCG(I)+(XJ*C(I)*G(I)))
     CG(I)=C(I)*G(I)
     SQRCG(I)=SQRT(CG(I))
     SCG(I)=S*SQRCG(I)
     ECLCG(I)=E*CG(I)*((LOG(CG(I)))/2.303)
     QP(I)=Q(I)+SCG(I)-ECLCG(I)
     Y(I)=(QP(I)-QZERO)/CG(I)
     FSQRD(I)=EXP((-2.303*A*SQRCG(I))/(1.+(B*AZ*SQRCG(I))))
     X(I)=FSQRD(I)*Q(I)
     C(I)=C(I)*1.0E+04
  13 PRINT 1013,C(I),SCG(I),ECLCG(I),QP(I),Y(I),X(I),Q(I)
1013 FORMAT(2F9.3,2F10.3,F10.1,2F10.3/)
  14 PRINT 1014
1014 FORMAT(///)
     GO TO 18
     END
```

```
C     CONDUCTANCE ERROR ANALYSIS, FUOSS-ONSAGER METHOD
C
C     VALUES OF CONSTANTS FROM FUOSS AND ACCASCINA, ELECTROLYTIC COND.
C     H = EXPERIMENTAL VALUE OF J(A)
    1 PUNCH 1001
 1001 FORMAT(42H CONDUCTANCE ERROR ANALYSIS    X - Y METHOD//)
    4 READ 1004
 1004 FORMAT(55H                                                       )
      PUNCH 1004
    6 READ 1006,N,QZ,D,T,ETA
 1006 FORMAT(I5,5X,4F10.0)
    8 READ 1008,H,AZ,XK
 1008 FORMAT(3F10.0)
      AZ=AZ*1.E-08
      SQRDT=SQRT(D*T)
      ALPHA=.8204E+06/(SQRDT**3)
      BETA=82.501/(ETA*SQRDT)
      S=(ALPHA*QZ)+BETA
      E1=6.7747E+12/((D**3)*(T**3))
      E2=.9977E+08/(ETA*(D**2)*(T**2))
      E=(E1*QZ)-E2
      A=3.6494E+06/(SQRDT**3)
      B=.50294E+10/SQRDT
   18 PUNCH 1018
 1018 FORMAT(44H     CONCENTRATION    LAMBDA    DELTA LAMBDA)
      SUMKA=0.
      SUMQZ=0.
      SUMJ=0.
      NDONE=0
   20 READ 1020,C,Q
 1020 FORMAT(2F10.0)
      C=C*1.E-04
      G=Q/(QZ-(S*(SQRT((C*Q)/QZ))))
      CG=C*G
      SCG=S*SQRT(CG)
      ECG=(E*CG*LOG(CG))/2.30258
      G=Q/(QZ-SCG+ECG+H*CG)
      CG=C*G
      SCG=S*SQRT(CG)
      ECG=(E*CG*LOG(CG))/2.30258
      FSQRD=EXP((-2.30258*A*SQRT(CG))/(1.+(B*AZ*SQRT(CG))))
      QP=Q+SCG-ECG
      Y=(QP-QZ)/CG
      X=FSQRD*Q
      CALKA=(H-Y)/X
      CALQZ=QP-H*CG+XK*CG*X
      CALQ=(QZ-SCG+ECG+H*CG)/(1.+XK*CG*FSQRD)
      DELQ=Q-CALQ
      CALJ=Y+XK*X
      DKASQ=(CALKA-XK)**2
      SUMKA=SUMKA+DKASQ
      DQZSQ=(CALQZ-QZ)**2
      SUMQZ=SUMQZ+DQZSQ
      DJSQ=(CALJ-H)**2
```

```
      SUMJ=SUMJ+DJSQ
      C=C*1.E+04
   80 PUNCH 1080,C,Q,DELQ
 1080 FORMAT(F15.4,F13.3,F12.3)
      NDONE=NDONE+1
      IF(N-NDONE)20,85,20
   85 G=N
      SIGKA=SQRT(SUMKA/(G-1.))
      SIGQZ=SQRT(SUMQZ/(G-1.))
      SIGJ=SQRT(SUMJ/(G-1.))
      AZ=AZ*1.E+08
      XJ=H+SIGJ
      XA=XJ*AZ/H
      SIGAZ=XA-AZ
   90 PUNCH 1090,XK,SIGKA
 1090 FORMAT(5X,22HASSOCIATION CONSTANT =F11.4,17H  STANDARD DEV. =F8.3
   92 PUNCH 1092,QZ,SIGQZ
 1092 FORMAT(5X,13HLAMBDA ZERO =F8.3,17H  STANDARD DEV. =F8.3)
   94 PUNCH 1094,H,SIGJ
 1094 FORMAT(8H      J =F11.4,17H  STANDARD DEV. =F11.4)
   96 PUNCH 1096,AZ,SIGAZ
 1096 FORMAT(5X,10HION SIZE =F8.3,17H  STANDARD DEV. =F8.3//)
      GO TO 4
      END
```

```
C     CALCULATION FOR INTERPOLATION OF ION SIZE
C
C     H = EXPERIMENTAL J(A)
C     USE MAXIMUM POSSIBLE VALUE FOR AZ ON DATA CARD 2
    1 TYPE 1001
 1001 FORMAT(/51HCALCULATION FOR INTERPOLATION OF ION-SIZE PARAMETER//)
    2 READ 1002
 1002 FORMAT(55H                                             1
      PRINT 1002
    3 READ 1003,QZ,D,T,ETA,AZ,H
 1003 FORMAT(6F10.0)
    4 TYPE 1004,QZ,H
 1004 FORMAT(//13HLAMBDA ZERO =F10.3,22H   EXPERIMENTAL J(A) =F10.3)
   11 PRINT 1011
 1011 FORMAT(//8X,4HJ(A),9X,8HION SIZE)
   15 AZ=AZ*1.E-08
      B=16.708E-04/(D*T*AZ)
      XLOG=LOG(0.50294E+10*AZ/SQRT(D*T))
      S1=5.8844E+12/((D*T)**3)
      S11=((2.*(B**2))+(2.*B)-1.)/B**3
      SIG1=S1*(S11+0.9074+XLOG)
      S2=0.67683E+08/(ETA*((D*T)**2))
      S22=0.38035E+12*AZ/(ETA*D*T)
      S222=0.8666E+08/(ETA*((D*T)**2))
      SIG2=S2+S22-(S222*(1.017+XLOG))
      XJ=(SIG1*QZ)+SIG2
      AZ=AZ*1.0E+08
   16 TYPE 1016,XJ,AZ
 1016 FORMAT(/F14.4,F13.2)
      IF(XJ-H) 18,18,17
   17 SAZ=AZ
      SXJ=XJ
      AZ=AZ-(AZ*.1)
      GO TO 15
   18 AZ=(SAZ-AZ)*(H-XJ)/(SXJ-XJ)+AZ
   20 TYPE 1020,AZ
 1020 FORMAT(//10HION SIZE =F7.2)
      PAUSE
      GO TO 1
      END
```

```
C     ANALYSIS OF SOLUBILITY DATA(DETERMINATION OF ACTIVITY COEFFICIENT)
C
C     SWITCH 1 OFF - THEORETICAL DEBYE-HUCKEL A USED IN CALCULATION
C     SWITCH 1 ON - TYPE IN DEBYE-HUCKEL A
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(10),CL1(10),A1P(10),B1P(10),P(10),A1C(10),B1C(10)
      DIMENSION CL(10),PI(10),XLI(10),AC(10),CKP(10),CLC(10),X(10),Y(10)
      DIMENSION ALPHA(10)
    1 TYPE 1000
 1000 FORMAT(/17HLOAD NEXT PROBLEM)
      PAUSE
      PUNCH 1001
 1001 FORMAT(53HDETERMINATION OF ACTIVITY COEFFICIENT FROM SOLUBILITY)
    2 READ 1002
 1002 FORMAT(55H                                                       )
      PUNCH 1002
    3 READ 1003,N,D,T,XK1,XK2,XK3,DSOLV,TOL
 1003 FORMAT(I5,5X,7F10.0)
      DO 5 I=1,N
    5 READ 1005,CKP(I),CLC(I)
 1005 FORMAT(E10.0,F10.0)
      TOL=TOL*.01
      SQRDT=SQRT(D*T)
      IF( SENSE SWITCH 1)8,7
    7 A=1.8246E+06/(SQRDT**3)
      GO TO 9
    8 ACCEPT 1008,A
 1008 FORMAT(F10.0)
    9 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 PUNCH 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)+SQRT((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=ABS(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=EXP(-4.60518*A*SQRT(AC(I)))
      IF(ABS(FSQRD(I)-FS)-.0001)199,199,185
  185 FSQRD(I)=FS
      GO TO 110
  199 CONTINUE
      GO TO 500
C     START CALCULATION 2
  200 PUNCH 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)+SQRT((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=ABS(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=EXP(-4.60518*A*SQRT(AC(I)))
      IF(ABS(FSQRD(I)-FS)-.0001)299,299,285
  285 FSQRD(I)=FS
      GO TO 210
  299 CONTINUE
      GO TO 500
C     START CALCULATION 3
  300 PUNCH 1300
 1300 FORMAT(14H CALCULATION 3/)
      DO 399 I=1,N
      FSQRD(I)=1.
  310 PI(I)=(-1.+SQRT(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=EXP(-4.60518*A*SQRT(AC(I)))
      IF(ABS(FSQRD(I)-FS)-.0001)399,399,385
  385 FSQRD(I)=FS
      GO TO 310
  399 CONTINUE
      GO TO 500
```

```
C     START CALCULATION 4
  400 PUNCH 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 PUNCH 1600
 1600 FORMAT(14H CALCULATION 5/)
      DO 699 I=1,N
      FSQRD(I)=1.
  610 PI(I)=(-1.+SQRT(1.+4.*XK1*FSQRD(I)*CKP(I)))/(2.*XK1*FSQRD(I))
      CL(I)=(-1.+SQRT(1.+4.*XK2*FSQRD(I)*CLC(I)))/(2.*XK2*FSQRD(I))
      AC(I)=PI(I)+CL(I)
      FS=EXP(-4.60518*A*SQRT(AC(I)))
      IF(ABS(FSQRD(I)-FS)-.0001) 699,699,685
  685 FSQRD(I)=FS
      GO TO 610
  699 CONTINUE
  500 DO 599 I=1,N
  510 X(I)=SQRT(AC(I))
      ALPHA(I)=PI(I)/CKP(I)
  599 Y(I)=(LOG(ALPHA(I)*CKP(I)))/2.30258
      ALPHO=PI(1)/CKP(1)
      TOL=TOL/.01
   32 PUNCH 1032,N,D,T
 1032 FORMAT(4H N =I3,9X,15HDIELECT.CONST =F6.2,9X,13HTEMPERATURE =F7.2)
   33 PUNCH 1033,DSOLV,TOL
 1033 FORMAT(21H DENSITY OF SOLVENT =F8.5,17X,5HTOL =F6.4)
   34 PUNCH 1034,XK1
 1034 FORMAT(39H ASSOCIATION CONSTANT FOR ELECTROLYTE =F8.2)
   36 PUNCH 1036,XK2
 1036 FORMAT(40H ASSOCIATION CONSTANT FOR SOLVENT SALT =F8.2)
   37 PUNCH 1037,XK3
 1037 FORMAT(44H ASSOCIATION CONSTANT FOR INTERFERING SALT =F8.2)
      IF(SENSE SWITCH 1)39,38
   38 PUNCH 1038,A
 1038 FORMAT(29H THEORETICAL DEBYE-HUCKEL A =E12.5/)
      GO TO 40
   39 PUNCH 1039,A
 1039 FORMAT(30H EXPERIMENTAL DEBYE-HUCKEL A =E12.5/)
   40 PUNCH 1040
 1040 FORMAT(52H  SOLUBILITY    CONC(LICL)  LOG(ALPHA*SOL)   SQRT(I))
      DO 42 I=1,N
   42 PUNCH 1042,CKP(I),CLC(I),Y(I),X(I)
 1042 FORMAT(1X,E11.4,F11.5,F15.4,F14.5)
   46 PUNCH 1046,ALPHO
 1046 FORMAT(/43H DEGREE OF DISSOCIATION (IN PURE SOLVENT) =F7.4)
      GO TO 1
   53 TYPE 1053
 1053 FORMAT(/45H CONCENTRATION OF SOLVENT SALT LESS THAN ZERO)
      GO TO 1
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  54 TYPE 1054
1054 FORMAT(/36H ASSOCIATION CONSTANT LESS THAN ZERO)
     GO TO 1
     END
```

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