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STUDIES OF EMF CELLS WITH LIQUID
JUNCTIONS BETWEEN DIFFERENT SOLVENTS

by

ANNA BERNE

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

1986

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

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Abstract

STUDIES OF EMF CELLS WITH LIQUID
JUNCTIONS BETWEEN DIFFERENT SOLVENTS

by

ANNA BERNE

Advisor: Professor Orest Popovych

Liquid-junction potentials, E_j , between electrolyte solutions in water and methanol-water solvents were interpreted using both existing equations and a new formulation developed here. The E_j 's were evaluated from the e.m.f. of cells with liquid junction, by considering the contribution of the transfer free energies, transport numbers, and activity coefficients of all the species crossing the junction. Cells with and without salt bridges were studied. The E_j was formally divided into E_j^i and $E_{j,s}$, which account, respectively, for the transport of the ions and the solvent molecules across the interface. An improved formulation for E_j^i was developed which accounts for the variation of the transport numbers of the ions crossing the boundary with the solvent composition across the diffusion layer. $E_{j,s}$ was estimated for junctions between pairs of HCl solutions, pairs of NaCl solutions, and for junctions with a concentrated aqueous KCl salt bridge. $E_{j,s}$ values between water and methanol-water solvents showed a dependence on the content of methanol, the concentration of the electroactive species and the nature of the current-carrying species.

Literature data from pH-cells with liquid-junction in methanol-water media were interpreted.

A new method for estimating transfer activity coefficients of single ions was tested for tetraalkylammonium cations using e.m.f. cells with a salt bridge of tetraalkylammonium perchlorate (RClO_4) between pairs of the following dipolar aprotic solvents: acetonitrile, N,N-dimethylformamide, dimethylsulfoxide, and propylene carbonate. Subsequently, a two-step procedure was developed, in which concentration-dependent $\log_m \gamma$ values of the tetraalkylammonium perchlorate ions obtained in the first step were used to interpret e.m.f. measurements of cells with a salt bridge of tetraalkylammonium picrate (RPI) in order to estimate transfer activity coefficients of the picrate ion.

A saturated solution of tetraphenylarsonium tetraphenylborate ($\text{Ph}_4\text{AsBPh}_4$) in DMSO and later in DMF was used as a salt-bridge between pairs of dipolar aprotic solvents in e.m.f. cells used for estimating transfer activity coefficients, of the sodium ions, $\log_m \gamma_{\text{Na}}$. The new values of $\log_m \gamma_{\text{Na}}$ were compared with the literature values, including those obtained with other salt-bridge electrolytes, thus allowing for the evaluation of the performance of $\text{Ph}_4\text{AsBPh}_4$ as an "ideal" salt-bridge electrolyte.

To my family.

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INTRODUCTION

Presentation of the Problem.

Introduction.

E.m.f. cells with liquid junction find many uses in electrochemistry. With the growing interest in nonaqueous solvent chemistry, methods developed previously for water are now applied to a variety of solvents. Measurements of pH with a glass electrode, the use of other ion-selective electrodes, potentiometric titrations, polarographic studies and studies of electrode kinetics are now conducted in solvents other than water. All of these methods require the use of a reference electrode. Very often that reference is the aqueous saturated calomel electrode, chosen for its stability, reproducibility and ease of preparation. However, the use of such an electrode introduces a liquid junction at the interface of two different solvents. E.m.f. cells with liquid junction are also useful because they can provide direct estimates of transfer free energies and transfer activity coefficients of single ions.

The reliability and accuracy of results obtained in any of these techniques and applications depend on how much we know about the relevant liquid-junction potential, E_j . Traditionally, chemists have been neglecting the contribution of E_j on the assumption that it can be rendered negligible by the interposition of a suitable salt bridge. This salt bridge has been almost invariably a saturated aqueous solution of potassium chloride. Although this approach has been

demonstrated to have merit in all-aqueous e.m.f. cells, opinion has gradually developed that the method would fail when applied to interfaces between different solvent media.

Objectives.

The primary objective of this dissertation research was to study e.m.f. cells with liquid junction between different solvent media in order to elucidate the factors that govern the liquid-junction potentials which arise at their interfaces. Measurements were made in methanol-water solvents with HCl and NaCl as the electrolytes. An improvement is being proposed to the existing formulation for liquid-junction potentials at the interface of two different solvents.

Another objective of this research was the development of a new method for the estimation of transfer activity coefficients of single ions. This method involves measurements of the e.m.f. of cells with a salt bridge between pairs of a number of dipolar aprotic solvents. The single ion for which transfer activity coefficient is being determined is a constituent of the salt-bridge electrolyte.

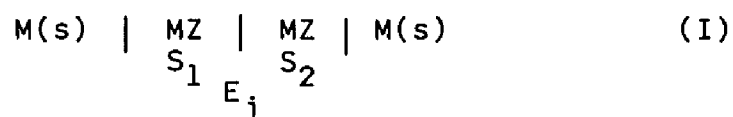
In addition, a new salt-bridge electrolyte, namely tetraphenylarsonium tetraphenylborate, was tested between pairs of dipolar aprotic solvents.

The Theory of the Electrochemical Potential of a Cell with Liquid Junction.

Types of E.m.f. Cells Employed.

In general, two types of cells with liquid junction are used in this work - (I) without a salt bridge and (II) with a salt bridge. The first type of cell is composed of two identical electrodes, reversible to either a cation M^+ , or an anion Z^- , added to solution in the form of the electrolyte MZ . One of the electrodes is in equilibrium with a solution of MZ in the reference solvent S_1 , and the other, with the same electrolyte MZ in solvent S_2 . The choice of solvent S_1 as the reference solvent is, of course, completely arbitrary.

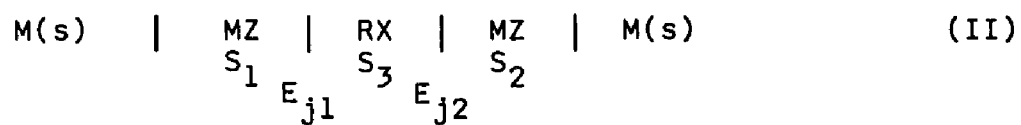
If the electrodes are reversible to the cation M^+ , this cell can be represented schematically as:



where S_1 and S_2 are two different solvents. In such a cell, there exists a liquid-junction potential E_j , at the interface of the two solutions of MZ .

The second type of cell used here differs from the first by the presence of a salt bridge between the half-cells in the two different solvents. The salt-bridge solution consists of an electrolyte RX present at a high concentration relative to the electroactive electrolyte MZ in a

solvent S_3 that is not necessarily the same as either of the electrode solvents:



In Cell II, two liquid junctions are present, one on each side of the salt bridge, giving rise to two liquid-junction potentials, E_{j1} and E_{j2} , respectively.

The E.m.f. of Cell I and II Formulated Without E_j .

General Remarks.

The potential of either Cell I or II is a sum of two terms, E' (sometimes referred to as E_N), and E_j . The latter represents the sum of all liquid-junction potentials in a given cell. For example, for Cell II, which has a salt bridge, $E_j = E_{j1} + E_{j2}$.

E' is the value that the potential of the cell would assume in the absence of a liquid junction. In other words, it can be simply expressed by the difference between the Nernst equations for two electrodes, so that for the cell with electrodes reversible to the cation M^+ and at 25°C we have:

$$E' = {}_2E_M^\circ + 59.16 \log {}_2a_+ - {}_1E_M^\circ - 59.16 \log {}_1a_+ \quad (1)$$

where the potentials are in millivolts. The symbols ${}_1a_+$ and ${}_2a_+$ stand for the molar ionic activities of the ion M^+ in the solvent S_1 and S_2 , respectively. The symbols ${}_1E_M^\circ$ and ${}_2E_M^\circ$ refer to the standard electrode potentials for the half-cell reaction $M^+ + e = M^0$ in solvent S_1 and S_2 , respectively. If the two solvents are chosen to be the same, the difference between the standard electrode potentials for the two half cells becomes zero and Equation 1 reduces to:

$$E' = 59.16 \log \frac{R^a_+}{L^a_+} \quad (2)$$

which represents a simple concentration cell, where a_+ and a_+ are the molar ionic activities of the cation M^+ in the solutions on the right and the left side of the cell, respectively. However, the standard electrode potentials of the same electrode in two different solvents are generally different. The correlation between the E^0 's and ion activities in different solvents is governed by the transfer free energies of single ions, which are defined and discussed in the next section.

Transfer free energy of single ions.

When an electrochemical series is determined in a given solvent, all electrode potentials are assigned relative to the arbitrary value of 0 volts for the potential of the standard hydrogen electrode in that solvent at all T . Similarly, when the activity of a solute i in a given solvent is considered, it is usually referred to its standard state in that solvent. In order to correlate the electrochemical series or to compare the activities of a solute in different solvents, we must use a single standard state. Usually, but not invariably, water is chosen as the reference solvent. The problem is reduced to one of evaluating the difference between the standard free energy of the solute i in the given solvent and in a reference solvent. This difference is often termed the standard free energy of transfer from the reference medium to the medium in which the property is determined. Symbolically we say that for a solute i :

$${}^1_2\Delta\bar{G}_t^\circ(i) \equiv {}_2\bar{G}_i^\circ - {}_1\bar{G}_i^\circ = RT\ln_m\gamma_i \quad (3)$$

The reference solvent, S_1 is often water. ${}_1\bar{G}_i^\circ$ and ${}_2\bar{G}_i^\circ$ are the partial molar standard free energies of the solute i in the two solvents, S_1 and S_2 , respectively. The symbol ${}_m\gamma_i$ is often referred to as either the transfer activity coefficient or the medium effect. The relationship in Equation 3 can also be formulated on the molarity or mole-fraction scale. Complete discussion of the conversions can be found

in (1). In this dissertation the molarity scale is used exclusively.

Final equation for E'.

Going back to the problem of correlating e.m.f. series in different solvents, we recall that $\Delta G^0 = -nFE^0$, where in reference to Cells I and II, $E^0 = {}_2E_M^0 - {}_1E_M^0$. Combining this fact with the expression for the standard free energy of the cell reaction for Cells I and II, $M^+(S_2) \rightarrow M^+(S_1)$ which is

$$\begin{aligned}\Delta G^0(\text{reaction}) &= {}_1G^0(M^+) - {}_2G^0(M^+) \\ &= -{}_1\Delta {}_2G_t^0(M^+) \\ &= -RT \ln {}_m\gamma_M\end{aligned}\quad (4)$$

we arrive at the following relationship for the e.m.f., referred to as E', of Cell I and II under the condition that liquid-junction potential is zero:

$$E' = 59.16 \log {}_m\gamma_M + 59.16 \log \frac{{}_2a_+}{{}_1a_+}\quad (5a)$$

where ${}_m\gamma_M$ is the transfer activity coefficient of the cation M^+ for the transfer of ion M^+ from a solvent S_1 to S_2 .

An analogous equation can be developed if the electrodes in Cell I or II are reversible to the anion Z^- . In that case:

$$E' = -59.16 \log {}_m\gamma_Z - 59.16 \log \frac{{}_2a_-}{{}_1a_-}\quad (5b)$$

To recapitulate, values of E' obtained by using Equations 5a or 5b account for the difference in the Nernstian

responses of the two electrodes comprising Cell I or II. That difference is a function of two parameters only:

1. the medium effect γ_m of the ion to which the electrodes are reversible
2. the conventional activity of the ion in each of the solvents.

The Liquid-junction Potential.

General Remarks.

When two solutions of electrolytes are brought into contact, there will be an interphase region in which the composition will vary from that of one of the end solutions to that of the other. The "make up" of this region will depend upon such factors as diffusion, convection and mixing. The methods by which such liquid junctions are formed concentrate on avoiding convection and mixing, so that any process that takes place in the region between the two end solutions is diffusion-controlled. If the two solutions differ in composition, some (or all) of the constituents on either side will experience a chemical potential gradient, which will cause a unidirectional drift of any given species towards the region of low chemical potential. There are two fundamentally separate reasons for that gradient, which relate to the two factors determining the activity of a given species i in solution. Those two factors are: 1. concentration, and 2. solvent. Thus, if there is a concentration difference for ion i between the two solutions, that ion will diffuse towards the side of low concentration. If the solvents are different, the chemical potential difference for any species i will determine the direction of its drift. That means, of course, that for a boundary between two solvents, the diffusion of all species may have to be con-

sidered, both charged and uncharged, including the molecules of each solvent diffusing into the other.

Now, an obvious fact has to be stated: an electrolyte solution contains both positive and negative ions. It is also a known fact that mobilities of different ions are almost never the same. If two electrolyte solutions are brought into contact and diffusion of ionic species takes place across the interface, the faster-moving ions (usually the cations) move ahead of the slower ones and a spatial charge separation occurs. The law of electroneutrality breaks down for the region in which diffusion takes place. However, that charge separation gives rise to a potential difference across the boundary, which opposes the separation. The faster-moving ions will experience an electric field which slows them down and the slow-moving ions are speeded up by the potential difference. Eventually, a steady state is reached, in which the total flux of positive ions into the volume enclosing the interphase region is equal to the total flux of negative ions entering that region. That steady state is possible only because of the initial occurrence of charge separation due to differences in ionic mobilities, which then creates a potential difference across that region. That potential difference is called a diffusion potential or a liquid-junction potential, E_j .

Historically, expressions needed to calculate E_j were derived in water only and thus related the value of E_j to

the differences in ion concentrations only. A more general formulation was needed for cases where a junction was formed between two different solvents. In the next two sections I will describe the approaches used for the formulation of E_j expressions for a single-solvent and a two-solvent junction, respectively.

Liquid-junction potential at a single-solvent interface.

The concept of unequal diffusion of positive and negative ions across the interfacial region has been supported recently (1981) in a study by Leckey and Horne (2). With the aid of a computer, they were able to perform numerical studies of E_j in a concentration cell as a function of time and to analyze the dependence of E_j on single-ion activities. The results also showed that for a single-solvent system, a steady-state situation is reached practically instantaneously ($\sim 10^{-8}$ sec.). The problems associated with the existence of E_j were apparent, of course, long before 1981. In 1930, Guggenheim (3) reviewed the theory of cells with liquid-liquid junctions. At that time, every study mentioned by Guggenheim, dealt with aqueous solutions only. Some authors (3,4,5,6) concentrated on the experimental design which would assure a stable and/or minimal E_j . Obviously, an intelligent evaluation of any such design was possible only if a formulation for E_j existed which would allow for comparison of theoretical and experimental values.

In order to formulate some expressions for E_j , a general equation is first required. A very good derivation and justification of a basic equation for the diffusion potential can be found in chapter 4 of "Modern Electrochemistry" by Bockris and Reddy (7). Following the presentation by Bockris and Reddy, the liquid-junction potential between two solutions in the same solvent is equal to:

$$\begin{aligned}
E_j &= - \frac{1}{F} \sum_i \int_{x=0}^{x=1} \frac{t_i}{z_i} \frac{dG_i}{dx} dx = \\
&= - \frac{RT}{F} \sum_i \int_{x=0}^{x=1} \frac{t_i}{z_i} \frac{d \ln a_i}{dx} dx = \\
&= - \frac{RT}{F} \sum_i \int_{x=0}^{x=1} \frac{t_i}{z_i} \frac{1}{f_i c_i} \frac{d(f_i c_i)}{dx} dx \quad (6)
\end{aligned}$$

where t_i and z_i are the transport number and charge of the ion i , f_i is the salt-effect activity coefficient of the ion i , the summation is performed over all ionic species crossing the boundary, and the integration is performed across the transition region of thickness l , from the homogeneous solution on the right to the homogeneous solution on the left. To carry out the integration, one must know:

1. How the concentrations c_i of all the species vary in the transition region,
2. How the activity coefficients f_i vary with c_i ,
3. How the transport numbers t_i vary with c_i .

The general case is too difficult to solve analytically, but several special cases can be solved. What follows is a brief summary of the conditions stipulated and the results obtained in solving Equation 6. An excellent discussion of this material can be found in "The Principles of Electrochemistry" by MacInnes (8).

Henderson's integration for the "mixture boundary"

Henderson (9) solved Equation 6 by making the following assumptions:

1. The junction consists of a continuous series of solutions produced by mixing the two solutions initially brought into contact (hence: "mixture boundary"). If x , the mixing fraction, is the proportion of the second solution at a particular point in the boundary, then the fraction of the first solution will be $(1-x)$ and x will vary between zero and unity.

2. The activity coefficient f_i is assumed to be unity or not a function of concentration of ion i .

3. The transport number t_i of the ion i can be expressed at any point in the boundary region as a function of the concentrations c_i and the mobilities u_i of all the ions present at that point.

When the appropriate substitutions are made, Equation 6 can be solved exactly and the following expression for E_j is obtained, which will be referred to from now on as $E_{j,H}$ (H for Henderson):

$$E_{j,H} = \frac{RT \sum_n \frac{u_i}{z_i} (c_i'' - c_i')}{F \sum_n u_i (c_i'' - c_i')} \ln \frac{\sum_n c_i' u_i}{\sum_n c_i'' u_i} \quad (7)$$

The end concentrations of the first and the second solutions are referred to as c' and c'' , and the mobilities of ions are assumed to be constant in that concentration range.

The Henderson equation has been found to be most useful because of its simplicity, although some doubt exists as to how close the boundary conditions come to reality.

Planck's integration for the "constrained diffusion" boundary.

Planck (10) proposed a boundary in which a porous plug separates the two solutions, which are constantly renewed to keep their concentrations constant. Presumably a stationary state is reached in the layer represented by the plug. The numerical value of E_j using Planck's solution is obtained either by a graphical method proposed by Planck himself, or by some sort of iteration. Today, much can be accomplished even with pocket calculators capable of performing such iterations (11), but there does not seem to be any advantage to using Planck's equation over Henderson's. It maybe interesting to point out that in a couple of simple junctions, both equations yield the same results and, in general, the differences between them amount to less than ~5 millivolts.

Taylor's integration for the "free diffusion" boundary

Taylor (12) tried to obtain an approximate solution for the type of junction as defined by the following condition: The transition layer should be initially short compared with the distance between the two electrodes, and unconstrained diffusion should be allowed to take place. Under these conditions, the length of the transition layer is always

increasing, but, if there is cylindrical symmetry, that is, if the gradients of the concentrations and of the electrical potential are throughout parallel to a fixed straight line, it appears that the potential difference is independent of time. The exact solution to Equation 6 with these boundary conditions is impossible and the approximate solution attempted by Taylor is interesting only from the theoretical point of view.

Graphical methods for computing diffusion potentials.

MacInnes (13) proposed a graphical method of evaluating the integral in Equation 6, if the transport numbers for relevant mixtures are known, the mean ion activity coefficients have been measured, and if a Henderson boundary is assumed. This technique depends, of course, on the availability of such data, but when used, provides us with another method for determining the plausibility of the various boundaries mentioned here.

Liquid-junction potential at a two-solvent interface.

Staverman (14), using nonequilibrium thermodynamics, derived a general expression for the liquid-junction potential E_j between any two solutions:

$$E_j = - \int_L^R \sum t_i^r d G_i \quad (8)$$

where the summation extends over all species, charged and uncharged, and the limits of integration are the two homogeneous solutions which form the junction. The reduced transport number t_i^r is defined as the number of moles of species i transported towards the cathode when a Faraday of charge flows in the external circuit of the cell. It is convenient to separate formally the contributions to E_j made by all the charged species from those made by the transfer of the solvent (or of any other uncharged species present in the solutions) across the boundary. This does not mean that each species contributes to E_j independently of others. In fact, there is evidence to the contrary. For the purpose of determining all the factors contributing to E_j this formal separation becomes useful and the equation for E_j can be written as follows:

$$E_j = - \frac{1}{F} \sum_i \int_L^R \frac{t_i}{z_i} dG_i + E_{j,s} \quad (9)$$

where t_i , z_i , and G_i are the transport number, charge and chemical potential of each ionic species, i , present in the

solution. The first term, often referred to as E'_j , involves summation over all charged species crossing the boundary while $E_{j,s}$ refers to the contribution made by the uncharged species, which are almost invariably the solvent molecules. In practice, of course, when the e.m.f. of any cell represented by Cell I is measured, it represents the sum of the three terms, that is:

$$E(I) = E' + E'_j + E_{j,s} \quad (10)$$

where E' accounts for the Nernstian response of the electrodes to one of the ions of the electrolyte MZ.

From Equation 10, it is clear that the ability to calculate E' and E'_j gives us immediate access to the value of $E_{j,s}$. It is also clear that the reliability of the $E_{j,s}$ value thus obtained is directly related to the validity of the E_j expressions and of the data used to calculate both E' and E'_j . It is one of the objectives of this thesis to examine more closely the formulations used in these calculations and perhaps to improve them.

Looking back at the expression for E'_j (Equation 9) and remembering that

$$G_i = G_i^0 + RT \ln a_i \quad (11)$$

we can write for E'_j of Cell I (without a salt bridge):

$$E'_j = - \frac{1}{F} \sum_i \int_1^2 \frac{t_i}{z_i} dG_i^0 - \frac{RT}{F} \sum_i \int_1^2 \frac{t_i}{z_i} d \ln a_i \quad (12)$$

Here, the limits of integration refer to the reference solvent S_1 (often water) on the left and solvent S_2 on the right. The first integral can be solved if t_i is assumed to be constant and independent of the solvent composition across the junction. The evaluation of the integral involves a summation of the transfer free energies of all the ions moving across the junction, each transfer free energy being multiplied by the appropriate transport numbers, and it will be referred to as $E_{j,G}$:

$$E_{j,G} = - \frac{1}{F} \sum \frac{t_i}{z_i} l_{\Delta}^2 G_t^{\circ}(i) \quad (13)$$

For a simple junction present in Cell I, given schematically by:



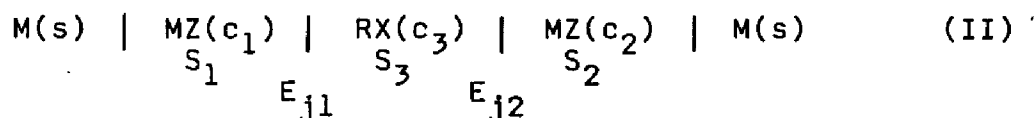
$E_{j,G}$ is equal to:

$$E_{j,G} = - \frac{1}{F} [t_M l_{\Delta}^2 G_t^{\circ}(M) - t_Z l_{\Delta}^2 G_t^{\circ}(Z)] \quad (13a)$$

A more interesting situation occurs when either junction present in Cell II (with a salt bridge) is considered. For the purpose of this discussion we chose the following junction:



In general, both cations (R^+ and M^+) and both anions (X^- and Z^-) have to be included in the calculation of $E_{j,G}$. However, if $c_1 \gg c_2$ (the proper salt-bridge condition), then the transport numbers of M^+ and Z^- in the transition layer are very small compared to those of R^+ and X^- and can be neglected. Under those conditions, the $E_{j,G}$ is completely dominated by the transfer free energies and transport numbers of the salt-bridge electrolyte, RX . An important fact has to be mentioned regarding the choice of the salt-bridge solvent. It can be easily shown that the total $E_{j,G}$ for Cell II does not depend on the identity of S_3 . The proof depends on the assumption that the transport numbers of individual ions do not change with the composition of the solvent. That is not always true, but if the changes are small enough, they can be neglected. Let us recall Cell II:



We assume that $c_1 \cong c_2$ (which can be controlled experimentally) and that $c_1 \ll c_3 \gg c_2$, so that $t_M \cong t_Z = 0$ and $t_R + t_X \cong 1$.

$E_{j,G}$ component of E_{j1} is equal to:

$$(E_{j,G})_1 = - \frac{1}{F} \{ t_R [{}_3G^0(R^+) - {}_1G^0(R^+)] - t_X [{}_3G^0(X^-) - {}_1G^0(X^-)] \} \quad (14a)$$

$E_{j,G}$ component of E_{j2} is equal to:

$$(E_{j,G})_2 = -\frac{1}{F} \{t_R[{}_2G^0(R^+) - {}_3G^0(R^+)] - t_X[{}_2G^0(X^-) - {}_3G^0(X^-)]\} \quad (14b)$$

If we combine both terms, remembering that t_R and t_X are the same for both junctions, we get:

$$E_{j,G} = -\frac{1}{F} \{t_R[{}_3G^0(R^+) - {}_1G^0(R^+) + {}_2G^0(R^+) - {}_3G^0(R^+)] - t_X[{}_3G^0(X^-) - {}_1G^0(X^-) + {}_2G^0(X^-) - {}_3G^0(X^-)]\} \quad (15)$$

When the addition is completed, the standard free energy terms referring to solvent S_3 vanish and we are left with an expression for $E_{j,G}$ which is a function of the transfer free energies of ions R^+ and X^- between the end solvents S_1 and S_2 only.

$$E_{j,G} = -\frac{1}{F} [t_R {}^1\Delta {}^2G_t(R^+) - t_X {}^1\Delta {}^2G_t(X^-)] \quad (16)$$

To complete the discussion of liquid-junction potential between different solvents Equation 12 must be recalled. The last term of that equation resembles very closely Equation 6, which is:

$$E_{j,H} = -\frac{RT}{F} \sum_i \int_{x=0}^{x=1} \frac{t_i}{z_i} \frac{d \ln a_i}{dx} dx \quad (6)$$

and the last term in Equation 12 is

$$- \frac{RT}{F} \sum_i \int_2^1 \frac{t_i}{z_i} d \ln a_i \quad (12a)$$

The basic difference between these two expressions is that in the first case the limits of integration involve solutions in the same solvent, while in the second case, the solutions are in two different solvents. In the present study, the approach to handling Equations 6 and 12a is twofold. Firstly, the Henderson equation is applied to Equation 12a using conventional activities instead of concentrations in the final expression for $E_{j,H}$. Since the transport numbers of ions often change from solvent to solvent, their average values in the two solvents are used here for each ion. Secondly, since some of these manipulations may be of questionable value, our effort is made to minimize the $E_{j,H}$ term. That can be accomplished in two ways:

1. In the case of Cell I, the concentrations of MZ in each solution are chosen to be as close to each other as possible.

2. In the case of Cell II, a salt bridge is used in conjunction with the equal concentrations of MZ in both solvents. A complete derivation of expression for $E_{j,H}$ for Cell II can be found in Appendix I.

Here is the final result:

$$E_{j,H(II)} = - \frac{RT}{F} (t_R - t_X) \ln \frac{2^{a_+}}{1^{a_+}} \quad (17)$$

It is clear that when $t_R = t_X$, $E_{j,H}$ will be equal to zero, but that does not mean that the E_j will vanish also. We have already seen that E_j between two different solvents has three components:

$$E_j = E_{j,G} + E_{j,H} + E_{j,s} \quad (18)$$

and all three have to be acted upon in a manner that would render them negligible or accounted for. The techniques chosen depend, of course, upon our understanding of all the factors contributing to E_j . The results obtained in this work will contribute to that understanding.

Methods for Estimating Transfer Free Energies of Single Ions.

Methods of Determining Thermodynamics Transfer Activity Coefficients.

Transfer activity coefficients of uncharged molecules, complete electrolytes and electroneutral combinations of ions can be calculated from experimental data without any extrathermodynamic assumptions. The most common methods of determining thermodynamic transfer free energies are discussed below. The reference solvent chosen for the discussion is water, but that is only because of historical precedent and convenience. Any other solvent could be used as a reference medium. For example, acetonitrile has been used as the reference medium for comparisons among organic solvents. The solvent chosen as reference must be clearly specified. Thus, the term ${}^{\text{MeCN}}\gamma_i^{\text{DMSO}}$ or ${}^{\text{MeCN}}\Delta^{\text{DMSO}}G_i^o$ refers to the transfer of solute i from acetonitrile (reference) to dimethylsulfoxide. It is a simple matter to convert the value of a transfer activity coefficient based on one reference solvent to another, if appropriate transfer activity coefficients are known. For example:

$${}^{\text{MeCN}}\Delta^{\text{DMSO}}G_i^o = W_{\Delta}^{\text{DMSO}}G_i^o - W_{\Delta}^{\text{MeCN}}G_i^o \quad (19)$$

where W represents H_2O .

Solubility Method.

When water and a nonaqueous solvent are both saturated with solute i, the chemical potentials of that solute in each solution are expressed by:

$${}_wG_i = {}_wG_i^{\circ} + RT \ln {}_w a_i \text{ (satd.)} \quad (20a)$$

$${}_sG_i = {}_wG_i^{\circ} + RT \ln {}_s a_i \text{ (satd.)} \quad (20b)$$

where ${}_w a_i \text{ (satd.)}$ and ${}_s a_i \text{ (satd.)}$ are the conventional activities of solute i in the aqueous and nonaqueous saturated solutions. The free energies of a solute in the solid state and in a saturated solution are equal. If neither solid forms a crystal solvate, both solutions are in equilibrium with the solute in the same solid state and thus their activities are equal:

$${}_wG_i = {}_sG_i \quad (21)$$

After substitutions and rearrangement the following equation is obtained:

$$\ln {}_m \gamma_i = \ln \frac{{}_w a_i \text{ (satd.)}}{{}_s a_i \text{ (satd.)}} \quad (22)$$

For an electrolyte, the activity of a saturated solution is equivalent to the solubility product, K_{sp} . Expressed in logarithmic form, Equation 22 becomes:

$$\log {}_m \gamma_i = p({}_s K_{sp}) - p({}_w K_{sp}) \quad (23)$$

While the estimation of transfer activity coefficients of simple ions requires some extrathermodynamic assumptions, it is possible to utilize that concept (of single ion medium effects) in formulating expressions for transfer activity coefficients for electroneutral combinations of ions. For example,

$$\log_m \gamma_{Cl} - \log_m \gamma_{Br} = \log_m \gamma_{AgCl} - \log_m \gamma_{AgBr} \quad (24)$$

For a symmetrical electrolyte (1:1, 2:2, etc.),

$$\log_m \gamma_{(\text{electrolyte})} = \log_m \gamma_{\pm}^2 = (\log_m \gamma_{+} + \log_m \gamma_{-}) \quad (25)$$

where $\log_m \gamma_{\pm}^2$ is the experimentally determined thermodynamic transfer activity coefficient of the complete electrolyte, and the r.h.s. represents the formal separation of that coefficient into contributions from the cation ($\log_m \gamma_{+}$) and the anion ($\log_m \gamma_{-}$).

There are several complications in the use of the solubility method. The first one has been mentioned already and it is the requirement that neither solvent form crystal solvates with the solute. The second complication arises from the fact that in solvents of low dielectric constant the possible association of ions may take place. In case of considerable ion-pairing, the solubility product must be expressed as

$$K_{sp} = c^2 \alpha^2 \gamma_{\pm}^2 \quad (26)$$

where c is the molarity, α is the degree of dissociation of

the ion pairs, and $\gamma_{\pm}$ is the salt-effect activity coefficient. The degree of dissociation is generally determined experimentally from electrolytic conductance measurements. A third complication involves obtaining values of salt-effect activity coefficients. In most cases, experimentally determined values of activity coefficients in nonaqueous solvents are not known. Calculations of these coefficients, using either the Debye-Huckel equation or a Davies equation, are commonly used for solutions of electrolytes of concentrations up to 10^{-2} molar. There is no acceptable method for determining activity coefficients of electrolytes at higher concentrations. Thus, the solubility method of determining transfer activity coefficients is suitable for electrolytes only slightly soluble in both solvents. The uncertainty of the activity corrections for solutions above 10^{-2} molar render the solubility method invalid for solutes, whose solubility exceeds that order of magnitude.

E.m.f. method.

Medium effects for electroneutral combinations of ions can be determined from e.m.f. measurements. The sums of the medium effects (in logarithmic form) of oppositely charged ions or the difference between medium effects of ions of like charge are accessible. The difference in standard free energies of solvation and hydration of species $\underline{i}$ corresponds to the energy of transfer of species $\underline{i}$ from the aqueous to the nonaqueous standard state. The standard free energy for the hydration reaction



is ${}_w\bar{G}_i^0$ and the standard free energy for the solvation reaction



is ${}_s\bar{G}_i^0$. The transfer of $\underline{i}$ from aqueous to nonaqueous standard states corresponds to



and the energy of transfer is

$${}_w\Delta^s\bar{G}_t^0(i) = {}_s\bar{G}_i^0 - {}_w\bar{G}_i^0 \quad (3a)$$

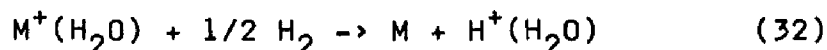
Standard free energies can be expressed in terms of single-electrode standard potentials via the equation

$$\bar{G}_i^0 = -nFE^0 \quad (30)$$

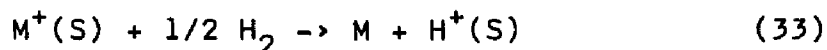
Thus, the transfer activity coefficient or medium effect for species i can be expressed in terms of single-electrode standard potentials

$$\ln_m \gamma_i = - \frac{nF}{RT} \Delta E_i^0 \quad (31)$$

where ΔE_i^0 is the standard potential corresponding to reaction 29. However, the only thermodynamic experimentally accessible standard potential of species i includes the standard potential of the reference species. For example, the experimental aqueous standard potential of the M^+ ion, ${}_wE^0(M, H_2O)$ in reality corresponds to the reaction

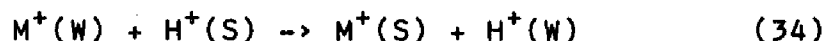


where the ${}_wE^0(H, H_2O)$ is directly related via Equation 30 to the standard energy of hydration of the hydrogen ion and is assigned value of zero volts. Similarly, in the nonaqueous solvent, the standard potential ${}_sE^0(M, S)$ corresponds to the reaction



where ${}_sE^0(H, S)$ is again assigned a value of zero. We might recall here that it is the arbitrary assignment of zero to the standard potential of the hydrogen electrode in every solvent which gives rise to as many experimentally determined electrochemical series as there are solvents in use, since in general ${}_1E^0(H, S_1) \neq {}_2E^0(H, S_2)$. When Equation 33 is

subtracted from Equation 32, the result represents the following reaction:



and with the use of Equation 30 we can write:

$${}_sE^0(M,S) - {}_wE^0(M,H_2O) = \frac{RT}{nF}(\ln_m \gamma_i - \ln_m \gamma_H) \quad (35)$$

When the species transferred according to Equation 29 is a negatively charged ion, Z^- , equation similar to Equation 35 can be developed:

$${}_sE^0(Z,S) - {}_wE^0(Z,H_2O) = \frac{RT}{nF}(\ln_m \gamma_Z + \ln_m \gamma_H) \quad (36)$$

Equations 35 and 36 illustrate the basic principle utilized in the e.m.f. method for determining transfer free energies of species i using e.m.f. cells without transference. The obvious requirement for the applicability of this method is that an electrode reversible to species i exist in both solvents. Furthermore, the difference between the experimentally accessible conventional standard potentials ${}_sE^0(i,S)$ and ${}_wE^0(i, H_2O)$ results in a value which represents some combination of the transfer activity coefficients for the ion of interest i and the reference ion, most frequently the hydrogen ion.

Distribution method.

The use of the distribution method for determination of transfer activity coefficients is quite limited. In cases where the two solvents are totally immiscible, the value of m^{γ}_i can be determined by extraction methods, because at equilibrium, the chemical potentials of solute i in the two phases are equal. The advantage of this method lies in the fact is that dilute solutions may be used, thus enabling one to neglect any uncertain corrections for salt-effect activity coefficients and the degree of dissociation required in the solubility method. However, in practice, most solvents of interest are miscible. In addition, so-called immiscible solvents are nevertheless saturated with each other at equilibrium. Thus, the solute is distributed not between two pure solvents, but between two media, each of which represents a different mixture of the two solvents.

Summary

Transfer activity coefficients of complete electrolytes or of electroneutral combinations of ions are commonly determined experimentally by two methods. The solubility method is practical for solutes which are only slightly soluble in both solvents of interest and form no crystal solvates. The e.m.f. method is useful for those species for which a reversible electrode exists in both solvents. The accuracy and precision of the transfer activity coefficients obtained with either method is a function of experimental factors. One such factor could be the accuracy of the method used to determine the concentration of a saturated solution of solute i; another factor might have to do with the method chosen for determining the salt-effect activity coefficients. However, none of these factors require any extrathermodynamic assumptions.

Transfer Activity Coefficients for Single Ions.

Introductory Remarks.

The physical significance of the energetic properties of single ions is no longer in dispute. A number of representative examples can be mentioned, supporting the contention that properties of single ions provide meaningful physico-chemical information. From conductivity, transference, and viscosity measurements of solutions of silver nitrate in mixtures of acetonitrile and water, Strehlow and Koepp (15) determined that silver ions are preferentially solvated by CH_3CN , when compared to the solvation of nitrate ions. Kim and Duschner (16) determined the thermodynamic formation constants of silver chloride complexes in mixed aqueous-ethanol solvents. With the aid of known medium effects for the chloride ion in the system, the medium effects for the silver ion and the silver chloride complex species were calculated and the preferential solvation of the silver and the chloride ion were interpreted further.

Izmaylov (17) estimated (by extrapolation methods) that the free energy of the proton is lower (more negative) in ammonia than in water by 23 kcal/mole. Strehlow (18,19) has repeatedly pointed out that whereas the transfer of alkali halides from water to ammonia involves energy changes of the order of a few kcal/mole, the corresponding transfer of acids is accompanied by $\Delta \bar{G}_t$ values in the vicinity of -20 kcal/mole. In view of Izmaylov's estimate that $\Delta \bar{G}_t^\circ(\text{H}^+) =$

-23 kcal/mole, it is clear that the proton dominates the energetics of the above transfer process, regardless of which anion is transferred along with it. Bockris and Reddy (7) compared the hydration enthalpies of salts with only one varying ion and came to the conclusion that the differences had to be attributed to the changes in hydration energies of the individual ions.

Very convincing evidence for the physical significance of the transfer activity coefficients for simple ions comes from Parker's (20) studies of transfer processes between trifluoroethanol (TFE) and hexamethylphosphoramide (HMPA). The silver ion is preferentially solvated by HMPA to such an extent that the $\Delta \bar{G}_t^\circ(\text{Ag}^+)$ from TFE (reference) to HMPA amounts to -22 kcal/mole ($\log_m \gamma_{\text{Ag}} = -16$). The reverse is true for the chloride ion, so that $\Delta \bar{G}_t^\circ(\text{Cl}^-) = +15.5$ kcal/mole ($\log_m \gamma_{\text{Cl}} = 11.4$). As a consequence of these extreme opposite preferences on the part of the Ag^+ and the Cl^- ions for TFE and HMPA, the corresponding transfer activity coefficient of AgCl is comparatively small ($\log_m \gamma_{\text{AgCl}} = 4.9$). Thus, a misleading view of relative ionic solvation in TFE and HMPA would be obtained if one relied solely on the thermodynamic transfer activity coefficients for the complete electrolyte.

It is clear that the problem with the energetic properties of single ions lies not in their physical significance, but in their accessibility.

Every approach to the problem of obtaining transfer activity coefficients for single ions requires the use of some extrathermodynamic assumption. Consequently, the accuracy of the resulting medium effects depends not so much on the experimental parameters (which can usually be controlled and measured with sufficient precision) but on the validity of a given assumption. Popovych (21-24), Alexander and Parker (25), and Berne (26) have reviewed some or all of the extrathermodynamic methods.

The results can be evaluated in the light of either the agreement among the final values of transfer activity coefficients for species i obtained by various methods (thus lending credence to those methods among which agreement is most pronounced) or by critical analysis of the validity of each assumption made. Basically, the methods can be divided into two broad categories: 1) those based on relationships between the sizes of ions and their solvation energies and 2) potentiometric methods with the assumption of negligible or calculable liquid junction potential. Among methods in the first group are extrapolation methods, calculations based on modified Born equations, and various empirical assumptions for reference solutes. In some methods, medium effects for single ions are estimated directly whereas in others, solvation energies for single ions are estimated first and then the medium effects are calculated from their differences. The method which at present finds most favor with many chemists working in this field is called the

reference-electrolyte method and will be described next as a representative of the whole group.

The reference-electrolyte method.

Historically, an effort was made to find an ion whose solvation free energy could be assumed to be essentially constant for a number of solvents and for which there existed a reversible electrode. Pleskov (27) chose rubidium as this "normal element" on the basis of its "large" radius ($1.49\text{\AA}$), small charge, low polarizability, and a minimal tendency toward specific interaction with solvents. Even though subsequent studies showed Pleskov's method to be rather inadequate, it pointed the way to the final general approach based on large solute species, namely the use of a reference electrolyte. Such an ideal 1:1 "reference electrolyte" would have large ions ($r > 4\text{\AA}$), with small surface charge densities, low polarizabilities; they would also not interact specifically with solvent molecules and would be as similar to each other as possible.

When the transfer activity coefficient of a complete reference electrolyte is known, it can then be separated into equal contributions from the positive and the negative ion, respectively:

$$\log_m \gamma_{\text{cation}} = \log_m \gamma_{\text{anion}} = 1/2 \log_m \gamma_{\text{reference electrolyte}} \quad (37)$$

The idea of apportioning measureable properties of an electrolyte between its ions is not new. MacInnes (28) suggested that the chloride ion activity in a solution of any chloride be considered the same as in a solution of potassium chloride at the same total concentration. In

essence, the MacInnes assumption relied on the activity of the chloride ion being equal to the activity of the potassium ion in a solution of potassium chloride, thus making KCl the first reference electrolyte. Fuoss and Hirsch (20) proposed the use of tetrabutylammonium tetraphenylborate and Coetzee and Cunningham (30) used tetraisoamylammonium tetraisoamylboride as the reference electrolyte in the evaluation of single ion conductivities in solvents where accurate transference data were not available.

The first use of a reference electrolyte to estimate transfer free energies for ions was reported in 1960. Grunwald, Baughman and Kohnstam (31) used tetraphenylphosphonium tetraphenylborate (Ph_4PBPh_4) to estimate free energy changes for the transfer of single ions between dioxane-water mixtures. Trisoamyl- n -butylammonium tetraphenylborate (TABPh_4) was used by Popovych (32) to determine transfer activity coefficients in methanol and the ASTM mixture, consisting of 50.0% toluene, 49.5% isopropanol and 0.5% water, by volume and by Popovych and Dill (33) in ethanol-water mixtures. Currently, the reference electrolyte of choice is tetraphenylarsonium tetraphenylborate ($\text{Ph}_4\text{AsBPh}_4$) (23,25,33-37). When the $\text{Ph}_4\text{AsBPh}_4$ assumption is applied, the transfer activity coefficient of the complete electrolyte is divided equally between its ions:

$$\log_m \gamma_{\text{Ph}_4\text{As}} = \log_m \gamma_{\text{BPh}_4} = 1/2 \log_m \gamma_{\text{Ph}_4\text{AsBPh}_4} \quad (38a)$$

Once the transfer activity coefficient is available for one

ion, values of $\log_m \gamma$ for other single ions can be calculated from available data, for example:

$$\log_m \gamma_K = \log_m \gamma_{K\text{BPh}_4} - \log_m \gamma_{\text{BPh}_4} \quad (38b)$$

$$\log_m \gamma_{\text{Cl}} = \log_m \gamma_{\text{KCl}} - \log_m \gamma_K \quad (38c)$$

$$\log_m \gamma_H = \log_m \gamma_{\text{HCl}} - \log_m \gamma_{\text{Cl}} \quad (38d)$$

While the transfer activity coefficient of $\text{Ph}_4\text{AsBPh}_4$ is not always easy to determine directly because of its extremely low solubility in water (the most popular reference solvent), it can be calculated from $\log_m \gamma$ values of other electrolytes, e.g.:

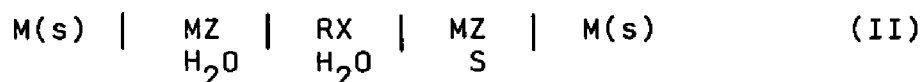
$$\begin{aligned} \log_m \gamma_{\text{Ph}_4\text{AsBPh}_4} = \\ \log_m \gamma_{\text{Ph}_4\text{AsPi}} + \log_m \gamma_{\text{KBPh}_4} - \log_m \gamma_{\text{KPi}} \end{aligned} \quad (38e)$$

which are accessible experimentally. Obviously, transfer activity coefficients for electroneutral combinations of ions must be available first, before they can be apportioned into single-ion values by the reference electrolyte assumption.

Existing potentiometric methods. Literature review.

The only experimental method which, in principle, can provide direct estimates for the transfer activity coefficients of single ions is potentiometry using e.m.f. cells with liquid junction.

Typically, Cell II is used, composed of the same metal electrode M in equilibrium with its ions M^+ in water and the nonaqueous solvent S, with a solution of a salt-bridge electrolyte RX inserted between the two end solutions:



If, for the sake of simplification, the activity of M^+ ions is adjusted to be equal in the two solvents, the potential of Cell II is given by:

$$E^0(II) = {}_sE^0 - {}_wE^0 + E_j \quad (39)$$

Recalling the definition of ${}_m\gamma$ from Equations 3 and 31, it follows that at 25°C:

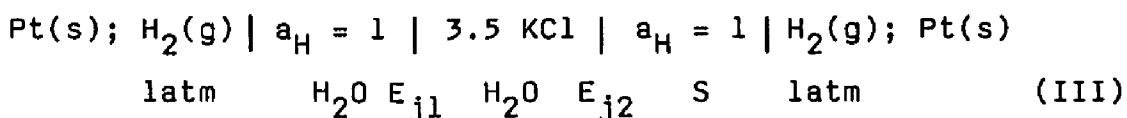
$$E^0(II) = 59.16 \log {}_m\gamma_M + E_j \quad (40)$$

where the potentials are in millivolts. Cell II can of course be employed using electrodes reversible to other than metal ions, e.g. H^+ or Cl^- , where they yield values of $\log {}_m\gamma_H$ or $\log {}_m\gamma_{Cl}$, respectively. It is clear that the potential of Cell II provides a direct measure of $\log {}_m\gamma_M$, provided the liquid-junction potential E_j is negligible or

calculable. What follows is a critical review of the existing approaches designed to deal with the E_j .

Negligible liquid-junction potential.

The assumption that the E_j at the interface of different solvents can be minimized by interposition of a concentrated-salt bridge was the first approach to the estimation of the transfer activity coefficients of single ions. In 1927, Bjerrum and Larsson (38) estimated the values of $\log_m \gamma_H$ in ethanol-water media from the e.m.f. measurements of cells composed of hydrogen electrodes in the nonaqueous media and a 3.5 N aqueous calomel electrode as the reference. They assumed that the E_j between the ethanol-water solutions and the aqueous KCl bridge solution could be neglected. In effect, their measurements could be represented by the following cell, composed of standard hydrogen electrodes (SHE) in water and in solvent s , separated by a salt bridge:



For the above cell, the potential E is given:

$$E(\text{III}) = 59.16 \log_m \gamma_H + E_{j1} + E_{j2} \quad (41)$$

Bjerrum and Larsson made several erroneous assumptions in their calculations. They did not account for incomplete dissociation of electrolytes in ethanol and ethanol-water

solvents. They used a cube root formula

$$\log f = -k c^{1/3} \quad (42)$$

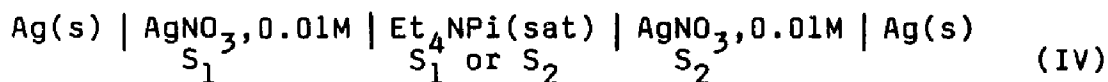
for estimating activity coefficients, which is not generally accepted anymore. The most significant error, however, lies in their assumption of negligible E_j . We may recall that for a simple junction between two different solvents the E_j is a sum of the following terms:

$$E_j = E_{j,G} + E_{j,H} + E_{j,s} \quad (18)$$

$E_{j,G}$ is a function of transfer activity coefficients and transport numbers of all ions crossing each boundary, $E_{j,H}$ accounts for differences in mobilities of those ions, and $E_{j,s}$ is responsible for contributions to E_j from the transport of the solvent molecules across the junctions. In the case of Cell III, the $E_{j,H}$ is indeed very small because of the presence of the salt bridge, but no such claim can be made about the value of $E_{j,G}$ and $E_{j,s}$, and thus the assumption of negligible E_j is invalid.

Oiwa (39) in 1957 used a cell similar to Cell III to estimate $\log_m \gamma_H$ values in methanol-water solvents. While he tried to account for the differences in ionic mobilities by the use of the Planck (10) equation, he, like Bjerrum and Larsson, failed to consider the effect of the transfer activity coefficients on the diffusion potential of such a cell.

Parker and coworkers (25,40-44) used the following cell to study the magnitude of the E_j between various solvents



where $\text{Et}_4\text{N}^+\text{Pic}^-$ is tetraethylammonium picrate.

In general, if the conventional activities of the AgNO_3 solutions are the same in both solvents, the following relationship is true:

$$E(\text{IV}) = 59.16 \log_m \gamma_{\text{Ag}} + E_j \quad (43)$$

By assuming negligible E_j Parker (40) and later Alexander, et al. (25) calculated $\log_m \gamma_{\text{Ag}}$ from the e.m.f. measurements of Cell IV for a number of solvent pairs. Parker then proposed that the assumption of negligible E_j be considered valid for those pairs of solvents for which the transfer activity coefficients for Ag^+ thus obtained were similar to those arrived at by other methods (such as the $\text{Ph}_4\text{As}^+\text{BPh}_4^-$ assumption). Using $\log_m \gamma_{\text{Ag}}$ values referred to as "our estimate" (resulting from a critical review of various data for $\log_m \gamma_{\text{Ag}}$ available for a given pair of solvents), Parker then calculated E_j via Equation 43. Table 1 lists the results for some representative pairs of solvents for which these calculations were performed. The $E(\text{IV})$ values listed were obtained within limits shown using any one of the three bridge solvents (S_1 , S_2 , and 50:50 $S_1:S_2$), and using AgClO_4 in place of AgNO_3 . The conclusion drawn from these calculations (and supported by a more thorough investigation in

(40)) was that the assumption of negligible E_j in Cell IV is valid only for interfaces between two dipolar aprotic solvents. "Negligible" here means less than 30 mV, which is important to remember when considering the uncertainty of $\log_m \gamma_{Ag}$ obtained from Equation 43. It is easily seen that an E_j value of ± 10 mV corresponds to a change of $\pm .17$ in the calculated value of the transfer activity coefficient for Ag^+ . Thus, saying that an E_j of 30 mV is negligible amounts to an uncertainty of ~ 0.5 in the value of $\log_m \gamma_{Ag}$.

TABLE 1

Transfer Activity Coefficients of Ag^+ Estimated by Parker
(40) and E_j Values of Cell IV Calculated Using $\log_m \gamma_{\text{Ag}}$.

S_1	S_2	$E(\text{IV})$	$\log_m \gamma_{\text{Ag}}^{S_1 S_2}$		$E_j, \text{ mV}$ (calculated using "our estimate")
			calculated if $E_j = 0$	"our estimate"	
H_2O	MeOH	75 ± 10	+1.5	+0.8	-40
H_2O	DMF	-90 ± 10	-1.3	-4.3	-180
MeOH	HMF	-190 ± 10	-3.6	-3.7	-5
MeCN	DMF	$+40 \pm 0$	+0.8	1.2	+20
MeCN	DMSO	-135 ± 5	-2.5	-1.9	+30
DMF	DMSO	-180 ± 10	-3.4	-3.1	+20
MeOH	MeCN	255 ± 5	-4.3	-6.3	-120

Finally, Parker (42,43) recommended a silver electrode immersed in a 0.01M AgClO_4 in acetonitrile, with a salt bridge of 0.1M $\text{Et}_4\text{N}^+\text{Pi}^-$ in MeCN, as a reference electrode for electrochemical work in nonaqueous solvents. From e.m.f. measurements of a cell similar to Cell IV, where one electrode was the proposed reference electrode, and the other electrode consisted of a silver wire immersed in 0.01M AgClO_4 in a number of solvents, all different from MeCN, Parker calculated for every solvent pair the E_j present at the interface of the two solvents. He subsequently proposed to correct the experimental measurements of e.m.f. cells utilizing his reference electrode by subtracting from them the value of E_j calculated for Cell IV, provided that the test solution concentration was less than 0.01M. That procedure is legitimate only if the E_j of the junction represented by 0.1M $\text{Et}_4\text{N}^+\text{Pi}^-$ in MeCN 0.01M (or less) MZ in S is constant both for decreasing concentrations of MZ as well as the variable identity of MZ. How valid is that assumption? Parker calculated the total diffusion potential in Cell IV from experimental parameters and without considering the individual factors contributing to it. Equation 18 states that E_j is a sum of three terms, $E_{j,G}$, which is a function of transfer activity coefficients and transport numbers of all ions crossing the boundary, $E_{j,H}$, which accounts for differences in mobilities of those ions, and $E_{j,s}$, which is responsible for contributions to E_j for the transport of the solvent molecules across the junction.

Could it be fortuitous that for some solvent pairs that sum is very small, even though the individual terms may be quite large? The answer to this question would permit a more enlightened use of Parker's electrode. The relative contributions to $E_{j,G}$ and $E_{j,H}$ made by the salt-bridge electrolyte RX as opposed to those made by the test solution electrolyte MZ, depend on their relative concentrations. In Cell IV that ratio is only 10:1, which means that the presence of MZ (such as AgClO_4) in the diffusion layer of the junction interphase cannot be ignored. It is also obvious that the contribution of MZ to the value of $E_{j,G}$ and $E_{j,H}$ will change not only with the concentration of MZ (via changing transport numbers for M^+ and Z^-) but with the identity of MZ (via mobilities and transfer activity coefficients of M^+ and Z^-). While a concentration ratio of 100:1 usually renders contributions from MZ negligible, that condition is not met in Parker's Cell IV. The third term of Equation 18, $E_{j,s}$, has been found to be a function both of the concentrations as well as the identities of electrolytes crossing the boundary. Even when the concentration and the nature of the salt-bridge electrolyte is fixed (as it would be in a reference electrode), no such claim can be made about the electrolyte MZ.

This author does not question the validity of Parker's results for $\log_m \gamma_{\text{Ag}}$ and for E_j obtained from e.m.f. measurements of Cell IV. However, applying these E_j values to cells where the concentration and/or the nature of the test

solution electrolyte MZ was changed is not justified without further investigation of all the factors contributing to the liquid-junction potential between different solvents.

Matsuura and coworkers (45-47) studied the behavior of several metal ions (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , Tl^+ , Ag^+) in DMSO, DMF and PC. They determined the values of the half-wave potentials for the alkali metals measured against the aqueous SCE (45). By assuming that a difference between two $E^{1/2}$ values is the same as the difference between the two respective E^0 values, an electrochemical series was established in each solvent, using Rb(Hg)/Rb^+ as the reference electrode in each case. The E^0 values corresponding to transfer free energies for the Rb^+ ion were calculated using the Born equation and compared with the experimental values of ${}_sE^{1/2}_{\text{Rb}} - {}_wE^{1/2}_{\text{Rb}}$. Because of a poor correlation between these two sets of values, a correction term was introduced corresponding to the E_j at the junction between the aqueous reference electrode and the polarographic solution. Subsequently, a different value for the E_j was obtained from the determinations of standard electrode potentials in these solvents (46). Table 2 lists the E_j values from both sources. Matsuura, et. al. attributes the different results to two factors. First, the concentration of the current-carrying electrolyte was varied ($0.1\text{M Et}_4\text{NPI}$ in polarographic studies and $0.01\text{M Et}_4\text{NPI}$ in the standard potential determinations); second, the polarographic half-wave potentials were not corrected for any changes due to the variation in

the diffusion constants and the salt-effect activity coefficients with the change of the solvent medium. This second factor relates to the assumption that electrochemical series can be established using half-wave potentials. While this is true in principle, the correlation between those two scales is not exact and all the factors relating E^0 and $E^{1/2}$ should be taken into account. It must be noted, however, that for the purpose of estimating transfer free energies of single ions, those factors appear to be very small, as the authors point out themselves while analyzing their results.

TABLE 2

Comparison of E_j Values Obtained for the Interface

KCl(sat) | $\text{Et}_4\text{N}^+\text{Pi}^-$.
 H_2O S

Solvent	$E_j(\text{mV})(a)$	$E_j(\text{mV})(b)$
DMSO	90	121
DMF	85	121
PC	4	37

a) results from (45). Conc. of $\text{Et}_4\text{N}^+\text{Pi}^- = 0.1\text{M}$

b) results from (46). Conc. of $\text{Et}_4\text{N}^+\text{Pi}^- = 0.01\text{M}$

Medium effects of several single ions were estimated (47) from the solubility products of thallium halides combined with the transfer free energies of cations obtained in (46). After comparing the values of $\log_m \gamma_{Ag}$ obtained via various extrathermodynamic assumptions, the conclusion was drawn that the method of the corrected rubidium scale (where the E_j is taken into account) yields reasonable results. Table 3 lists some of the medium effects for single ions obtained by Matsuura, et al. (47) as well as $\log_m \gamma$ values reported in (84) and included here for comparison.

Liquid-junction potential included.

We see that, historically, transfer activity coefficients of single ions were at first obtained by neglecting or minimizing the E_j , but with time an effort was made to correct for even a "negligible" liquid-junction potential. Goldberg (48) and Goldberg and Popovych (49) have used both approaches in their study of the medium effects for Na^+ and H^+ ions between a number of dipolar aprotic solvents. The following cell was used:

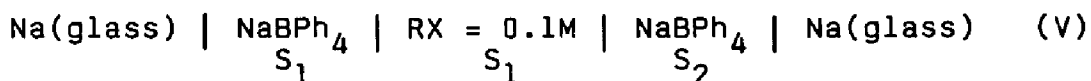


TABLE 3

Medium Effects for Some Single Ions ($\log_m \gamma$) (Molar Scale).

Reference Solvent is Water (47).

Ion	$\log_m \gamma$ for transfer to		
	DMSO	DMF	PC
K^+	-1.24(-2.13)*	-0.35(-1.69)*	+2.07(+1.03)*
Na^+	-1.14	+0.07	+3.74
Ag^+	-5.15(-6.15)*	-2.28(-3.03)*	+3.69(1.83)*
ClO_4^-	-1.22	-1.22(0.07)*	

*Values in parenthesis are from ref. 84.

One objective of their study was to compare the effect of the salt-bridge electrolytes $(\text{tab}^+)(\text{BPh}_4^-)$ (chosen because the transport numbers of its ions were shown to be equal in a number of media), $\text{Et}_4\text{N}^+\text{Pi}^-$, and $\text{Et}_4\text{N}^+\text{ClO}_4^-$ (which were used historically) on the estimation of the transfer activity coefficients of the sodium ion, $\log_m \gamma_{\text{Na}}$, and of the hydrogen ion, $\log_m \gamma_{\text{H}}$, from the e.m.f. of cells with liquid junction between different dipolar solvents using the assumption of negligible E_j . The second objective was to calculate the magnitude of E_j from Equation 18 for those systems where the relevant data were available and to apply such calculated corrections to the measured e.m.f., in order to arrive at more refined values of $\log_m \gamma$. It is important to note that the value of $E_{j,s}$, which would account for the solvent contribution to E_j (Equation 9), was assumed to be zero in every case. The transport numbers and $\log_m \gamma$ values necessary for the E_j calculations were available only for $\text{Et}_4\text{N}^+\text{ClO}_4^-$. While interpreting the various results for $\log_m \gamma_{\text{Na}}$ obtained using the three salt-bridge electrolytes, with or without corrections for E_j , the authors arrived at one far-reaching conclusion: with an independent (prior) knowledge of the values for $\log_m \gamma_{\text{Na}}$, $\log_m \gamma_{\text{R}}$ or $\log_m \gamma_{\text{X}}$, and of all the relevant transport numbers, it is possible to estimate the transfer activity coefficient of the ion X^- or R^+ (whichever is the unknown) of a highly soluble salt-bridge electrolyte from the e.m.f. measurements of Cell V.

New Method for Estimating Transfer Free Energies of Single Ions.

To illustrate this new method of estimating transfer activity coefficients of single ions, we will first apply Equation 10 to Cell V, with E_j expressed as the sum of E_j^I and $E_{j,s}$:

$$E(V) = E' + E_j^I + E_{j,s} \quad (10)$$

where

$$E' = 59.16 \log_m \gamma_{Na} + 59.16 \log \frac{2^{a_{Na}}}{1^{a_{Na}}} \quad (5)$$

and

$$E_j^I = E_{j,G} + E_{j,H} \quad (18a)$$

When the appropriate substitutions are made, with the simplifying assumption that $s^{a_{Na}}$ and $w^{a_{Na}}$ are equal (although that is not mandatory in order to perform the calculations), the following equation is obtained:

$$\begin{aligned} E(V) = & 59.16 \log_m \gamma_{Na} \\ & - 59.16 [t_R \log_m \gamma_R - t_X \log_m \gamma_X] \end{aligned} \quad (44)$$

The last step is the rearrangement of Equation 44, so that an expression for $\log_m \gamma_R$ is obtained:

$$\log_m \gamma_R = \frac{1}{t_R \times 59.16} [59.16 \log_m \gamma_{Na} - E(V) - t_X \log_m \gamma_X] \quad (45)$$

A similar expression can be arrived at for $\log_m \gamma_X$, if that is the desired quantity. Equation 45 illustrates the principle underlying this new method for estimating transfer activity coefficients of single ions. The existing methods rely on the combination of one of the two factors present for both solvents: 1) low solubility of the complete electrolytes or 2) existence of an electrode reversible to the ion of interest. The new method does not require the second condition and is eminently suitable for ions forming highly soluble electrolytes; in fact, its reliability should improve with increased solubility of the salt-bridge electrolyte, RX.

Studies of $E_{j,s}$, the Solvent Contribution to the Liquid-junction Potential. Literature Review.

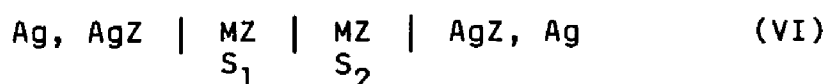
Introductory Remarks.

From the moment electrochemists started using non-aqueous solvents and dealt with interfaces between different solvents, they had to become aware of factors that did not exist when the same solvent was present throughout the e.m.f. cells. One such factor is the difference in the solvation energies of ions in different solvents. We have already seen (Equations 12, 13, and 16) how the transfer free energies of single ions contribute to the diffusion potential at the interface of two solvents. The presence of this factor can also be understood intuitively if we recall that the diffusion potential is due to migration of ions caused by a chemical potential gradient, which in case of solutions in different solvents is a function both of the different solvation energies as well as the different conventional activities of the ions forming the junction. That each solvent could contribute in some other way to the diffusion potential was only suspected by Staverman (14) in 1952, when he developed a general expression for the liquid-junction potential E_j between any two solutions (Equation 8). Staverman's equation formally included contributions to E_j made by the transfer of any uncharged species across the boundary. However, no experimental evidence existed for the presence of this $E_{j,s}$ and furthermore, no mechanism was

proposed by which the transfer of uncharged molecules could give rise to an electrical potential difference.

Alfenaar et al.

In 1967, Alfenaar, de Ligny and Remijnse (50) presented the first physical evidence for the existence of an $E_{j,s}$. The following cell was used in their study:



The concentrations of MZ in S_1 and S_2 were chosen very low and equal, so that the e.m.f. of Cell VI could be written as:

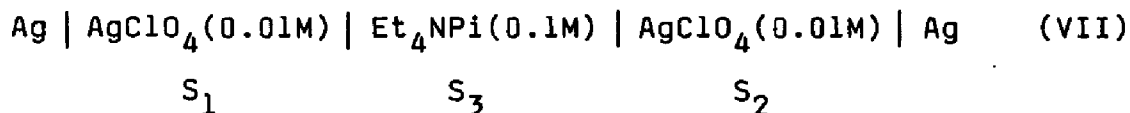
$$E(\text{VI}) = -59.16 t_M \log_m \gamma_{\text{MZ}} + E_{j,s} \quad (46)$$

With the availability of $\log_m \gamma_{\text{MZ}}$ between water and methanol-water mixtures and of the t_M values for those solvents, the estimates of $E_{j,s}$ were calculated for junctions between water and a series of MeOH-H₂O mixtures. The significance of the nature of the electrolyte MZ was also tested by using LiCl, NaCl, KCl, RbCl, CsCl, KBr and KI. No effort was made to vary the concentration of MZ and that is a shortcoming of this study. The evidence presented clearly supported the existence of $E_{j,s}$ and its dependence on the nature of the two solvents as well as the nature of the electrolyte crossing the boundary between them. It is important, however, to note that any estimate of $E_{j,s}$ obtained here depends on the accuracy of the transfer activity coefficient of MZ as well as on the details of the experimental design, e.g. on how "equal" were the activities of MZ in the two solutions, and if not exactly equal, then how was the difference accounted

for? None of these questions are answered in this study and therefore the resulting $E_{j,s}$ values can only be considered as rough estimates.

Parker, et al.

Cox, Parker, and Waghorne (51) used the following cell with a salt bridge in their study of $E_{j,s}$:



The e.m.f. measurements of Cell VII were interpreted in the light of changing the salt-bridge solvent, S_3 . By assuming that the transport numbers of both Et_4N^+ and Pi^- ions are equal to each other in all the solvents used here and that the current is carried only by those two ions. Cox, et al. (51) showed that the e.m.f. of Cell VII is given by:

$$\begin{aligned} E(\text{VII}) = & \frac{RT}{F} \ln \frac{2^{a_{\text{Ag}}}}{1^{a_{\text{Ag}}}} - \frac{0.5}{F} 1_{\Delta}^2 G_t^{\circ}(\text{Et}_4\text{N}^+) \\ & + \frac{0.5}{F} 1_{\Delta}^2 G_t^{\circ}(\text{Pi}^-) + E_{j,s} \end{aligned} \quad (48)$$

Cox et. al. (51) further assumed that the transfer free energies of Et_4N^+ and Pi^- ions are equal for all the pairs of solvents studied and therefore any changes in the e.m.f. of Cell VII will be due to changes in $E_{j,s}$.

We may recall that $E_{j,s}$ is expressed as a function of changes in the free energy of the solvents as they cross the boundary

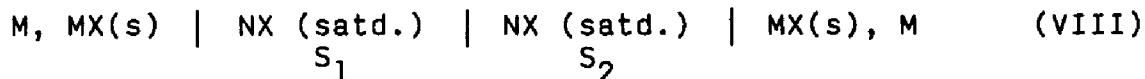
$$E_j = \int_L^R \sum_{\text{all species}} t_i^F dG_i \quad (8)$$

$$E_j = - \frac{1}{F} \sum_{\text{ions}} \int_L^R \frac{t_i}{z_i} dG_i + E_{j,s} \quad (9)$$

Because of lack of data on the transfer free energies for the various solvents, Cox et. al. (51) proposed to study the e.m.f. of Cell VII as a function of the total enthalpies of transfer for the two junctions, $S_1 S_3$ and $S_3 S_2$. By comparing the free energy of solution, the enthalpy of solution, and the e.m.f. values for various combinations of solvents S_1 , S_3 , and S_2 they arrived at the following conclusion: for junctions formed between dipolar aprotic solvents (that is excluding water, methanol and formamide) the value of $E_{j,s}$ should be very small. It is clearly a qualitative statement and it will remain such for the results presented in their work, because some of the assumptions made by Cox and his coworkers do not hold up under close inspection. The main objection is to the assumption that the only current-carrying species present is the salt-bridge electrolyte, $\text{Et}_4\text{N}^+\text{Pi}^-$. With a $\text{Et}_4\text{N}^+\text{Pi}^-:\text{AgClO}_4$ concentration ratio of only 10 to 1, that is not very likely and the contribution from Ag^+ and ClO_4^- ions both to $E_{j,G}$ and to $E_{j,H}$ has to be included. Thus, the complete equation for the e.m.f. of Cell VII should contain terms accounting for the presence of Ag^+ and ClO_4^- ions in both diffusion layers, and the assumption that those terms remain constant with changing solvent S_3 needs to be proven before Equation 48 can be used as described.

Murray and Aikens.

Much light on the nature of $E_{j,s}$ was shed by Murray and Aikens (52). They used the following cell in their study of the contribution of solvent transport to the liquid-junction potential between electrolytes in different solvents:



It can be shown (Appendix 2) that in the absence of solid solvates formed by MX with either solvent, the e.m.f. of this cell can be represented by the equation:

$$E_{\text{cell}} = - \frac{t_N}{F} \Delta G_t(NX)_{\text{satd.}} + E_{j,s} \quad (47)$$

Since both solutions are saturated with NX, solid crystals of NX must be present in both solvents. If those crystals do not form a solid solvate with either solvent, then $\Delta G_t(NX) = 0$ and the e.m.f. of Cell VIII is a direct measure of $E_{j,s}$. The following parameters were evaluated in the study of Murray and Aikens (52).

1) The effect on $E_{j,s}$ of varying the electrolyte, by using sat. solutions of LiCl and KCl as NX and showing dependence of $E_{j,s}$ on the identity of NX.

2) The method of forming a junction, such as a frit, stopcock, or capillary, and the junction compartment (no effect except for stability).

3) The types of solvents used. Solvent pairs were formed between water, acetonitrile, propylene carbonate,

acetone, methanol, and ethanol and the resulting $E_{j,s}$ values were tabulated.

4) The dependence of $E_{j,s}$ on the cell life. For most junctions, the e.m.f. rose for the first 40 minutes and remained stable for many hours. This was not true for junctions with acetone, where a great deal of turbulence was observed.

Murray et. al. proposed a mechanism which could explain how the transport of uncharged solvent species contributes to liquid-junction potential. Murray and Aikens wrote (52):

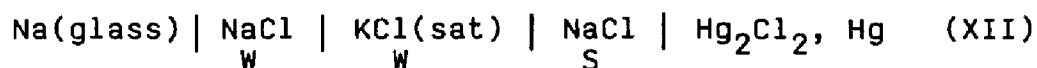
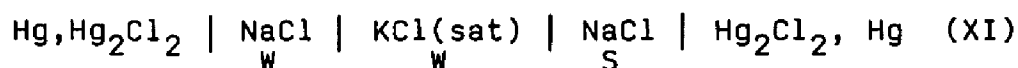
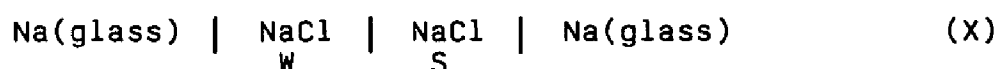
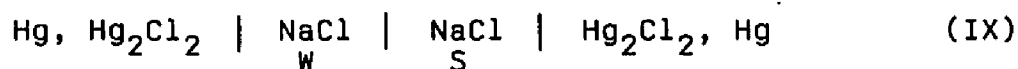
"We consider it likely that the source of the solvent contribution to the total liquid-junction potential is the transfer of solvated ions across the solvent-solvent boundary as a consequence of the chemical potential gradient which exists for solvent species. That is to say, in Cell VIII, the ions themselves have no tendency to diffuse since their chemical potential gradient across the solution-solution interface is zero;...however, the solvent species will tend to diffuse and, since ions are solvated by these species, some ions will also tend to be carried across the boundary with the solvent molecules. If solvated cations and anions do not diffuse at the same rate, then charge separation will occur, and the potential gradient will gradually increase across the solvent-solvent boundary until it is large enough to just counter the chemical potential gradient which led to the flow of solvated ions--at this point, a steady state will exist and the potential gradients will no longer increase. That is to say, the liquid-junction potential will become constant."

This explanation of the solvent-solvent diffusion potential is analogous to that employed by Bockris (7) and used by this author to explain the liquid-junction potential occurring between two different electrolyte solutions in the solvent.

The value of $E_{j,s}$ for the H_2O -MeOH junction with KCl obtained by Murray and Aiken (52) is about one-third of that obtained by Alfenaar et al. (50). While the Alfenaar calculation may be in error due to uncertainties in t_K and $H_2O \Delta^{MeOH} G_t^o(KCl)$, it is unlikely that these uncertainties are large enough to cause the observed difference. Rather, it is more likely that the value of $E_{j,s}$ depends not only on the nature, but also on the concentration of the current-carrying species present and that $E_{j,s}$ decreases significantly with increasing electrolyte concentration.

Goldberg

Goldberg (48) investigated this concentration dependence in his study of liquid-junction potentials between water and a series of methanol-water solvents. Four different e.m.f. cells:



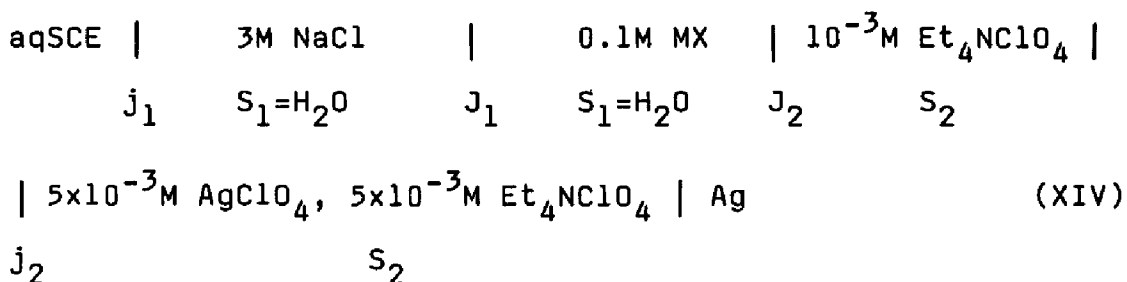
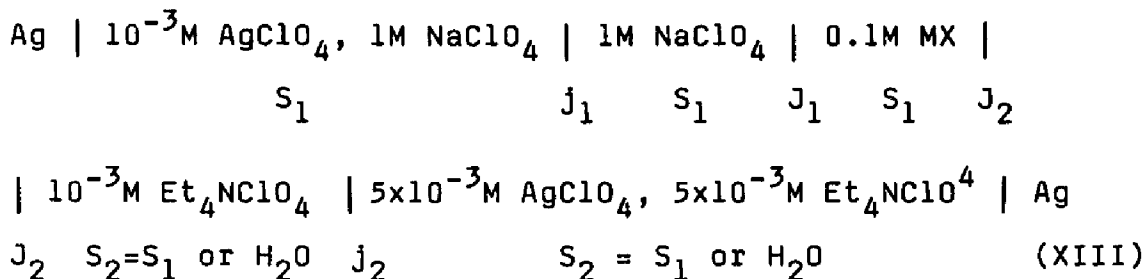
were studied, with concentrations of NaCl ranging from saturated to $3 \times 10^{-3} \text{M}$. Solvent S was varied from 50 to 90% methanol. For each cell, an equation was developed for the evaluation of $E_{j,s}$ in terms of the measured e.m.f. of that cell and other thermodynamic data.

The results showed a clear inverse dependence of $E_{j,s}$ on the concentration of the current-carrying species, as illustrated by $E_{j,s}$ values obtained for the saturated NaCl solutions vs. $3 \times 10^{-3} \text{M}$ solutions. $E_{j,s}$ was also shown to increase with the increasing concentration of methanol, which was not surprising, since that corresponds to an increasing dissimilarity between the solvent S and the reference solvent, water. Goldberg's results and assumptions

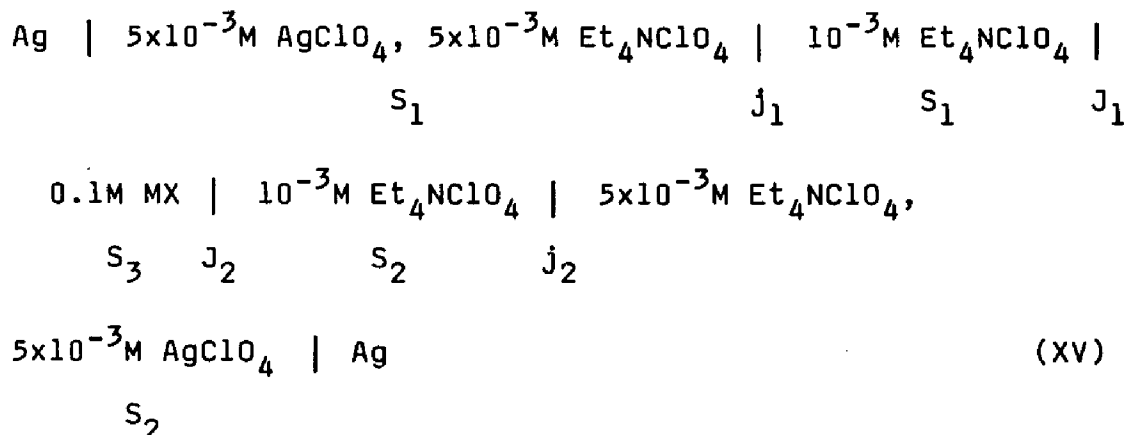
will be discussed in more detail later, in relation to the present work in methanol-water solvents.

Izutsu, et al.

Izutsu and coworkers (53-57) have studied extensively some of the factors determining the E_j between two solvents. E.m.f. values of the following cells were measured while changing the solvents S_1 and S_2 and the electrolyte MX:



where the solvents used were H_2O , MeOH , MeCN , PC , DMSO and DMF and MX was Me_4NClO_4 , Et_4NClO_4 , Pr_4NClO_4 , Bu_4NClO_4 , LiClO_4 , NaClO_4 , $\text{Mg}(\text{ClO}_4)_2$, $\text{Ba}(\text{ClO}_4)_2$, Et_4NPI , Et_4NBr , Et_4NBr , Et_4NCl , or Et_4NNO_3 . The measured e.m.f. values were corrected for the E_j at j_1 , j_2 and J_1 , which were calculated using the Henderson equation. The change in the corrected e.m.f. values with the change of MX corresponds to the change in the E_j at J_2 . The variation in e.m.f. was also studied as a function of the salt-bridge solvent S_3 in the following cell:



The results of the first paper (53) pointed out that there was a component to E_j at J_2 which could not be accounted for in the usual way, i.e., by $E_{j,G}$ or $E_{j,H}$ calculations. In other words, the existence of an $E_{j,s}$ was supported once more. The second paper (54) dealt with the effects of varying solvents on the value of $E_{j,s}$. The results showed that the value of the $E_{j,s}$ for a given solvent combination was almost independent of the kinds of ions crossing the junction, if those ions were only weakly solvated. When highly solvated ions were complexed with crown ethers, the e.m.f. of Cell XV changed with S_3 the same way as when the cation was large and weakly solvated (55). A correlation was also found between the $E_{j,s}$ changes and the Lewis acid-base properties as well as the mutual heats of solution of the solvents at the junction. By correlating the e.m.f. values of Cells XIII, XIV, and XV with the various parameters introduced, Izutsu monitored the changes in $E_{j,s}$ with the changed parameters. No effort was made to estimate the magnitude of $E_{j,s}$ for any particular junction. In addition, the term "constant", or "almost independent" refers to cases

where the variation may be as much as 5-10mV. While that is not a large figure, it points to the existence of factors not accounted for here. The final two papers (56,57) considered the effect on $E_{j,s}$ of using a mixed solvent as a salt-bridge solvent S_3 and/or as one of the end solvents, S_1 or S_2 .

The large body of data was analyzed in a variety of ways and the conclusions drawn from all five papers can be listed as follows:

- 1) There is a component of a liquid-junction potential between two solvents that is caused by the solvent-solvent interactions.

- 2) That component (call it $E_{j,s}$) does not depend on the identity of the electrolyte in the diffusion layer only if the ions are solvated very weakly by the solvents.

- 3) A correlation can be found between the magnitude of $E_{j,s}$ and some properties of the solvents forming the junction. Evidence also suggests that that correlation is a function of the compositions of the solvents on both sides of the junction and is almost independent of the way the solvents are mixed in the interfacial region.

By using only weakly solvated ions in their studies, Izutsu and coworkers believe that they could interpret the observed $E_{j,s}$ values in terms of solvent-solvent interactions only. However, the effect of varying solvation cannot be denied and has to be investigated. Could it be that the $E_{j,s}$ observed is a function of two factors: one, which

accounts for solvent-solvent interactions and therefore is solute-independent and two, which deals with the transport of those solvent molecules that are part of the solvation shells of the ions crossing the junction (that factor would be negligible when the ions are solvated only weakly)? Clearly, more data are needed along with careful interpretation of the results.

EXPERIMENTAL

Preparation of Solvents.

Acetonitrile (MeCN).

Acetonitrile was purified by the method of Coetzee, et al. (58). ACS Reagent-Grade acetonitrile (Fisher or Mallinckrodt) was first treated with silica gel for ~0.5 hour and decanted, then stirred with CaH_2 for about two days and decanted. Approximately five L of the decantate from these treatments were used to charge a distillation flask. The solvent was fractionally distilled from fresh P_2O_5 using a 30-cm Vigreux column. The first and the last 10% were discarded and the middle fraction collected.

Dimethylformamide (DMF).

Certified ACS, spectra-analyzed N,N-dimethylformamide (Fisher) was fractionally distilled under reduced pressure using a 30-cm Vigreux column. The first and the last 10% were rejected. For working with AgClO_4 it was necessary to redistill the purified DMF one more time, again collecting only the middle 80% fraction.

Dimethylsulfoxide (DMSO).

Certified ACS-Grade dimethylsulfoxide (Eastman) was fractionally distilled over CaH_2 under reduced pressure using a 30-cm Vigreux column. The first and the last 10% were discarded and the middle 3 L, collected.

N-Methylformamide (NMF).

N-Methylformamide (Eastern Chemical) was used without any further purification.

Methanol (MeOH).

Spectra-analyzed methanol (Fisher Scientific) was used without any further purification. Methanol-water mixtures were prepared volumetrically using approximate required amounts of spectraanalyzed methanol and deionized water. The density of the solvent mixtures was determined gravimetrically in quadruplicate using calibrated 100-mL volumetric flasks. The exact weight percentage was determined from a plot of density vs. weight percent methanol prepared from literature data (59). Appendix 3 contains a table of densities of methanol-water solvents.

Propylene Carbonate (PC).

Propylene carbonate (Eastman or MCB Reagents) was distilled over CaH_2 under reduced pressure using a 30-cm vigreux column as suggested in (60). Only the middle 80% of the total charge were collected. For work with AgClO_4 , the purified PC was distilled twice under reduced pressure, again retaining only the middle fraction in each distillation.

Preparation and Purification of Solutes.

Tetramethylammonium Picrate (Me_4NPi).

Tetramethylammonium picrate was prepared by the metathesis of hot picric acid with tetramethylammonium bromide or hydroxide, both solutions prepared in water. Upon cooling the reaction mixture, long and thick needles of Me_4NPi formed, which were filtered, washed, and recrystallized twice from 95% ethanol. The solid Me_4NPi was dried in a vacuum oven at 60°C for a few hours.

Tetraethylammonium Picrate (Et_4NPi).

Tetraethylammonium picrate was prepared exactly as Me_4NPi , except that Et_4NOH was used instead of Me_4NOH .

Tetrapropylammonium Picrate (Pr_4NPi).

Tetrapropylammonium picrate was prepared by adding hot aqueous solution of Pr_4NOH to a hot aqueous solution of HPi . A viscous layer formed when the hot solutions were mixed. Upon cooling, that separate layer solidified and also short, narrow, yellow needles precipitated. Both solids were filtered together, washed, recrystallized twice from ethanol, and dried in the vacuum oven at $\sim 50^\circ\text{C}$ overnight.

Tetrabutylammonium Picrate (Bu_4NPi).

Tetrabutylammonium picrate was prepared from either 25% solution of Bu_4NOH in MeOH or a concentrated solution of

Bu_4NBr in MeOH mixed with an equimolar solution of HPi in MeOH. Cold water was added slowly to the resulting mixture, until cloudiness appeared. Upon cooling, the precipitate was filtered, washed and eventually recrystallized three times from EtOH. The original decantate was allowed to decrease in volume by slow evaporation, until more precipitate was formed, filtered, and added to the first batch. The process of evaporation was repeated a few times in order to recover as much Bu_4NPi as possible from the original reaction mixture. The recrystallization procedure, as well as the actual synthesis was again complicated by the appearance of a viscous layer whenever the solutions were hot enough. When the hot solutions were allowed to cool slowly, the viscous layer increased and eventually solidified into one large chunk. In order to prevent this and at the same time to obtain a reasonable yield from each recrystallization, the concentrated Bu_4NPi solution in EtOH was cooled quickly in an ice bath. Since this procedure does not ensure crystals of the highest purity, the recrystallization was performed three times, instead of the usual two. The final product was dried in a vacuum oven at -40°C overnight.

An accurately weighed sample of each tetraalkylammonium picrate synthesized in our laboratory was dissolved in 95% EtOH and analyzed spectrophotometrically for the picrate ion. The analysis was performed on a Cary 17 Model spectrophotometer using the picrate absorbance at its peak at 355 nm. In 95% EtOH, the absorptivity of the picrate ion, Pi^- ,

is 1.59×10^4 (61). The solutions were diluted to give an absorbance of ~ 1 . When the observed and calculated absorbances were compared, they differed usually by less than 1.5%. Since each compound was analyzed in this manner only once, the results were deemed sufficiently accurate for the purpose of identifying each picrate. The previous speculation (62) that the viscous layer was a by-product resulting from some oxidation reaction proved to be in error. It is this author's belief that the very concentrated solution of $\text{Bu}_4\text{N}^+\text{Pic}^-$ (or $\text{Pr}_4\text{N}^+\text{Pic}^-$) in hot EtOH upon slow cooling produces either a solution of EtOH in $\text{Bu}_4\text{N}^+\text{Pic}^-$ or a layer of liquid $\text{Bu}_4\text{N}^+\text{Pic}^-$, which then solidifies into one solid chunk. The quick cooling employed here allows the formation of small crystals without going through the intermediate liquid state. It would be possible, of course, to avoid this difficulty by recrystallizing $\text{Bu}_4\text{N}^+\text{Pic}^-$ using EtOH at lower temperature at which the viscous layer does not appear, but a test run showed that the yield in such a procedure (which depends on the difference in solubility of $\text{Bu}_4\text{N}^+\text{Pic}^-$ between cold and hot solutions) was extremely poor.

Tetramethylammonium Perchlorate ($\text{Me}_4\text{N}^+\text{ClO}_4^-$).

Tetramethylammonium perchlorate, suitable for polarography, (Frederick Smith Chemical Co.) was used without further purification.

Tetraethylammonium Perchlorate (Et_4NClO_4).

Tetraethylammonium perchlorate (Eastman) was recrystallized twice from 95% ethanol and dried overnight in the vacuum oven at 60°C .

Tetrapropylammonium Perchlorate (Pr_4NClO_4).

Tetrapropylammonium perchlorate (Eastman) was treated in a manner identical to Et_4NClO_4 .

Tetra-n-butylammonium Perchlorate (Bu_4NClO_4).

Tetra-n-butylammonium perchlorate (Eastern Chemical) was recrystallized twice from 95% ethanol. The solutions were slowly cooled to room temperature and then placed in ice to increase the yield. The final product was dried in a vacuum oven at room temperature for several days and then at 40°C for several hours.

Silver Perchlorate (AgClO_4).

Anhydrous, reagent grade silver perchlorate (Frederick Smith Chemical Co.) was used without any further purification. It was stored in a vacuum dessicator and kept away from light.

Sodium Chloride (NaCl).

Certified ACS sodium chloride (Fisher Scientific Co.) was dried in a vacuum oven at 80°C overnight prior to its being used in making solutions in $\text{MeOH-H}_2\text{O}$ solvents.

Sodium Tetraphenylborate (NaBPh_4).

Sodium tetraphenylborate (Eastern Chemical) was dissolved in dry acetone (3g of NaBPh_4 to 10 mL of acetone), toluene was added until the solution turned slightly opalescent, the solution was filtered, and the filtrate warmed on a hot plate until needle-like crystals precipitated. This procedure was performed twice and the resulting crystals were dried in a vacuum oven at 50°C for several days.

Tetraphenylarsonium Tetraphenylborate ($\text{Ph}_4\text{AsBPh}_4$).

Tetraphenylarsonium tetraphenylborate was prepared by adding, slowly and with stirring, an ethanolic solution of sodium tetraphenylborate to an equimolar ethanolic solution of tetraphenylarsonium chloride. Immediately a very thick, white mixture was formed, which was filtered and washed several times with hot acetone. An attempt was made to dissolve some of the precipitate in hot acetone so as to produce crystals upon cooling, but the amount of acetone required was prohibitively high. It was decided that for the purposes of this investigation thorough washing of $\text{Ph}_4\text{AsBPh}_4$ was sufficient, since both Ph_4AsCl and NaBPh_4 are very soluble in acetone, while Ph_4AsPh_4 is not. The product of this procedure was dried in a vacuum oven at 60°C for several days, accompanied by breaking up of large clumps of $\text{Ph}_4\text{AsBPh}_4$ that formed at first.

Sodium Picrate (NaPi).

Sodium picrate was prepared by adding an equivalent amount of a solution of sodium hydroxide in water to a hot solution of picric acid in 1:1 methanol-water mixture. Upon cooling and adding more cold water, needles of NaPi formed. The precipitate was washed by decantation, recrystallized twice from 1:1 ethanol-water mixture, and finally dried in a vacuum oven overnight at room temperature.

Silver Chloride (AgCl).

Silver chloride was precipitated from a hot aqueous solution of high-purity silver nitrate to which an aqueous solution of sodium chloride was added. The precipitate was washed by decantation with water containing some nitric acid and dried in a vacuum oven at 80°C for several hours.

E.m.f. Measurements.

Potentiometers and Amplifiers Systems.

The variety of galvanic cells employed in this investigation necessitated the use of appropriate e.m.f. measuring devices. When both electrodes were of low impedance (such as two calomel electrodes, or two silver electrodes), a Keithley 169 multimeter was used to measure the voltage.

For calibration of sodium glass electrodes (Fisher Scientific 13-639-20) and hydrogen glass electrodes (Fisher Scientific 13-639-3) a Delta-matic pH meter, model 135A, was used, which is specifically designed to handle only one electrode of high impedance.

Cells consisting of two high-impedance electrodes required the use of a series of operational amplifiers placed between the cell and the Keithley digital voltmeter. Figure 1 shows the circuit diagram of the amplifier system. The gain of the amplifier system was 3.00. Keithley Instruments Model 301 solid-state operational amplifiers were used as amplifiers A and B; an Analog Devices 40J amplifier was used as amplifier C.

Because of the slow drift of the first amplifier circuit, an improved version of this circuit was used in some of the later measurements (Figure 2), where two Analog Devices 52K amplifiers were used. The gain of this amplifier system was 2.99. All cell voltages measured using

either amplifier system in the circuit have been corrected for this amplification factor.

FIGURE 1

Circuit Diagram of the First Amplifier System.

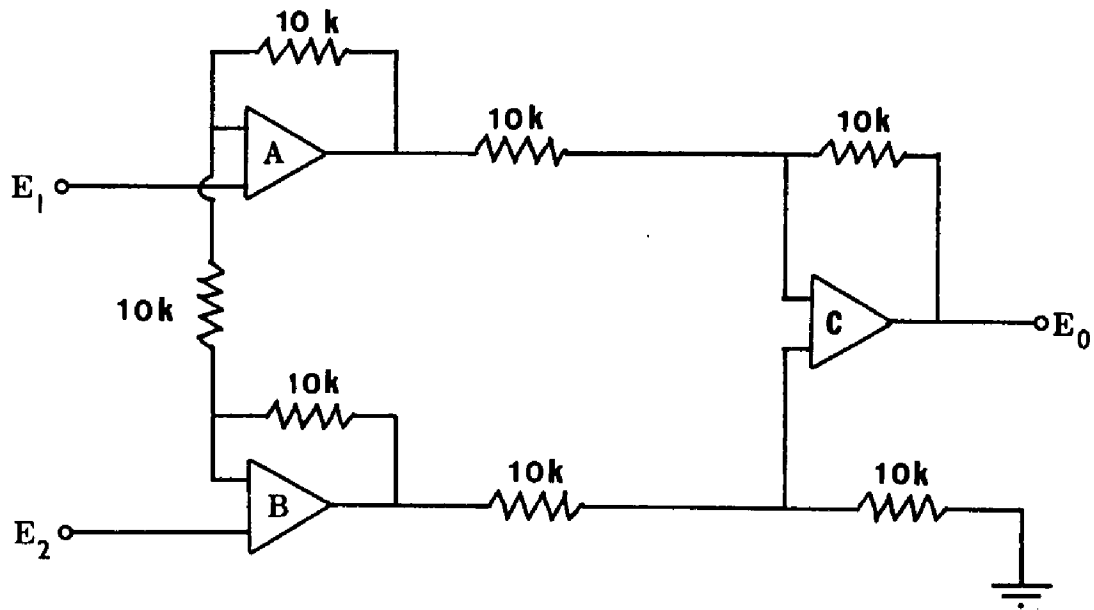
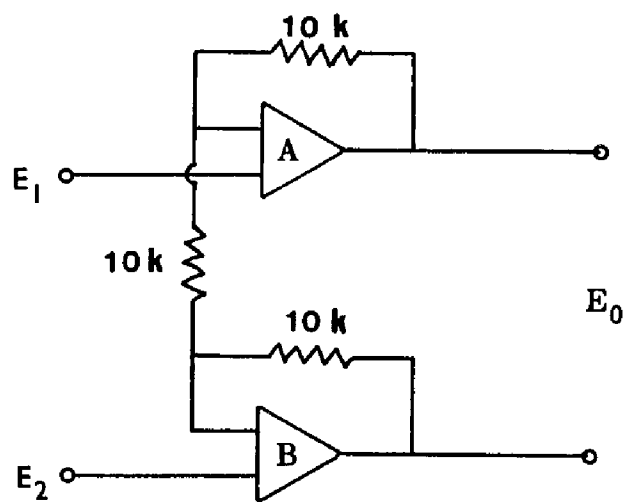


FIGURE 2

Circuit Diagram of the Second Amplifier System.



Cell Design.

The basic e.m.f. cell used in this investigation was similar to the one used earlier by Goldberg (48).

A junction between two solutions was formed by the use of a sleeve-type component, shown in Figure 3. A glass tube of precision bore enclosed a stainless-steel tube. The bottom of the glass tube was finely ground to make a socket of exact fit over a half-sphere ground-glass ball. The ground-glass ball was connected to the stainless-steel tube by a Teflon-coated stainless-steel wire fashioned through a Teflon support. The Teflon support was composed of two parts: part A contained the Teflon wires and screwed into part B which fitted snugly in the ground-glass ball (Figure 3).

The electrochemical cell consisted of a jacketed container (~100mL) with a plastic (polyethylene) screw cap. The jacket allowed for circulation of water from a constant-temperature water bath. The temperature of the water was kept constant at $25.00^{\circ} \pm 0.01^{\circ}$ by using a Yellow Springs Instruments Co. Model 72 proportional temperature controller. The actual bath temperature was verified by means of a certified National Bureau of Standards thermometer. A typical assembly is illustrated in Figure 4. There were several interchangeable plastic tops available, differing from each other by the number and the size of the round openings drilled in them. When the main container was filled with a salt-bridge solution, two sleeve-type components would be

FIGURE 3

Detailed Illustration of Sleeve-Type Electrode Compartment.

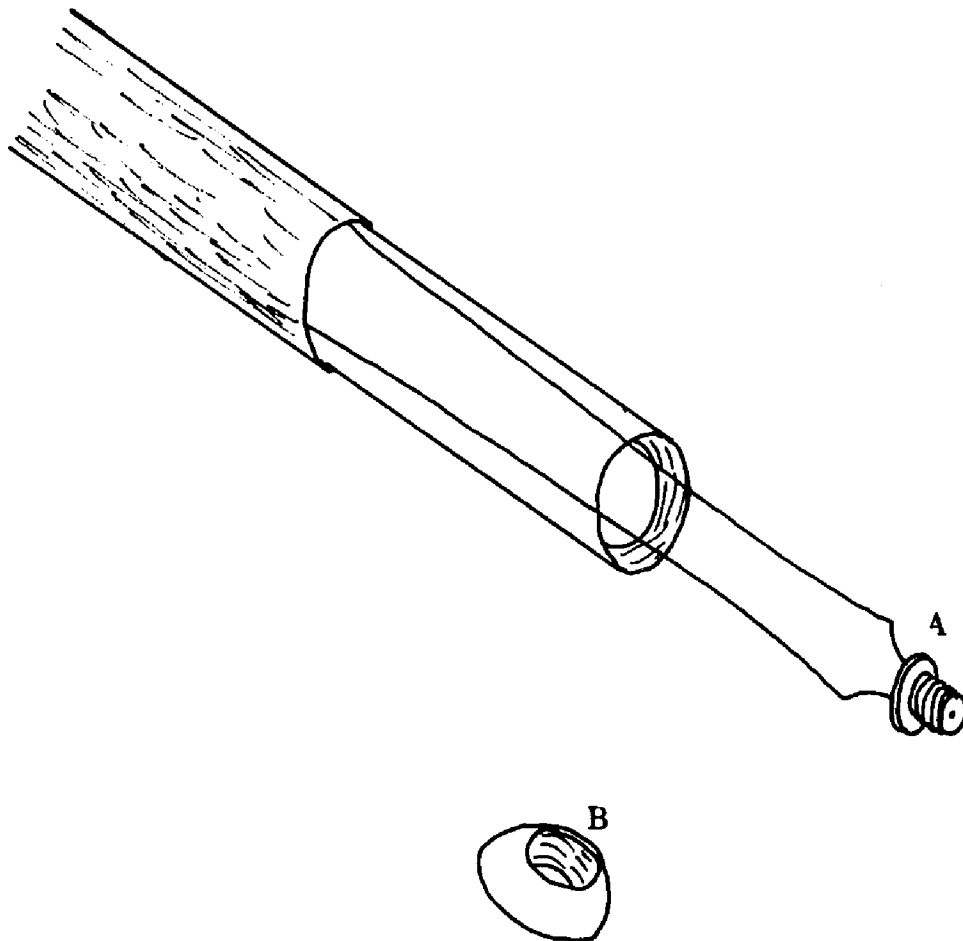
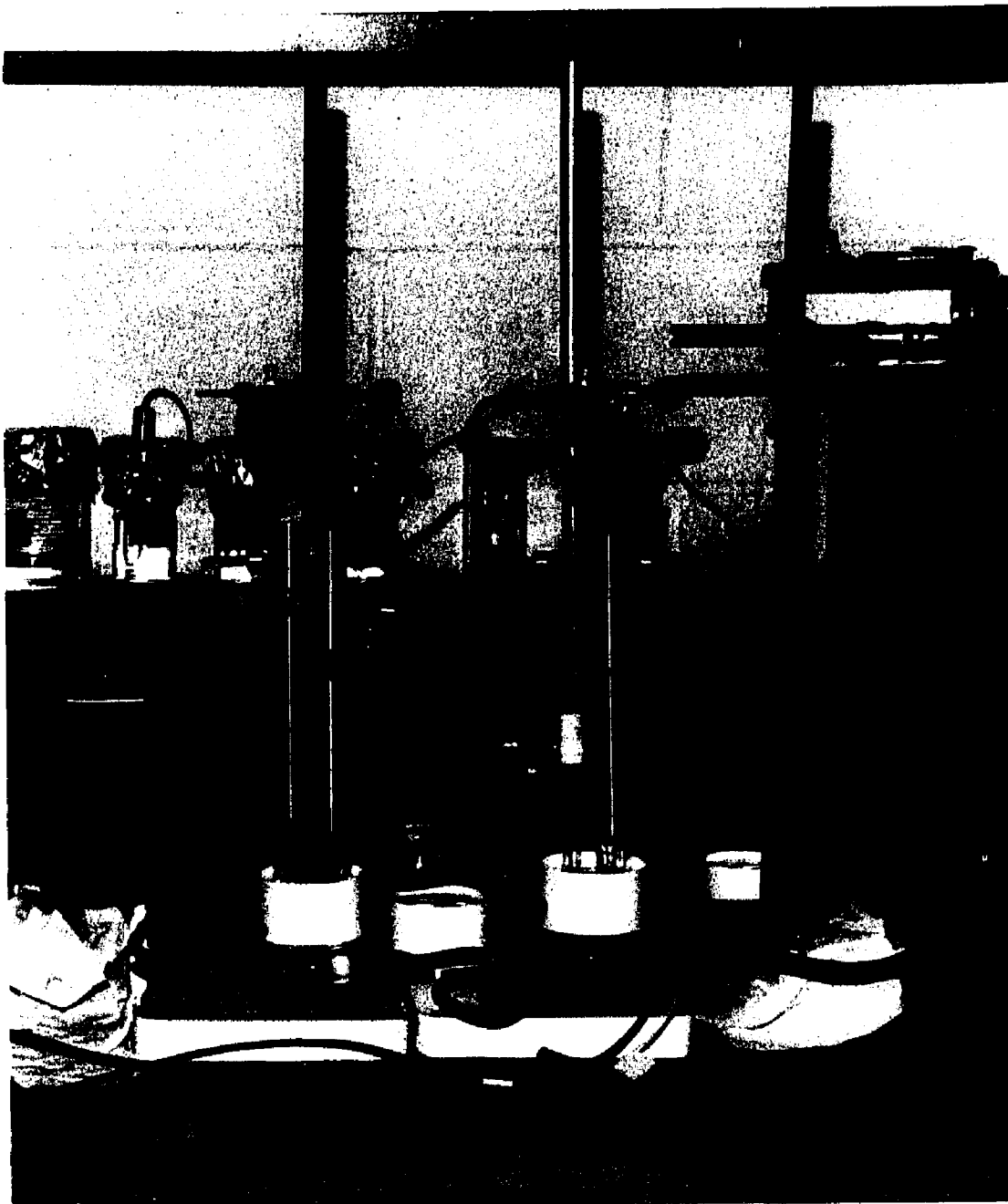


FIGURE 4

Illustration of the Sleeve-Type Cell.



filled with the end solutions, carefully lowered through round openings of the plastic top into the salt-bridge solution and clamped into place. The appropriate electrodes (silver wire, calomel or glass electrodes) were then inserted from the top into each of the sleeves. For a single-junction cell (without a salt bridge) only one sleeve was required, filled with one end solution, while the other end solution was placed directly in the cell container and the appropriate electrode was immersed in the solution through a small opening in the plastic top. When two glass electrodes were used in the same cell, it was found that the cell voltage was stabilized by the presence of a platinum electrode connected to the ground of the amplifier circuit. The openings in the plastic tops were made with a minimum clearance necessary for the placement of the electrodes and/or the sleeves. This was done to minimize exposure of the solutions to air, since some of the solvents used in this research were hygroscopic. The sleeves were usually filled with the appropriate solution using pipettes. Each sleeve was carefully washed with acetone and dried before being used again.

The stability of the cell voltage was related mainly to the amount of leakage of any solution from the sleeve into the main container. Ideally, no leakage should have been present, but a compromise had to be reached regarding the smoothness and the fit between the socket and the half-sphere ground-glass ball, so that diffusion of both solu-

tions (inside and outside the sleeve) was possible along the surface of contact, but without appreciable flow of solution, which would result in a constantly renewed diffusion layer. The criterion for stability decided upon was to be a change in the cell e.m.f. of 0.1mV or less in ten minutes. The time required for the voltage to stabilize differed for different cell designs. Cells with salt bridges usually took longer, up to two hours, before the voltage reached a plateau. Single-junction cells sometimes reached the final e.m.f. after only ten minutes and could remain there for several hours.

While the individual cell voltages were stable within the described limits, the reproducibility of the e.m.f. of a particular cell was a different matter. Whenever possible, more than one e.m.f. determination was made and the reported uncertainty reflects the lack of reproducibility and not the instability of an individual e.m.f. determination. When no uncertainty is reported, it means that only a single determination was performed.

Electrodes.

Silver electrode.

The silver electrode was constructed from a 99.99% silver wire for electrodes (Fisher Scientific) inserted into a rubber stopper which fitted into the stainless steel tube of the sleeve. The wire was cleaned with very fine sand paper and a silver polishing paper was used until the surface was smooth and shiny.

Sodium and hydrogen glass electrodes.

The sodium and hydrogen glass electrodes were used in a variety of solvents. Each electrode was pre-soaked at least overnight in the solvent in which it was to be used next and then calibrated prior to its use in a cell. An effort was made to time the calibration procedure as close as possible to the day on which the e.m.f. measurements were to be taken, because the response factor (slope of the calibration curve) of a given glass electrode could change with time.

Calomel electrodes.

Calomel electrodes were used, two at a time, for e.m.f. determinations, and one at a time as reference electrodes. The basic design consisted of a long glass tube with two small openings near the bottom, on the opposite side of each other. The bottom of the tube was filled with triply-distilled mercury. A platinum wire sealed in a very narrow glass tube was immersed completely in the pool of mercury and the whole assembly was topped with a rubber cap. Electrical contact was made with an insulated platinum wire, pushed through an opening in the cap to the bottom of the narrow glass tube, where a drop of mercury allowed for contact with the platinum electrode. A quantity of mercury was placed in a separate container with some mercurous chloride and shaken vigorously. This action produced a very thin film (bloom) of a mixture of mercury and mercurous chloride, which could be scraped up on a spatula and placed on top of the mercury at the bottom of the larger tube. Appropriate solution was placed inside the tube through the openings. Solutions could be changed by rinsing the surface of mercury several times using a medicine dropper. Calomel electrodes assembled this way were stable for at least one day and reproducible. After too many solution changes, the "bloom" was rinsed away and a fresh electrode had to be prepared. The agreement among several calomel electrodes tested in the same solution was better than 0.2 millivolts.

The above procedure for the preparation and use of the calomel electrode was adapted from Ives and Janz (63).

Calibration of glass electrodes in methanol-water solvents.

The calibration of glass electrodes in methanol-water solvents was performed without a salt bridge. The reference electrode (which was the calomel electrode) was in direct contact with the test solution. The procedure used to determine the response of a glass electrode when the potential of the reference electrode changes with the activity of the test solution will be described in detail later.

Reference electrodes used in calibration of sodium glass electrodes in aprotic solvents.

The calibration of sodium glass electrodes in the aprotic solvents used here required several different reference electrodes, each designed with a salt bridge of 0.1M $\text{Et}_4\text{N}^+\text{Pi}^-$ in the appropriate solvent, so that its potential was assumed constant while the activity of the test solution was varied. The basic design of the calibration cell was the same for all the solvents where a salt bridge was used. First a U-shaped container was filled with the salt-bridge solution. A glass tube with a very fine porosity frit in the bottom was inserted into one arm. That tube was filled with a test solution and the glass electrode was immersed in it. Another tube, also with a very fine frit at the bottom, was inserted into the other arm. That tube was filled with the solution containing ions to which the reference electrode was reversible in the solvent of interest. The reference electrode immersed in that solution completed the assembly.

The reference electrode used in DMSO, NMF, and PC consisted of a silver wire immersed in 0.001M solution of tetraphenylphosphonium chloride. Saturation was assured by the use of ultrasonic waves on a solvent in the presence of solid silver chloride. In acetonitrile, the reference electrode was a silver wire in 0.01M solution of silver nitrate. Calomel electrode placed in a saturated solution of potas-

sium chloride was used in DMF. References regarding these electrodes can be found in the literature (64,65).

RESULTS AND DISCUSSION

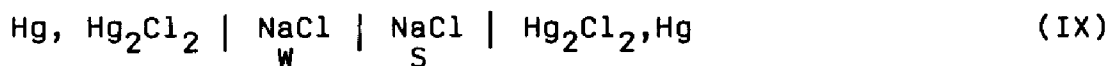
Studies of the Liquid-junction Potential at the Interfaces
Between Water and Methanol-Water Solvents.

Description of the Cells Used and the General Equations for
Their E.m.f.

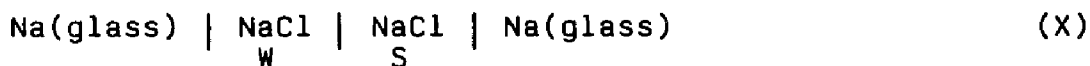
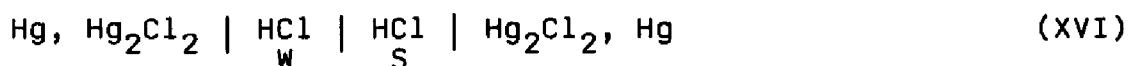
The e.m.f. of a galvanic cell with liquid junction can be viewed as a sum of three terms, E' (Equations 5a and 5b), E_j' (Equations 9 and 12) and $E_{j,s}$ (Equation 9). In this part of the investigation, cells were used for which there were enough data to calculate both E' and E_j' . Thus, by combining these calculated values with the experimental e.m.f.'s for these cells, it was possible to evaluate the $E_{j,s}$ for each junction. Table 4 lists all the cells used here. Cells IX-XII are identical to the ones used by Goldberg (48). The symbol W indicates that water is the solvent, S stands for methanol-water mixtures, which were prepared at ~10% (by weight) intervals. Solutions of sodium chloride were prepared in 50, 60, 70, 80, and 90% methanol. In order to study the effect of concentration on the E_j and $E_{j,s}$, the molarity of NaCl was also varied from $\sim 1 \times 10^{-1} M$ to $\sim 3 \times 10^{-3} M$, but kept approximately equal for both half cells. The exact concentrations were known from the weights of NaCl used. Solutions of hydrogen chloride were prepared in 30 - 90% methanol-water mixtures, also at 10% intervals. The concentration of HCl was varied from $1 \times 10^{-1} M$ to $1 \times 10^{-3} M$. The exact concentration of each HCl stock solution was determined by titration with a standard solution of sodium

TABLE 4

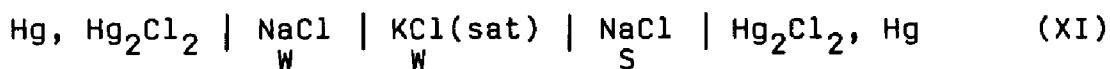
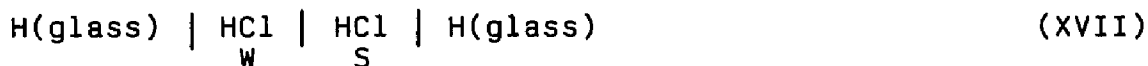
List of the Cells Used to Study Liquid-junction Potentials
Between Two Different Solvents.



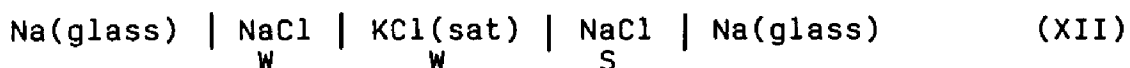
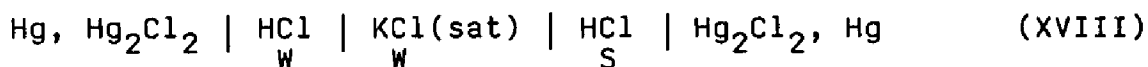
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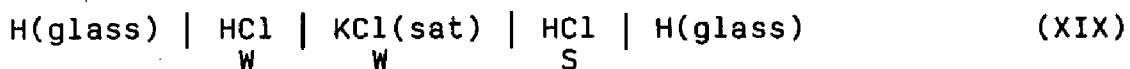
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hydroxide, using phenolphthalein to detect the end point. The calomel electrodes used here were prepared in the manner described above (experimental). The sodium and the hydrogen glass electrodes were checked for their response and the results of this calibration procedure will be discussed later.

The cells were chosen so that comparisons between them could shed some light on the factors used to calculate their e.m.f.'s. For example, $E_{j,s}$ values calculated using cells IX and XVI (or X and XVII, or XI and XVIII, or XII and XIX) show the effect (if any) of changing the nature of one of the ions participating in the junction formation, that is the effect of replacing sodium ion Na^+ with the hydrogen ion H^+ . Comparisons made between pairs of cells such as IX and XI, XVI and XVIII, X and XII, and finally XVII and XIX, illustrate the effect of the salt bridge on the calculated E_j and $E_{j,s}$. Last, but not least, a comparison of E_j and $E_{j,s}$ values obtained from cells such as IX and X, XVI and XVII, XI and XII, XVIII and XIX, leads to a careful examination of the term E' used in each calculation, since for every pair of cells mentioned, the junction is the same (that is the E'_j and $E_{j,s}$ terms do not change) and the only difference is the type of electrode used.

What follows is a list and general description of all the equations normally used to calculate E' , E'_j , and $E_{j,s}$ for cells IX-XII and XVI-XIX. Sources and/or calculations

of all the parameters mentioned here will be described in detail in the next section.

As mentioned before (Equation 1), E' is the difference between the potentials of the two electrodes comprising the cell, ignoring the E_j . For Cells IX, XVI, XI, and XVIII, all of which use calomel electrodes, E' was calculated by:

$$E' = -59.16 \log_m \gamma_{Cl} - 59.16 \log \frac{s^a_{Cl}}{w^a_{Cl}} \quad (49)$$

where $\log_m \gamma_{Cl}$ is the transfer activity coefficient of the chloride ion (molar scale) between water and the methanol-water solvent, and w^a_{Cl} and s^a_{Cl} refer to conventional activities of the chloride ion in water and methanol-water solutions, respectively. E' is calculated in millivolts. The E' for cells using hydrogen glass electrodes (that is, Cells XVII and XIX) was calculated by

$$E' = 59.16 \log_m \gamma_H + m_s \log_s a_H - m_w \log_w a_H \quad (50)$$

where $\log_m \gamma_H$ is the transfer activity coefficient of the hydrogen ion, w^a_H and s^a_H are the conventional activities of the hydrogen ions in water and methanol-water solvent, respectively, and the m_s and the m_w constants refer to the slopes, also called Nernstian factors, obtained in the calibration procedure of the hydrogen glass electrodes in methanol-water solvent and water. For Cells X and XII, which are sodium glass electrodes, E' is similar to that for the hydrogen glass electrodes (i.e., Equation 50), except for

the presence of a small correction factor Δ resulting from different values of the y-intercepts in the calibration curves for each sodium glass electrode:

$$E' = 59.16 \log_m \gamma_{Na} + m_s \log_s a_{Na} - m_s \log_w a_{Na} + \Delta \quad (51)$$

Here $\log_m \gamma_{Na}$ is the transfer activity coefficient for sodium ion, $_w a_{Na}$ and $_s a_{Na}$ are the conventional activities of the sodium ions in water and methanol-water solvents, and the m_s and m_w constants are obtained in the calibration procedure of the sodium glass electrodes. There exist explicit equations for only two terms of the liquid-junction potential at the interface of two solvents, namely $E_{j,G}$ (Equation 12), which accounts for differences in solvation energies and transport numbers of all ions crossing the boundary, and $E_{j,H}$ (Equation 7), which accounts for differences in mobilities of those ions. When applied to the four different junctions present among the cells used in this study, they lead to the following equations:

a) For a simple junction between sodium chloride solutions, $NaCl | NaCl$, it follows that:

$$\begin{matrix} W & S \end{matrix}$$

$$E_{j,G} = 59.16 (t_{Na} \log_m \gamma_{Na} - t_{Cl} \log_m \gamma_{Cl}) \quad (52)$$

where t_{Na} is the transport number of the sodium ion in sodium chloride, averaged over the two solvents (that is, $t_{Na} = (_w t_{Na} + _s t_{Na})/2$), and $t_{Cl} = 1 - t_{Na}$.

$$E_{j,H} = -59.16 (t_{Na} - t_{Cl}) \log \frac{s^a_{NaCl}}{w^a_{NaCl}} \quad (53)$$

where w^a_{NaCl} and s^a_{NaCl} are the conventional mean ionic activities of NaCl solutions in water and the given mentha-nol-water solvent.

b) For a simple junction between hydrogen chloride solutions, $HCl_W | HCl_S$, expressions parallel to Equations 52 and 53 were obtained:

$$E_{j,G} = -59.16(t_H \log_m \gamma_H - t_{Cl} \log_m \gamma_{Cl}) \quad (54)$$

where $t_{Cl} = 1 - t_H$ and

$$E_{j,H} = -59.16(t_H - t_{Cl}) \log \frac{s^a_{HCl}}{w^a_{HCl}} \quad (55)$$

c) For a junction involving a salt bridge of saturated aqueous KCl between sodium chloride solutions in water and given methanol-water mixture, $NaCl_W | KCl(sat)_W | NaCl_S$, the following expression was derived:

$$E_{j,G} = 59.16(0.5146 \log_m \gamma_{Cl} - 0.4854 \log_m \gamma_K) \quad (56)$$

where 0.5416 and 0.4854 are, respectively, transport numbers of the chloride ion and the potassium ion in the saturated aqueous solution of KCl, obtained by extrapolation of the data reported by Miller (66).

In the presence of a saturated KCl salt bridge, $E_{j,H}$ was assumed to be zero. Both $E_{j,G}$ and $E_{j,H}$ expressions were

derived using the assumption that only the salt-bridge electrolyte contributes to the diffusion potential. In order to test that assumption, a sample calculation of $E_{j,H}$ was made using the complete Henderson equation as applied to a saturated KCl salt-bridge junction between 0.1M solutions of HCl in water and 90% methanol, giving the result of 1.5mV. Since that number would be even smaller for less concentrated HCl solutions as well as for junctions between water and methanol-water solvents of lower methanol content the assumption of KCl being the only current-carrying species seems to be valid here.

d) For a salt-bridge junction between hydrogen chloride solutions, $\text{HCl} \underset{W}{|} \text{KCl(sat)} \underset{W}{|} \text{HCl} \underset{S}{|}$, Equation 56 was used to calculate $E_{j,G}$, and $E_{j,H}$ was again assumed to be zero, since the assumption in c) is equally valid here.

Finally, $E_{j,s}$ values were obtained by subtracting all the calculable terms from the experimental e.m.f. values:

$$E_{j,s} = E(\text{cell})^{\text{exp}} - E' - E_j' \quad (57)$$

which is only a rearrangement of Equation 10.

Table 5 can be used as a reference to all the equations used to calculate the $E_{j,s}$ values for junctions between water and methanol-water solvents.

TABLE 5

Reference List of Equations Used to Calculate E' , $E_{j,G}$, and $E_{j,H}$ for Cells Listed in Table 4.

Cell #	Equation for E'	Equation for $E_{j,G}$	Equation for $E_{j,H}$
IX	49	52	53
XVI	49	54	55
X	51	52	53
XVII	50	54	55
XI	49	56	--
XVIII	49	56	--
XII	51	56	--
XIX	50	56	--

Calculations Based on the Existing Formulations.

In order to use Equations 52-56 in the calculations of E_j and $E_{j,s}$ for the junctions between water and methanol-water solvents studied in this investigation, the following parameters had to be available from the literature or determined experimentally:

a) Transfer activity coefficients of H^+ , Na^+ , K^+ , and Cl^- ions between water and methanol-water solvents.

b) Salt-effect activity coefficients for NaCl and HCl solutions in water and methanol-water solvents.

c) Transport numbers of Na^+ ions in NaCl solutions and of H^+ ions in HCl solutions in all methanol-water solvents and of K^+ ions in a sat. KCl solution in water.

d) The Nernstian factors, m_s and m_w , for every hydrogen and sodium glass electrode used in this investigation.

What follows is a detailed account of the procedures used to obtain these parameters, and a presentation of the final calculations of E' , E'_j , and $E_{j,s}$.

Transfer activity coefficients of single ions.

In order to obtain the transfer activity coefficients of the single ions needed for the present calculations, which were $\log_m \gamma_{Na}$, $\log_m \gamma_K$, $\log_m \gamma_H$, and $\log_m \gamma_{Cl}$, the available data had to be examined and correlated. The final values were all converted to molar scale, and large-scale graphs were made for each medium effect as a function of wt % methanol which were subsequently used to interpolate those values to the experimental concentrations of methanol. Transfer activity coefficients of tetraphenylarsonium picrate (67), potassium tetraphenylborate and potassium picrate (68) were used to calculate the medium effect of the BPh_4^- ion, using Equation 38e. With the knowledge of transfer activity coefficient of one ion it became possible to calculate $\log_m \gamma$ for other ions, using known medium effects for complete electrolytes, such as potassium chloride (69-71), sodium chloride (70,71), and hydrogen chloride (72). The results of the calculations and interpolations to even wt % methanol-water compositions were eventually published (73). Table 6 lists transfer activity coefficients of all the ions relevant to this study, reported at even wt % methanol intervals. The actual values used were obtained by interpolation to the exact solvent composition.

TABLE 6

Transfer Activity Coefficients of K^+ , Na^+ , H^+ , and Cl^- Ions
in Methanol-Water Solvents (Water Reference-Molar Scale)
(73).

Wt % MeOH	$\log_m \gamma_{K^+}$	$\log_m \gamma_{Na^+}$	$\log_m \gamma_{H^+}$	$\log_m \gamma_{Cl^-}$
100	1.72	1.57	1.80	2.37
90	1.70	1.51	0.53	1.86
80	1.58	1.44	-0.08	1.47
70	1.39	1.35	-0.11	1.15
60	1.22	1.16	-0.10	0.88
50	0.99	1.00	-0.06	0.68
40	0.87	0.89	0.07	0.42
30	0.70	0.72	0.11	0.26
20	0.48	0.59	0.20	0.06
10	0.20	0.27	0.08	0.05

Salt-effect activity coefficients

Salt-effect activity coefficients for sodium and chloride ions in NaCl solutions were calculated using the Debye-Huckel equation:

$$\log y = - \frac{A I^{1/2}}{1 + B a^{\circ} I^{1/2}} \quad (58)$$

where y is the ionic activity coefficient of the Na^+ or Cl^- ion, a° is the ion-size parameter chosen to be $4.6\text{\AA}$ for both ions in all methanol-water solvents as well as for water. The value of $a^{\circ}=4.6\text{\AA}$ was used by Paabo, Bates and Robinson (72) to calculate $\log y_{\text{Cl}}$ in the establishment of pH scales in methanol-water solvents. I is the ionic strength of each NaCl solution (equal in this case to the molarity), and the parameters A and B were calculated for each solvent by:

$$A = \frac{1.8246 \times 10^6}{(\epsilon T)^{3/2}} \quad (59)$$

and

$$B = \frac{50.29 \times 10^8}{(\epsilon T)^{1/2}} \quad (60)$$

where $T = 298.15\text{K}$, and ϵ is the dielectric constant of the solvent. Appendix 4 lists values of ϵ as a function of % MeOH at even % intervals, taken from (59). A large-scale graph was used to interpolate those values to the experimental composition of methanol-water mixtures.

The ionic activity coefficients obtained via Equation 58 were used to calculate the activities of both sodium and chloride ions in solution, when the electrolyte was sodium chloride. With solutions of HCl, the approach was somewhat different. The assumption which was made for NaCl solutions that the activities of cation and anion are essentially the same because of their similar size is not valid for HCl solutions. Oiwa (74) reported the results of experimental determination of activity coefficients of HCl solutions, y_{HCl} , both as a function of HCl concentration (from 0.1 to 0.0005m) as well as of concentration of methanol in its aqueous mixtures (20, 40, 60, 80, 90 wt %). By a series of interpolations from large-scale graphs, first plotting y_{HCl} values as a function of wt % methanol (one graph for each concentration of HCl) and interpolating to experimental wt % MeOH, then taking those values and plotting them against the HCl concentrations, the activity coefficients y_{HCl} for all the concentrations of HCl used here in all of the methanol-water solvents were obtained. For each HCl solution, the ionic activity coefficient of the chloride ion, y_{Cl^-} was calculated using Equation 58, with the a again chosen to be $4.6\text{\AA}$. Finally, the ionic activity coefficient of the hydrogen ion, y_{H^+} , was calculated using the relationship

$$y_{\text{H}^+} = \frac{y_{\text{HCl}}^2}{y_{\text{Cl}^-}} \quad (61)$$

The activity coefficients of hydrogen ion and chloride ion, y_{H^+} and y_{Cl^-} , were then used to calculate the ionic activities of both ions in HCl solutions. Table 7 illustrates the significance of these calculations by listing some of the activities obtained here. While in most cases the differences are very small, omitting this procedure by using a $y_{\pm}$ value for the activity coefficient of the hydrogen ion would result in subsequent error of as much as 2.5mV, when that activity coefficient is used in e.m.f. calculations.

TABLE 7

Salt-Effect Activities (in Logarithmic Form) of Hydrogen and Chloride Ions in HCl Solutions.

Wt % MeOH	C_{HCl}	$-\log a_{\text{H}^+}$	$-\log a_{\text{Cl}^-}$
29.89	0.9648×10^{-1}	1.145	1.153
	0.9648×10^{-2}	2.074	2.072
	0.9648×10^{-3}	3.034	3.035
40.20	0.9616×10^{-1}	1.169	1.168
	0.9616×10^{-2}	2.083	2.080
	0.9616×10^{-3}	3.038	3.039
50.45	0.9667×10^{-1}	1.185	1.183
	0.9667×10^{-2}	2.088	2.085
	0.9667×10^{-3}	3.038	3.040
60.08	0.9699×10^{-1}	1.199	1.202
	0.9699×10^{-2}	2.097	2.093
	0.9699×10^{-3}	3.039	3.041
70.12	0.9706×10^{-1}	1.216	1.226
	0.9706×10^{-2}	2.116	2.104
	0.9706×10^{-3}	3.044	3.045
80.40	0.9667×10^{-1}	1.229	1.259
	0.9667×10^{-2}	2.125	2.120
	0.9667×10^{-3}	3.050	3.052

TABLE 7 (con't.)

Wt % MeOH	C_{HCl}	$-\log a_{H^+}$	$-\log a_{Cl^-}$
90.14	0.9644×10^{-1}	1.256	1.299
	0.9644×10^{-2}	2.141	2.140
	0.9644×10^{-3}	3.056	3.060

Transport numbers.

For the fairly dilute solutions of NaCl and HCl (from $1 \times 10^{-1} \text{M}$ to $1 \times 10^{-3} \text{M}$) transport numbers at infinite dilutions were used. They were calculated from the few available data (75) of limiting single ion conductances λ^0 for H^+ , Na^+ , and Cl^- , listed in Table 8, using the relationship:...

$$t_+^0 = \frac{\lambda_+^0}{\lambda_+^0 + \lambda_-^0} \quad (62)$$

which holds for any 1:1 electrolyte in a solution with no other electrolyte present. From the available literature data, transport numbers for Na^+ ions in NaCl solutions could be calculated only for water, 64% MeOH and 100% MeOH. These results were then plotted as a function of the concentration of MeOH. A smooth curve (Figure 5) was drawn through the three points to be used later for interpolation to the experimental composition of methanol-water mixtures. While obtaining a curve using only three points may not really be valid, the shape of the resulting curve was roughly parallel to that drawn using the t_{Na} values for 0.05m NaCl solutions, available for a number of methanol-water solvents (76), as opposed to the limiting values.

TABLE 8

Limiting Equivalent Conductances of H^+ , Na^+ , and Cl^- Ions in Methanol-Water Solvents (68).

Wt % MeOH	$\lambda_{H^+}^{\circ}$	$\lambda_{Na^+}^{\circ}$	$\lambda_{Cl^-}^{\circ}$
100	146.12	45.22	52.38
64	---	29.57	37.05
0	349.82	50.11	76.34

FIGURE 5

Transport Numbers of Na^+ in NaCl Solutions in Methanol-Water Solvents.

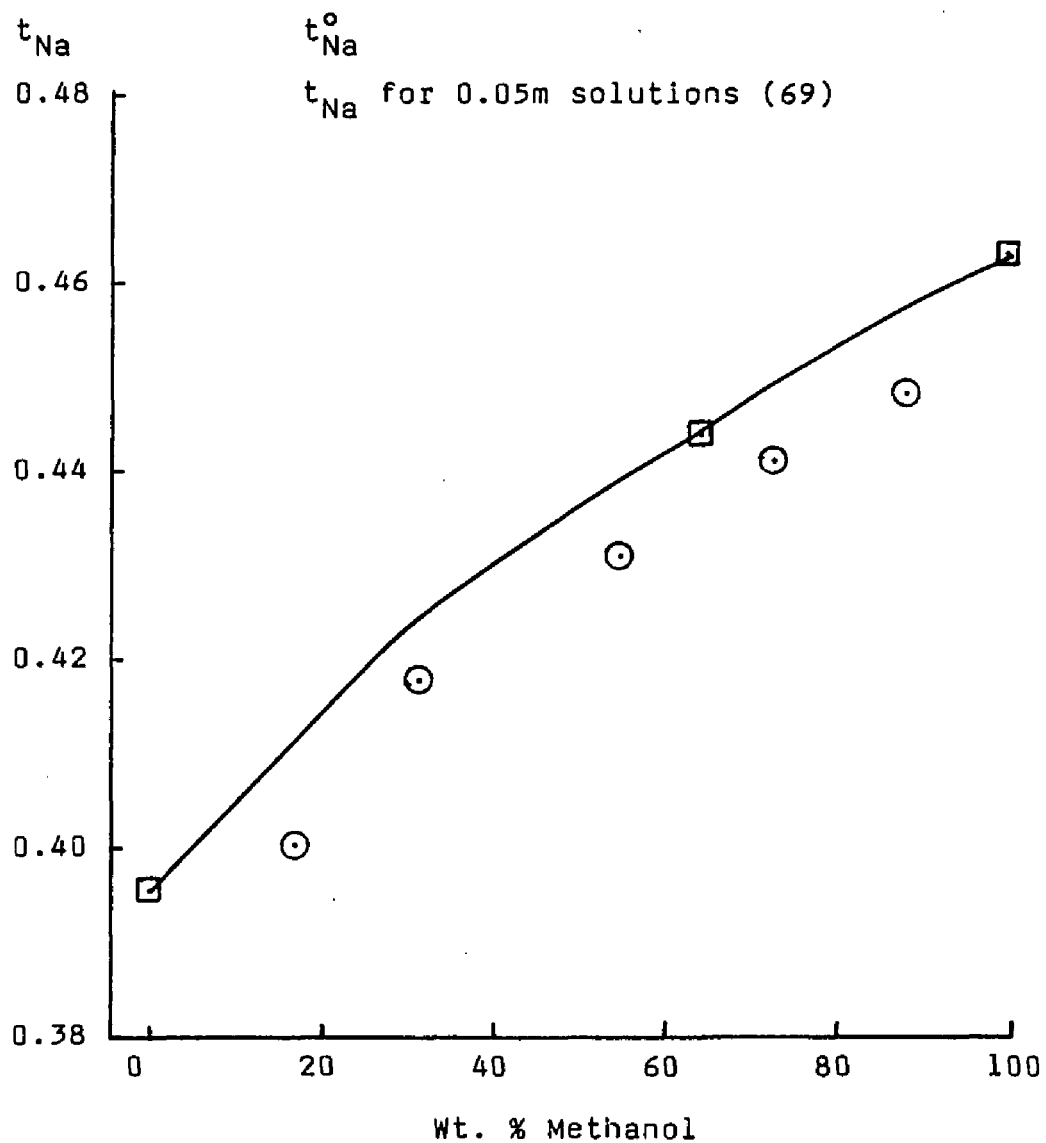
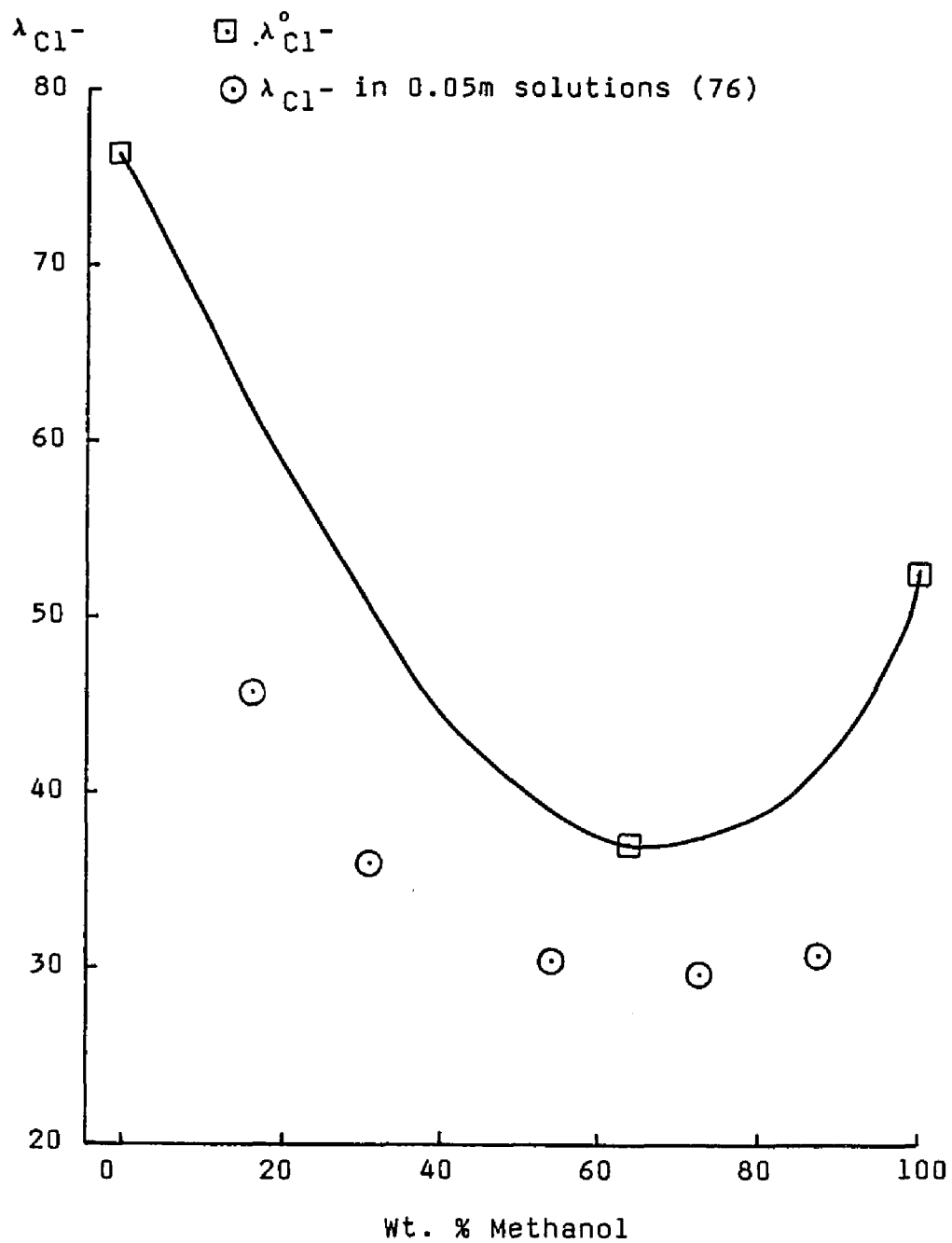


FIGURE 6

Limiting Equivalent Conductance of Cl^- , $\lambda_{\text{Cl}^-}^{\circ}$, in Methanol-
Water Solvents.



The procedure for obtaining transport numbers of H^+ and Cl^- in HCl solutions was more complicated due to lack of data. Shedlovsky, et al. (77) and De Lisi, et al. (78) determined the limiting conductances of HCl throughout the range of MeOH-H₂O solvents. The three known values for λ_{Cl}° (Table 8) were plotted as a function of solvent composition and a smooth curve was drawn through them (Figure 6). The shape of the curve was determined by the data for λ_{Cl}° obtained for 0.05m solutions by Longworth (76). (The procedure was analogous to that described already for t_{Na}° .)

A large-scale version of the graph in Figure 6 was used to get λ_{Cl}° values in methanol-water solvents for which Λ_{HCl}° were known (77,78); λ_H° values were calculated by difference ($\lambda_H^{\circ} = \Lambda_{HCl}^{\circ} - \lambda_{Cl}^{\circ}$), the t_H° values were obtained using Equation 62 and plotted as a function of solvent composition to allow for interpolation to experimental MeOH-H₂O composition. The results are shown in Table 9 and Figure 7. As can be seen, while the transport numbers of Na^+ change rather smoothly with solvent composition (Figure 5), the corresponding values for H^+ go through a very pronounced minimum. Although the precision of the calculated t_H° values may be questioned due to the lack of experimental data for λ_{Cl}° in the region of the minimum, its presence in the view of this author is supported by enough evidence.

While the validity of using limiting transport numbers without relating them to the actual concentration of each ion might be questioned, it can be examined for aqueous

solutions of KCL. Miller (66) in 1966 determined t_K values for KCl solutions ranging from $1 \times 10^{-4}M$ to $3M$. By extrapolating in both directions two values of the t_K were obtained: t_K was found to be 0.4905, t_K for a saturated solution was estimated to be 0.4854, the difference being about 1%. There is general agreement (75) that transport numbers are very insensitive to the concentration of the electrolyte.

TABLE 9

Limiting Equivalent Conductances of HCl and Cl⁻ and Limiting Transport Numbers of H⁺ in HCl in Methanol-Water Solvents.

Wt % MeOH	$\Lambda_{\text{HCl}}^{\circ}$ (a)	$\lambda_{\text{Cl}}^{\circ}$ (b)	t_{H}° (c)
0	426.16	76.34*	0.8210
10	343.2	63.7	0.8144
20	278.3	52.8	0.8103
40	190.1	41.1	0.7838
60	138.7	37.2	0.7318
64		37.05*	0.718
80	108.0	38.0	0.6482
90	103.2	41.3	0.5998
95.79	108.1	45.9	0.5754
100	198.5	52.38*	0.7361
82.29	108.32	38.5	0.6446
92.52	105.33	43.1	0.5908
94.46	106.87	44.6	0.5826
96.32	110.88	46.5	0.5806
98.05	119.81	48.5	0.5952
99.44	149.01	50.8	0.6591

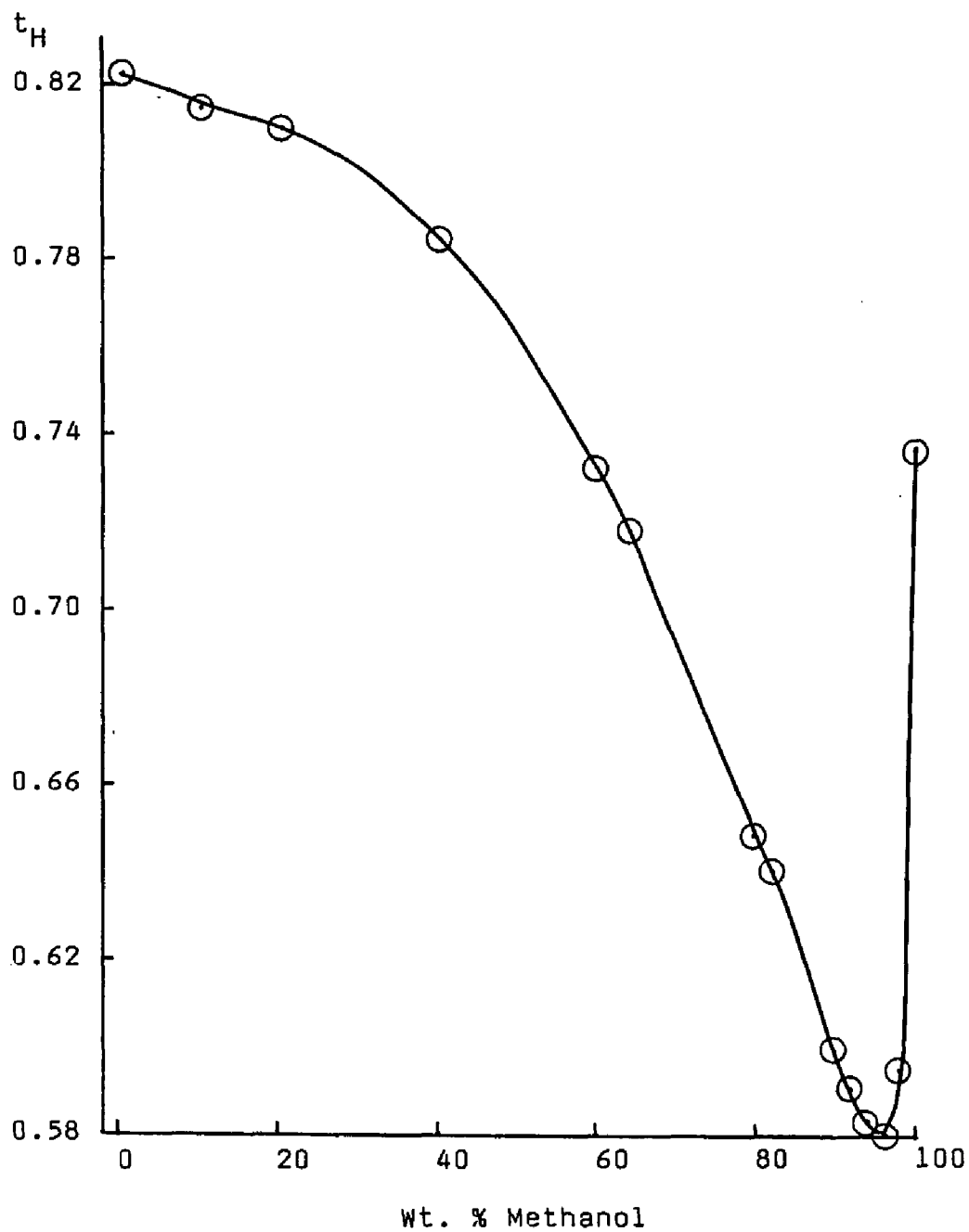
(a) determined by (77) and (78)

(b) interpolated using Figure 6, except for *, available from (75)

(c) calculated using Equation 62

FIGURE 7

Limiting Transport Number of H^+ , t_H^0 , in HCl Solutions in Methanol-Water Solvents.



Equation 56 was used previously (48) with both transport numbers, t_K and t_{Cl} , equated to 0.5. Table 10 shows the results of using Equation 56 either with $t_K = t_{Cl} = 0.5$ or with $t_K = 0.4854$ and $t_{Cl} = 0.5146$. While the effect is not very large in absolute magnitude, it can represent as much as 65% error (in the case of 90% MeOH) in the $E_{j,G}$ value used in later calculations. The relevance of such an error will be examined when the final $E_{j,s}$ values are calculated.

TABLE 10

Equation 56 [$E_{j,G} = 59.16(t_{Cl} \log_m \gamma_{Cl} - t_K \log_m \gamma_K)$] Calculated
Using $t_K = t_{Cl} = 0.5$ (Column A) or $t_K = 0.4854$ and $t_{Cl} =$
 0.5146 (Column B).

~Wt % MeOH	A(mV)	B(mV)	B-A(mV)
30	-12.90	-12.08	0.82
40	-13.34	-12.22	1.12
50	-9.23	-7.77	1.46
60	-9.97	-8.15	1.82
70	-6.95	-4.76	2.19
80	-2.90	-0.25	2.65
90	4.73	7.81	3.08
100	19.23	22.76	3.53

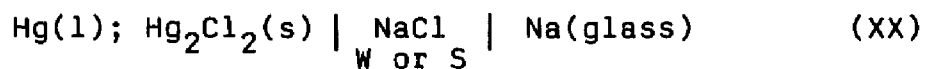
Calibration of glass electrodes.

Sodium glass electrodes

Several sodium glass electrodes were employed in this study. All of them were calibrated first in aqueous NaCl solutions to test their response. While one of them (#7) was chosen for exclusive use in water, others were used and calibrated in methanol-water solvents of varying composition. The calibration solutions ranged in concentration from $1 \times 10^{-1} \text{M}$ to $6 \times 10^{-4} \text{M}$ NaCl. The mean ionic activities of NaCl in these solutions were calculated using the Debye-Huckel equation (Equation 58) for the activity coefficient.

The calibration procedure was repeated several times during the few months of taking the e.m.f. measurements. The results showed that the glass electrode changes its characteristics with time and therefore an effort was made to coordinate those changes with the dates on which the e.m.f. measurements were made. In other words, the calibration of the two sodium glass electrodes which would be used in the actual calculations of $E_{j,s}$ had to coincide in time with the e.m.f. measurements of the cell in which those two electrodes were simultaneously used.

The reference electrode used in the calibration procedure was a calomel electrode and the calibration cell can be represented by:



According to the manufacturer (Fisher Scientific) the response of the sodium glass electrode is given by:

$${}_sE_{\text{Na(glass)}} = {}_sE_{\text{Na(glass)}}^{\circ} + m_s \log {}_s a_{\text{Na}} \quad (63)$$

where S stands for any solvent, including water. The response of the calomel electrode is given by

$${}_sE_{\text{calomel}} = {}_sE_{\text{cal}}^{\circ} - 59.16 \log {}_s a_{\text{Cl}} \quad (64)$$

Combining Equations 63 and 64 results in an equation relating e.m.f. of Cell XX to the mean ionic activity of NaCl solution, when the substitution ${}_s a_{\text{Na}} = {}_s a_{\text{Cl}} = {}_s a_{\pm}$ is made:

$$E(\text{XX}) - 59.16 \log {}_s a_{\pm} = m_s \log a_{\pm} + {}_sE_{\text{Na(glass)}}^{\circ} - {}_sE_{\text{cal}}^{\circ} \quad (65)$$

This equation can be simplified to the form:

$$y = m_s x + b \quad (66)$$

where

$$y = E(\text{XX}) - 59.16 \log {}_s a_{\pm} \quad (66a)$$

$$x = \log {}_s a_{\pm} \quad (66b)$$

and

$$b = {}_sE_{\text{Na(glass)}}^{\circ} - {}_sE_{\text{cal}}^{\circ} \quad (66c)$$

A plot of y values obtained in the calibration against the logarithm of the mean ionic activity of NaCl should result in a straight line, whose slope is equal to the Nernstian factor m_s and whose intercept with the y-axis, b , provides

us with an estimate of the standard potential of Cell XX in solvent S. There was usually a slight deviation from linearity at the lower concentrations of NaCl, and some points were rejected. The values of m_s , ${}_sE^0(XX)$ and ${}_wE^0(XX)$ for each electrode used in the final calculations are listed in Table 11, along with the correlation coefficient, R, which is an indicator of the linearity of the electrode response (perfectly linear response having an R equal exactly to one). Since every electrode was calibrated in water and later several electrodes at a time were calibrated in the same solvent, it became apparent that every electrode used in a particular solvent gave different value of $E^0(XX)$ in that solvent. These differences imply different values of ${}_sE^0\text{Na(glass)}$ for every electrode used. We may recall that Equation 4 is obtained from Equation 1 via the following relationship:

$${}_2E^0 - {}_1E^0 = 59.16 \log_m M \quad (67)$$

which is true only if each individual electrode of the same type (here M/M^+) has the same standard electrode potential in a given solvent S. Glass electrodes, unfortunately, do not behave that way. However, when the $E^0(XX)$ values obtained using two labelled sodium glass electrodes were compared in every solvent (including water), the differences between the $E^0(XX)$ values in each solvent were fairly constant ($\pm 2\text{mV}$) for a given pair of electrodes and could be used as a correlation factor Δ as seen in Equation 51. In

practice, the value of Δ was calculated from the $E^0(\text{XX})$ values obtained in water, according to the expression:

$$\Delta = {}_X E^0(\text{XX}) - {}_7 E^0(\text{XX}) \quad (68)$$

where subscript 7 refers to the electrode #7, chosen as the reference electrode in water, and the subscript X refers to the sodium electrode later used in the solvent of interest. Table 12 lists the values used in this investigation.

TABLE 11

Characteristics of Sodium Glass Electrodes Used in Methanol-
Water Solvents.

Electrode #	Wt % MeOH	$E^0_s(XX)$	$E^0_w(XX)$	m_s	R
1	50.58	222.4	126.7	57.95	0.9999
3	59.36	256.7	138.5	59.21	0.9999
5	89.76	332.8	129.8	60.48	0.9999
	88.96	337.2	132.2	58.67	0.9999
	60.27	252.2	132.2	59.11	0.9999
7	0.0		127.8	56.32	0.9998
8	68.95	278.0	128.2	58.10	0.9999
	69.73	278.3	133.4	60.47	0.9999
9	79.94	308.8	138.3	60.17	0.9999
	79.69	307.2	138.3	59.42	0.9998

TABLE 12

Correction Term Δ Determined for Sodium Glass Electrodes
Used in Methanol-Water Solvents.

Wt % MeOH	(in mV)
50	-1.1
60	4.4
70	5.6 } two different 0.4 } Na(glass) electrodes
80	10.5
90	4.4 } two different 2.0 } Na(glass) electrodes

The results of calibration of sodium glass electrodes can be interpreted in such a way that will show whether the glass electrodes behave thermodynamically in these media. Cell XX is a cell without transference and can be used to calculate transfer activity coefficients for electroneutral combinations of ions. In this case, two such electroneutral combinations can be evaluated.

First, a value for $\log_m \gamma_{\text{NaCl}}$ can be calculated from

$$\log_m \gamma_{\text{NaCl}} = \frac{1}{59.16} ({}_s E^0(\text{XX}) - {}_w E^0(\text{XX})) \quad (69)$$

Second, a value for $(\log_m \gamma_{\text{Na}} - \log_m \gamma_{\text{H}})$ can be obtained if standard electrode potentials of the calomel electrode in solvent S and in water are known. The following expression was derived for this purpose:

$$\log_m \gamma_{\text{Na}} - \log_m \gamma_{\text{H}} = {}_s E^0(\text{XX}) - {}_w E^0(\text{XX}) + {}_s E_{\text{Cal}}^0 - {}_w E_{\text{Cal}}^0 \quad (70)$$

It can be shown that either E_{Cal}^0 or E_{AgCl}^0 data can be used in Equation 70, and the latter were chosen due to their availability in the literature (75). Furthermore, since transfer activity coefficients for the sodium ion are available for methanol-water solvents (73), it is possible to calculate $\log_m \gamma_{\text{H}}$ and compare it with the known values:

$$\log_m \gamma_{\text{H}} = \log_m \gamma_{\text{Na}} - \text{Eq. 70} \quad (71)$$

Results from applying Equations 69, 70, and 71 to the e.m.f. values obtained in the calibration of sodium glass

electrodes in methanol-water solvents are listed in Table 13. The $\pm$ uncertainty indicates the standard deviation of each value, based on several individual determinations using different glass electrodes. The agreement between the values obtained here are the accepted literature values for both medium effects, that is for H^+ as well as NaCl is excellent.

TABLE 13

Transfer Activity Coefficients of NaCl and H⁺ Calculated
from E.m.f.'s of Cell XX in Methanol-Water Solvents.

Wt % MeOH	$\log_m \gamma_{\text{NaCl}}$ calc	$\log_m \gamma_{\text{NaCl}}$ lit. (70,71)	$\log_m \gamma_{\text{H}}$ calc	$\log_m \gamma_{\text{H}}$ lit. (73)
50	1.62 $\pm$ 0.00	1.68	-0.01	-0.05
60	2.07 $\pm$ 0.04	2.06	-0.12 $\pm$ 0.04	-0.10
70	2.49 $\pm$ 0.06	2.48	-0.14 $\pm$ 0.08	-0.11
80	2.88 $\pm$ 0.02	2.90	-0.06 $\pm$ 0.01	-0.08
90	3.41 $\pm$ 0.05	3.36	0.49 $\pm$ 0.03	0.50

Hydrogen Glass Electrodes.

Hydrogen glass electrodes were first calibrated in water, using a saturated calomel electrode as the reference. Two buffers were used, 0.05m solution of potassium tetroxalate ($p_{a_H} = 1.679$), and 0.05m solution of potassium hydrogen phthalate ($p_{a_H} = 4.008$). Since the y-intercepts of the hydrogen electrodes were all within 0.5mV of each other, the correction factor was assumed to be zero. Electrodes chosen for work in the methanol-water solvents were calibrated using HCl solutions in the respective solvents. Formulations analogous to Equations 65-66c were used to calculate the Nernstian response of each electrode. Activities of individual ions, that is hydrogen and chloride ions, were used instead of the mean ionic activity $a_{\pm}$. The procedure for obtaining the conventional activities of H^+ and Cl^- ions in HCl solution was described in the experimental section of this thesis. The m_s values used in each solvent are listed in Table 14.

TABLE 14

Characteristics of Hydrogen Glass Electrodes Used in Methanol-Water Solvents.

Electrode #	Wt % MeOH	$E^0_s(XX)$	m_s	R
1	90.14	512.70	58.78	0.99998
2	0.0		58.39	
3	80.40	476.9	60.60	0.999
4	70.12	454.90	58.95	0.99998
5	60.08	455.6	66.68	1.000
	40.20	433.3	61.83	1.000
6	50.45	435.7	60.98	1.000
	29.89	421.35	59.64	1.000

Final values of E' , E'_j and $E_{j,s}$ for Methanol-Water Solvents.

Presentation of the Results.

The results of e.m.f. measurements of Cells IX-XII and XVI-XIX and of calculations of E' , E'_j , and $E_{j,s}$ are listed in Tables 15 and 16. While the actual composition of each solvent was carefully determined and all solvent-dependent parameters were interpolated to the exact experimental solvent composition, in the final discussion only round figures for % MeOH will be used. The actual compositions are always within 0.5% of the round values and the terms calculated here do not change measurably for such small changes in solvent composition. Every line in Table 15 and 16 corresponds to a single determination of $E_{j,s}$. In the study involving NaCl solutions, the e.m.f. of a particular cell was determined only once. The e.m.f.'s of cells using HCl solutions were determined usually in triplicate. The values of E_{exp} reported in Table 16 are the mean values obtained for each cell. In order to facilitate the analysis of $E_{j,s}$ results, a summary of $E_{j,s}$ values is presented in Table 17 for NaCl system and in Table 18, for HCl system. A single value is reported for each electrolyte concentration, which is either the original value found in Tables 15 and 16 or the mean of more than one value.

TABLE 15

Experimental and Calculated Parameters for Cells using NaCl
in Methanol-Water Solvents (Molar Scale, 25°C, mV).

Cell	$\sim C_{\text{NaCl}}$	E_{exp}	E'	E'_j	$E_{j,s}$
90% MeOH					
IX (cal, simple)	1×10^{-1}	-50.8	-99.2	22.9	25.4
	3×10^{-2}	-51.2	-102.5	23.5	27.7
	3×10^{-2}	-51.1	100.5	22.6	26.8
	3×10^{-3}	-52.4	-106.8	24.1	30.2
	3×10^{-3}	-54.2	-104.7	23.2	27.3
X (Na(glass), simple)	1×10^{-1}	127	77.4	22.9	26.5
	3×10^{-2}	132	79.3	23.5	29.2
	3×10^{-2}	131	82.7	22.6	25.7
	3×10^{-3}	141	80.7	24.1	36.1
	3×10^{-3}	137	84.6	23.2	29.2
XI (cal, salt bridge)	1×10^{-1}	-76.5	-99.2	7.4	15.3
	3×10^{-2}	-80.0	-102.5	7.4	15.0
	3×10^{-2}	-79.1	-100.5	6.9	14.5
	3×10^{-3}	-87.1	-106.8	7.4	12.3
	3×10^{-3}	-85.6	-104.7	6.9	12.2
XII (Naglass, salt bridge)	1×10^{-1}	103	77.4	7.4	18.4
	3×10^{-2}	106	79.3	7.4	19.3
	3×10^{-2}	104	82.7	6.9	14.4
	3×10^{-3}	106	80.7	7.4	17.9
	3×10^{-3}	108	84.6	6.9	16.5

TABLE 15 (con't.)

Cell	$\sim C_{NaCl}$	E_{exp}	E'	E'_j	$E_{j,s}$
		80% MeOH			
IX (cal, simple)	1×10^{-1}	-44.9	-77.9	12.0	21.0
	3×10^{-1}	-44.3	-78.9	12.2	22.4
	3×10^{-2}	-49.2	-84.1	13.3	21.5
	3×10^{-3}	-44.6	-82.1	12.7	24.8
	3×10^{-3}	-51.4	-87.5	14.2	22.3
X (Na(glass), simple)	1×10^{-1}	112	83.5	12.0	16.5
	3×10^{-2}	113	83.0	12.2	17.8
	3×10^{-2}	122	87.6	13.3	21.1
	3×10^{-3}	116	83.1	12.7	20.2
	3×10^{-3}	124	87.9	14.2	22.3
XI (cal, salt bridge)	1×10^{-1}	-67.2	-77.9	-0.7	11.4
	3×10^{-2}	-66.6	-78.9	-0.7	12.9
	3×10^{-2}	-72.4	-84.1	-0.5	12.1
	3×10^{-3}	-66.8	-82.1	-0.7	16.0
	3×10^{-3}	-75.2	-87.5	-0.5	12.8
XII (Na(glass), simple)	1×10^{-1}	92	83.5	-0.7	9.1
	3×10^{-2}	91	83.0	-0.7	8.7
	3×10^{-2}	99	87.6	-0.5	11.9
	3×10^{-3}	93	83.1	-0.7	10.5
	3×10^{-3}	102	87.9	-0.5	14.6

TABLE 15 (con't.)

Cell	$\sim C_{NaCl}$	E_{exp}	E'	E'_j	$E_{j,s}$
		70% MeOH			
IX (cal, simple)	1×10^{-1}	-39.4	-61.4	4.4	17.6
	3×10^{-2}	-38.3	-61.9	4.5	19.1
	3×10^{-2}	-40.7	-62.6	4.4	17.6
	3×10^{-3}	-38.7	-64.4	4.9	20.8
	3×10^{-3}	-42.0	-65.2	4.8	18.4
X (Na(glass), plain)	1×10^{-1}	91.4	74.6	4.4	12.4
	3×10^{-2}	91.7	73.1	4.5	14.1
	3×10^{-2}	94.3	73.8	4.4	16.1
	3×10^{-3}	94	71.5	4.9	17.6
	3×10^{-3}	96.0	73.0	4.8	18.2
XI (cal, salt bridge)	1×10^{-1}	-58.4	-61.4	-5.0	8.0
	3×10^{-2}	-56.9	-61.9	-5.0	10.0
	3×10^{-2}	-59.4	-62.6	-5.3	8.5
	3×10^{-3}	-65.1	-64.4	-5.0	4.3
	3×10^{-3}	-62.1	-65.2	-5.3	8.4
XII (Na(glass), salt bridge)	1×10^{-1}	74.6	74.6	-5.0	5.0
	3×10^{-2}	73.0	73.1	-5.0	4.9
	3×10^{-2}	76.0	73.8	-5.3	7.5
	3×10^{-3}	74.0	71.5	-5.0	7.5
	3×10^{-3}	77.3	73.0	-5.3	9.6

TABLE 15 (con't.)

Cell	$\sim C_{NaCl}$	E_{exp}	E'	E'_j	$E_{j,s}$
		60% MeOH			
IX (cal, simple)	1×10^{-1}	-34.7	-48.4	0.9	12.8
	3×10^{-2}	-34.6	-50.0	1.2	14.2
	3×10^{-2}	-36.3	-51.6	1.4	13.8
	3×10^{-3}	-34.2	-53.2	1.7	17.3
	3×10^{-3}	-35.7	-53.7	1.8	16.2
X (Na(glass), simple)	1×10^{-1}	74	66.2	0.9	6.9
	3×10^{-2}	75	66.4	1.2	7.4
	3×10^{-2}	80.7	73.3	1.4	6.0
	3×10^{-3}	84	65.8	1.7	16.5
XI (cal, salt bridge)	1×10^{-1}	-50.3	-48.4	-8.2	6.4
	3×10^{-2}	-50.6	-50.0	-8.2	7.6
	3×10^{-2}	-52.8	-51.6	-8.2	7.0
	3×10^{-3}	-49.6	-53.2	-8.2	11.8
	3×10^{-3}	-54.0	-53.7	-8.2	6.1
XII (Na(glass), salt bridge)	1×10^{-1}	59	66.2	-8.2	1.0
	3×10^{-2}	58	66.4	-8.2	-0.2
	3×10^{-2}	63.7	73.3	-8.2	-1.5
	3×10^{-3}	62	65.8	-8.2	4.5

TABLE 15 (con't.)

Cell	$\sim C_{NaCl}$	E_{exp}	E'	E'_j	$E_{j,s}$
		50% MeOH			
IX (cal, simple)	1×10^{-1}	-26.7	-36.7	-1.8	11.7
	3×10^{-2}	-27.2	-37.8	-1.6	12.3
	3×10^{-2}	-27.9	-38.7	-1.1	11.9
	3×10^{-3}	-26.8	-39.3	-1.4	13.8
	3×10^{-3}	-29.9	-40.2	-0.9	11.2
X (Na(glass), simple)	1×10^{-1}	55.9	52.9	-1.8	4.8
	3×10^{-2}	57.4	53.3	-1.6	5.7
	3×10^{-2}	59.8	53.4	-1.1	7.6
	3×10^{-3}	57.2	53.2	-1.4	5.4
	3×10^{-3}	60.1	53.3	-0.9	7.7
XI (cal, salt bridge)	1×10^{-1}	-38.6	-36.7	-7.8	5.9
	3×10^{-2}	-39.7	-37.8	-7.8	6.0
	3×10^{-2}	-40.4	-38.7	-7.9	6.2
	3×10^{-3}	-38.9	-39.3	-7.8	8.2
	3×10^{-3}	-42.7	-40.2	-7.9	5.4
XII (Na(glass), salt bridge)	1×10^{-1}	43.7	52.9	-7.8	-1.4
	3×10^{-2}	45.7	53.3	-7.8	0.3
	3×10^{-2}	47.0	53.4	-7.9	1.5
	3×10^{-3}	45.5	53.2	-7.8	0.2
	3×10^{-3}	46.2	53.3	-7.9	0.8

TABLE 16

Experimental and Calculated Parameters for Cells Using HCl
in Methanol-Water Solvents (Molar Scale, 25°C, mV).

Cell	$\sim C_{HCl}$	E_{exp}	E'	E'_j	$E_{j,s}$
90% MeOH					
XVI (cal, simple)	1×10^{-1}	-59.0 ± 0.0	-99.9	-13.4	27.5
	1×10^{-1}	-58.9 ± 1.9	-99.8	13.2	27.6
	1×10^{-2}	-61.1	-105.6	11.2	33.3
	1×10^{-2}	63.0	-105.4	11.0	31.4
	1×10^{-3}	63.7 ± 0.9	-108.6	9.9	35.0
	1×10^{-3}	-55.6 ± 1.0	-108.4	9.6	43.3
XVII (H(glass), simple)	1×10^{-1}	39.2 ± 0.1	21.4	13.4	4.4
	1×10^{-1}	44.7 ± 0.4	21.8	13.2	9.7
	1×10^{-2}	47.0	26.2	11.2	9.6
	1×10^{-2}	47.9	26.6	11.0	10.3
	1×10^{-3}	51.9 ± 4.9	29.3	9.2	12.7
	1×10^{-3}	52.4 ± 0.1	29.6	9.6	13.2
XVIII (cal, salt bridge)	1×10^{-1}	-81.0 ± 0.0	-99.9	7.8	11.1
	1×10^{-1}	-80.4 ± 1.8	-99.8	7.8	11.6
	1×10^{-2}	-89.8 ± 0.8	-105.6	7.8	8.1
	1×10^{-2}	-83.7	-105.4	7.8	13.9
	1×10^{-3}	-97.4 ± 3.0	-108.6	7.8	3.4
	1×10^{-3}	-95.0 ± 2.6	-108.4	7.8	5.6

TABLE 16 (con't.)

Cell	$\sim C_{HCl}$	E_{exp}	E'	E'_j	$E_{j,s}$
XIX (H(glass), salt bridge)	1×10^{-1}	14.8 ± 1.8	21.4	7.8	-14.4
	1×10^{-1}	23.0 ± 0.1	21.8	7.8	-6.6
	1×10^{-2}	18.4 ± 2.0	26.6	7.8	-15.6
	1×10^{-2}	25.7 ± 0.7	26.6	7.8	-8.7
	1×10^{-3}	22.4 ± 1.3	29.3	7.8	-14.6
	1×10^{-3}	22.6	29.6	7.8	-14.8
80% MeOH					
XVI (cal, simple)	1×10^{-1}	-46.0 ± 0.3	-79.9	30.5	3.4
	1×10^{-1}	-46.8 ± 0.2	-80.0	30.4	2.8
	1×10^{-2}	-49.8 ± 0.0	-84.2	28.4	6.0
	1×10^{-2}	-50.0 ± 0.4	-83.4	28.4	5.5
	1×10^{-3}	-49.2 ± 0.4	-86.6	27.2	10.2
	1×10^{-3}	-50.8 ± 0.8	-86.2	27.1	8.3
XVII (H(glass), simple)	1×10^{-1}	23.1 ± 0.1	-15.9	30.5	8.5
	1×10^{-1}	27.8 ± 0.7	-15.6	30.4	13.0
	1×10^{-2}	23.7 ± 1.5	-13.3	28.4	8.6
	1×10^{-2}	31.1 ± 0.3	-13.2	28.4	15.9
	1×10^{-3}	28.2 ± 0.1	-12.6	27.2	13.5
	1×10^{-3}	32.2 ± 0.4	-12.3	27.1	17.4

TABLE 16 (con't.)

Cell	$\sim C_{HCl}$	E_{exp}	E'	E'_j	$E_{j,s}$
XVIII (cal, salt bridge)	1×10^{-1}	-66.1 ± 0.1	-79.9	-0.3	14.0
	1×10^{-1}	-67.7 ± 0.0	-80.0	-0.3	12.6
	1×10^{-2}	-74.1 ± 1.6	-84.2	-0.3	10.4
	1×10^{-2}	-72.2 ± 0.7	-83.4	-0.3	4.9
	1×10^{-3}	-81.9 ± 1.3	-86.6	-0.3	4.9
	1×10^{-3}	-69.7 ± 1.2	-86.2	-0.3	16.9
XIX (H(glass), salt bridge)	1×10^{-1}		-15.9	-0.3	
	1×10^{-1}	5.5 ± 0.1	-15.6	-0.3	21.4
	1×10^{-2}	4.9 ± 1.8	-13.3	-0.3	18.4
	1×10^{-2}	7.6 ± 1.1	-13.2	-0.3	21.2
	1×10^{-3}		-12.6	-0.3	
	1×10^{-3}	11.7 ± 0.6	-12.3	-0.3	24.4
70% MeOH					
XVI (cal, simple)	1×10^{-1}	-36.0 ± 0.2	-62.1	25.2	0.9
	1×10^{-2}	-39.2 ± 0.2	-65.5	23.2	3.1
	1×10^{-3}	-45.3 ± 1.8	-67.3	22.1	-0.1
XVII (H(glass), simple)	1×10^{-1}	16.4 ± 0.6	-15.3	25.2	6.5
	1×10^{-2}	18.8 ± 0.7	-11.3	23.2	6.9
	1×10^{-3}	18.7 ± 1.1	-9.4	22.1	6.0
XVIII (cal, salt bridge)	1×10^{-1}	-57.4 ± 0.7	-62.1	-4.8	9.4
	1×10^{-2}	-61.1 ± 0.1	-65.5	-4.8	9.2
	1×10^{-3}	-66.4 ± 0.5	-67.3	-4.8	5.6

TABLE 16 (con't.)

Cell	$\sim C_{HCl}$	E_{exp}	E'	E'_j	$E_{j,s}$
XIX (H(glass), salt bridge)	1×10^{-1}	-5.5 ± 0.7	-15.3	-4.8	14.6
	1×10^{-2}	-3.7 ± 1.1	-11.3	-4.8	12.3
	1×10^{-3}	-8.6 ± 0.9	-9.4	-4.8	5.6
60% MeOH					
XVI (cal, simple)	1×10^{-1}	-28.2 ± 0.2	-47.8	20.1	-0.4
	1×10^{-2}	-31.1 ± 0.1	-50.4	18.1	1.2
	1×10^{-3}	-34.2 ± 0.7	-51.8	17.2	0.3
XVII (H(glass), simple)	1×10^{-1}	10.3 ± 0.6	-22.8	20.1	13.2
	1×10^{-2}	12.9 ± 0.1	-25.9	18.1	20.7
	1×10^{-3}	13.8 ± 0.1	-31.9	17.2	28.4
XVIII (cal, salt bridge)	1×10^{-1}	-46.3 ± 0.7	-47.8	-8.2	9.6
	1×10^{-2}	-48.3 ± 0.5	-50.4	-8.2	10.3
	1×10^{-3}	-52.9 ± 0.3	-51.8	-8.2	7.0
XIX (H(glass), salt bridge)	1×10^{-1}	-9.7 ± 1.6	-22.8	-8.2	21.4
	1×10^{-2}	-5.2 ± 1.1	-25.9	-8.2	28.8
	1×10^{-3}	-7.4 ± 0.2	-31.9	-8.2	32.6
50% MeOH					
XVI (cal, simple)	1×10^{-1}	-23.6 ± 0.2	-37.3	15.2	-1.5
	1×10^{-2}	-27.7 ± 0.1	-39.3	12.7	-1.1
	1×10^{-3}	-38.0 ± 0.4	-40.3	12.0	-9.7

TABLE 16 (con't.)

Cell	$\sim C_{HCl}$	E_{exp}	E'	E'_j	$E_{j,s}$
XVII (H(glass), simple)	1×10^{-1}	8.8 ± 0.2	-13.1	15.2	6.7
	1×10^{-2}	9.7 ± 0.1	-11.4	12.7	8.4
	1×10^{-3}	9.6 ± 0.4	-12.4	12.0	10.0
XVIII (cal, salt bridge)	1×10^{-1}	-38.2 ± 1.5	-37.3	-7.8	6.9
	1×10^{-2}	-39.9 ± 0.7	-39.3	-7.8	7.2
	1×10^{-3}	-59.3 ± 5.6	-40.3	-7.8	13.9
XIX (H(glass), salt bridge)	1×10^{-1}	-7.3 ± 1.0	-13.1	-7.8	13.6
	1×10^{-2}	-2.5 ± 1.5	-11.4	-7.8	16.6
	1×10^{-3}	-3.9 ± 1.9	-12.4	-7.8	16.3
40% MeOH					
XVI (cal, simple)	1×10^{-1}	-18.3 ± 0.3	-22.5	3.9	0.3
	1×10^{-2}	-20.1 ± 0.3	-23.9	2.4	1.5
	1×10^{-3}	-20.1 ± 1.7	-24.6	1.8	2.7
XVII (H(glass), simple)	1×10^{-1}	9.4 ± 0.2	-4.9	3.9	10.4
	1×10^{-2}	10.3 ± 0.3	-4.5	2.4	12.4
	1×10^{-3}	10.1 ± 0.4	-6.7	1.8	15.0
XVIII (cal, salt bridge)	1×10^{-1}	-29.1 ± 0.3	-22.5	-12.2	5.6
	1×10^{-2}	-31.1 ± 1.7	-23.9	-12.2	5.0
	1×10^{-3}	-33.0	-24.6	-12.2	3.9

TABLE 16 (con't.)

Cell	$\sim C_{HCl}$	E_{exp}	E'	E'_j	$E_{j,s}$
XIX (H(glass), salt bridge)	1×10^{-1}	-1.6 ± 0.0	-4.9	-12.2	15.5
	1×10^{-2}	-2.1 ± 2.0	-4.5	-12.2	14.7
	1×10^{-3}	1.6 ± 2.6	-6.7	-12.2	20.6
30% MeOH					
XVI (cal, simple)	1×10^{-1}	-15.0 ± 0.3	-13.8	-0.9	-0.2
	1×10^{-2}	-16.8 ± 0.5	-14.2	-2.0	-0.6
	1×10^{-3}	-10.6 ± 1.3	-15.3	-2.4	7.1
XVII (H(glass), simple)	1×10^{-1}	6.2 ± 0.0	1.7	-0.9	5.4
	1×10^{-2}	6.7 ± 0.2	3.1	-2.0	5.6
	1×10^{-3}	7.2 ± 0.0	2.7	-2.4	6.9
XVIII (cal, salt bridge)	1×10^{-1}	-24.9 ± 0.9	-13.8	-12.1	1.0
	1×10^{-2}	-22.5 ± 1.3	-14.2	-12.1	3.7
	1×10^{-3}	-12.7 ± 0.3	-15.3	-12.1	14.7
XIX (H(glass), salt bridge)	1×10^{-1}	-3.8 ± 0.2	1.7	-12.1	6.5
	1×10^{-2}	-0.3 ± 0.9	3.1	-12.1	8.7
	1×10^{-3}	3.5 ± 0.3	2.7	-12.1	13.0

TABLE 17

Calculated $E_{j,s}$ for Cells Using NaCl in Methanol-Water Solvents (in mV).

Wt % MeOH	C_{NaCl}	simple junction		salt-bridge junction	
		(IX) cal	(X) Na(glass)	(XI) cal	(XII) Na(glass)
90	1×10^{-1}	25.4	26.5	15.3	18.1
	3×10^{-2}	27.3	27.5	14.8	16.9
	3×10^{-3}	28.8	32.7	12.3	17.2
80	1×10^{-1}	21.0	16.5	11.4	9.1
	3×10^{-2}	22.0	19.5	12.5	10.3
	3×10^{-3}	23.6	21.3	14.4	12.6
70	1×10^{-1}	17.6	12.4	8.0	5.0
	3×10^{-2}	18.4	15.1	9.3	6.2
	3×10^{-3}	19.6	17.9	6.4	8.6
60	1×10^{-1}	12.8	6.9	6.4	1.0
	3×10^{-2}	14.0	6.7	7.3	-0.9
	3×10^{-3}	16.8	16.5	9.0	4.5
50	1×10^{-1}	11.7	4.8	5.9	-1.4
	3×10^{-2}	12.1	6.7	6.1	0.9
	3×10^{-3}	12.5	6.6	6.8	0.5

TABLE 18

Calculated $E_{j,s}$ for Cells Using HCl in Methanol-Water
Solvents (in mV).

Wt % MeOH	C_{HCl}	simple junction (XVI)	junction (XVII)	salt-bridge junction (XVIII)	junction (XIX)
		cal	H(glass)	cal	H(glass)
90	1×10^{-1}	27.6	7.1	11.4	-10.5
	1×10^{-2}	32.4	10.0	11.0	-12.2
	1×10^{-3}	39.2	13.0	4.5	-14.7
80	1×10^{-1}	3.1	10.8	13.3	19.9
	1×10^{-2}	6.2	12.3	11.3	21.2
	1×10^{-3}	9.3	15.5	10.9	24.4
70	1×10^{-1}	0.9	6.5	9.4	14.6
	1×10^{-2}	3.1	6.9	9.2	12.3
	1×10^{-3}	-0.1	6.0	5.6	5.6
60	1×10^{-1}	-0.4	13.2	9.6	21.4
	1×10^{-2}	1.2	20.7	10.3	28.8
	1×10^{-3}	0.3	28.4	7.0	32.6
50	1×10^{-1}	-1.5	6.7	6.9	13.6
	1×10^{-2}	-1.1	8.4	7.2	16.6
	1×10^{-3}	-9.7	10.0	13.9	16.3
40	1×10^{-1}	0.3	10.4	5.6	15.5
	1×10^{-2}	1.5	12.4	5.0	14.7
	1×10^{-3}	2.7	15.0	3.9	20.6

TABLE 18 (con't.)

Wt % MeOH	C_{HCl}	simple junction	simple junction	salt-bridge	salt-bridge
		(XVI) cal	(XVII) H(glass)	(XVIII) cal	(XIX) H(glass)
30	1×10^{-1}	-0.2	5.4	1.0	6.5
	1×10^{-2}	-0.6	5.6	3.7	8.7
	1×10^{-3}	7.1	6.9	14.7	13.0

Some remarks regarding E' and E_j' .

Several observations can be made regarding the magnitude of E' , E_j' , and $E_{j,s}$. The E' value is due primarily to the transfer free energy of the electroactive ion, so it can be as large as -104 mV for a cell using calomel electrodes in 90% MeOH, or as small as 2mV for a cell using hydrogen glass electrodes in 30% MeOH. The range of values for E_j' illustrates clearly that a priori assumptions can be quite misleading. For example, for a simple junction between NaCl solutions in water and 90% MeOH, E_j' is calculated to be approximately 23mV, which, when referred to the more detailed experimental notes, is attributed mostly to $E_{j,G}$, that is, to the effect of the transfer activity coefficients and respective transport numbers of the Na^+ and Cl^- ions crossing the boundary. Coincidentally, the $E_{j,s}$ value calculated for this case is approximately 28mV, which cannot be discounted as a product of uncertainties in the other values used to calculate it. (More detailed discussion of these uncertainties will follow later.)

The values of E_j' for simple junction between NaCl solutions change in a consistent manner as the methanol content decreases. That behavior is not necessarily obvious, because even though the transfer activity coefficients of Na^+ and Cl^- ions decrease fairly uniformly with lowered methanol content, the differences between them are very sensitive to the actual shape of the change of each $\log_m \gamma$ with solvent composition. In addition to that, the

t_{Na} value decreases with decreasing methanol content, while t_{Cl} obviously increases at the same time (recall that $t_{Cl} = 1 - t_{Na}$). The final E'_j for a simple junction between two NaCl solutions, which as we said earlier is mainly a function of $E_{j,G}$

$$E_{j,G} = 59.16 (t_{Cl} \times \log_m \gamma_{Cl} - t_{Na} \log_m \gamma_{Na}) \quad (52)$$

is a result of interplay of several trends and in this case a gratifyingly uniform behavior is observed.

That is not the case for a simple junction between HCl solutions. Here the E'_j starts at -13mV for 90% MeOH, rises to 30mV in 80% MeOH, and then slowly decreases with the decreasing methanol content. The differences between transfer activity coefficients for H^+ and Cl^- ions again have to be modified by the effect of the transport numbers of both ions (Equation 54, similar to 52) and in the final analysis it seems that the properties of the hydrogen ion dominate the E'_j values calculated for a simple junction between HCl solutions in two solvents.

Results of calculations of E'_j for a salt-bridge junction illustrate the failure of use of a saturated aqueous KCl solution as a bridge which would eliminate a liquid-junction potential between solutions in different solvents. As can be seen in Tables 15 and 16, the calculated E'_j values for a salt-bridge junction range from +8mV to -12mV. We have already shown that the relative concentration of KCl to the electrolyte in the half-cell renders the $E_{j,H}$ term for

such a junction extremely small (at most $\sim 1\text{mV}$). Obviously, the E_j^i value for a salt-bridge junction is dominated by the $E_{j,G}$ term. Any effort to find a perfect salt-bridge electrolyte has to take into account not only the mobilities, but also the transfer free energies of the ionic constituents of such an electrolyte.

Discussion of $E_{j,s}$ values obtained in this study

The $E_{j,s}$ values calculated for the various cells range from $\sim 30\text{mV}$ to -15mV . Those values are generally of the same order of magnitude as the E_j^i values encountered in this work. The relationship between the exact value of $E_{j,s}$ and the other parameters used to calculate it depends on several factors, discussed next.

We mentioned earlier that comparisons between $E_{j,s}$ values obtained from various cells can be made in such a way that only one factor is varied and its effect can be ascertained. The effect of using calomel electrodes instead of glass electrodes, the effect of using HCl instead of NaCl as the electrolyte on both sides of the junction, and the effect of the salt bridge can all be investigated. In order to illustrate and to determine the extent of changes in $E_{j,s}$ values in terms of the factors mentioned, several graphs were drawn of $E_{j,s}$ values as a function of solvent composition. Since the same trends were observed for all concentrations of NaCl and HCl, the results from using the $1 \times 10^{-1}\text{M}$

solutions were chosen for the graphs, since that would also allow for direct comparison between NaCl and HCl systems.

Figures 8-11 illustrate the $E_{j,s}$ values for the same junction obtained with calomel or glass electrodes used as the indicator electrodes. Theoretically, the liquid-junction potential, including its component $E_{j,s}$, obtained for a particular junction from e.m.f. measurements should be independent of the electrodes used to measure that e.m.f. Any differences, therefore, between these results relate in some way to the $E_{j,s}$ calculations and formulations. Analysis of these formulations may shed some light on the validity of any assumptions made in deriving them.

FIGURE 8

$E_{j,s}$ of Cells IX and X in Methanol-Water Solvents.

(Effect of Using Na(glass) Electrodes Instead of Calomel Electrodes; NaCl | NaCl Junction.)

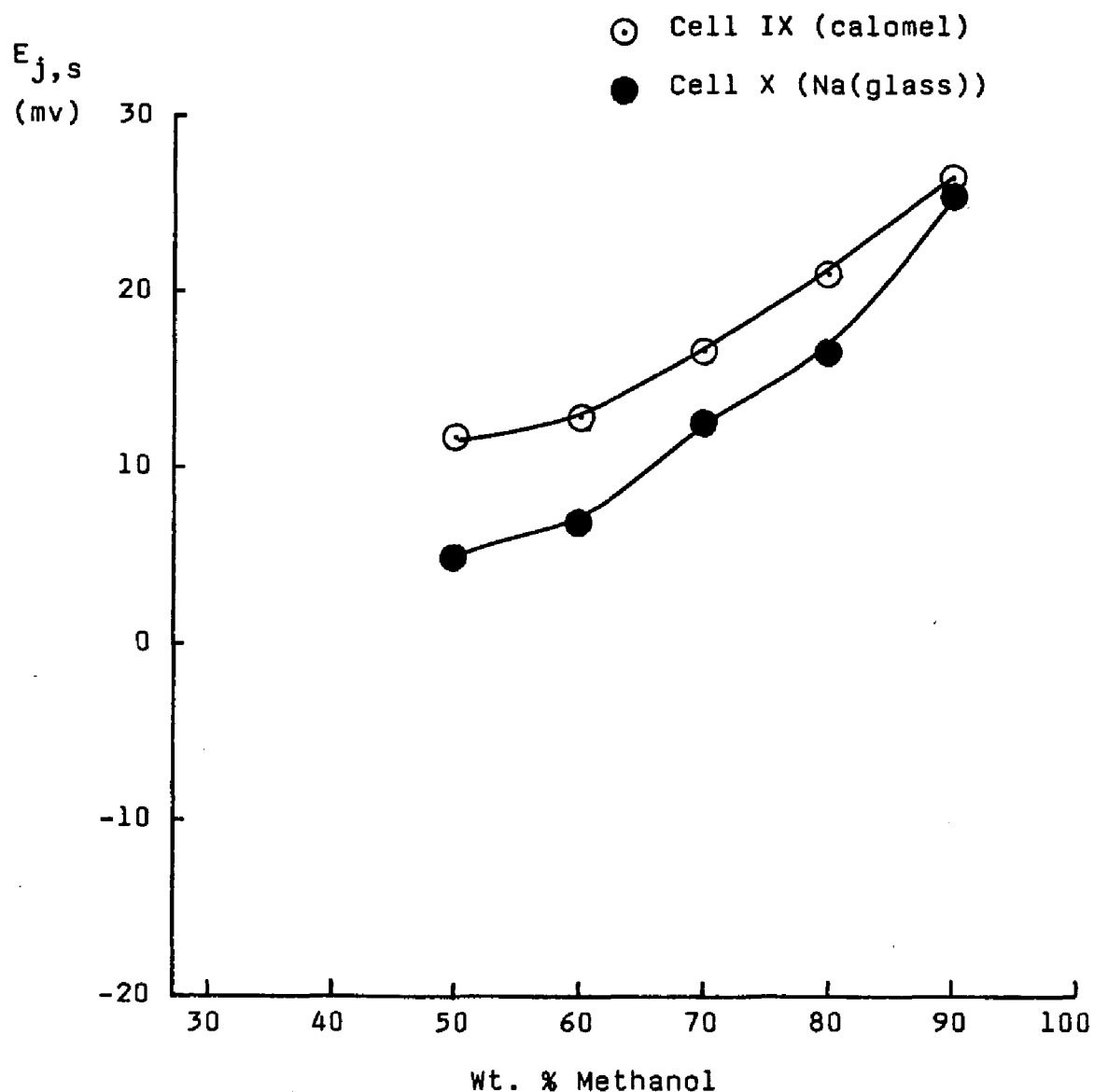


FIGURE 9

$E_{j,s}$ of Cells XI and XII in Methanol-Water Solvents.
(Effect of Using Na(glass) Electrodes Instead of Calomel
Electrodes; NaCl | KCl(sat.) | NaCl Junction.)

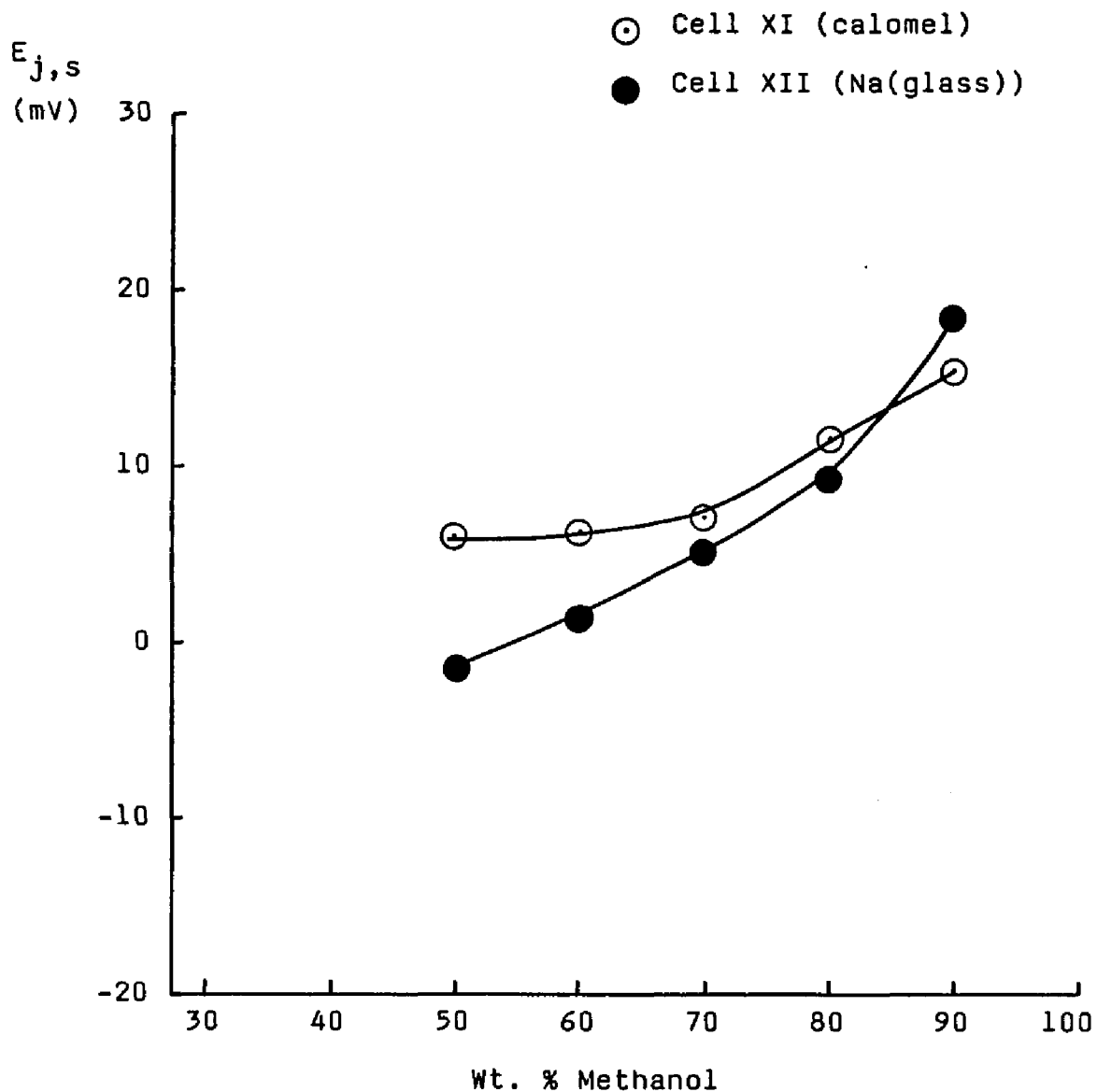


FIGURE 10

$E_{j,s}$ of Cells XVI and XVII in Methanol-Water Solvents.

(Effect of Using H(glass) Electrodes Instead of Calomel Electrodes; HCl | HCl Junction.)

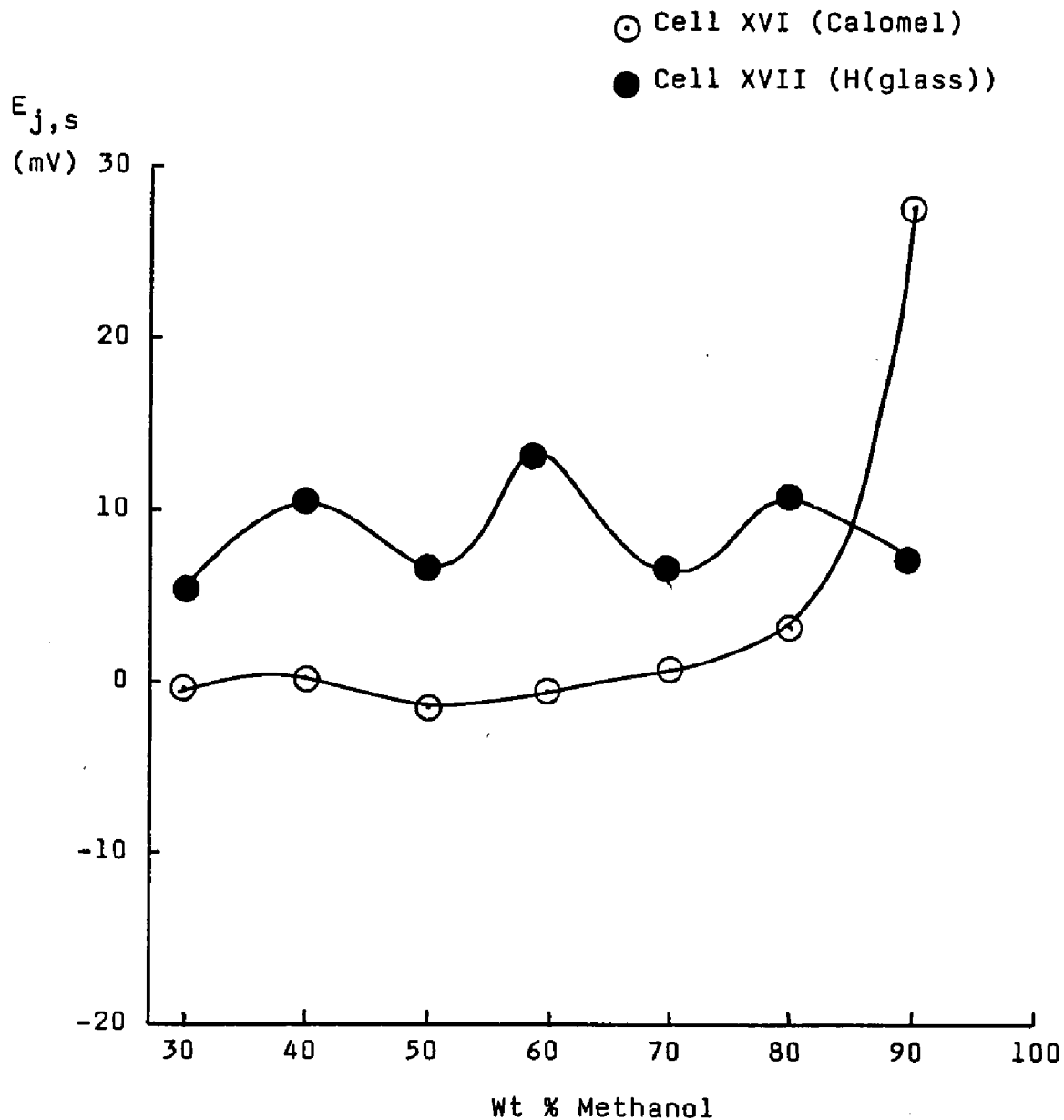
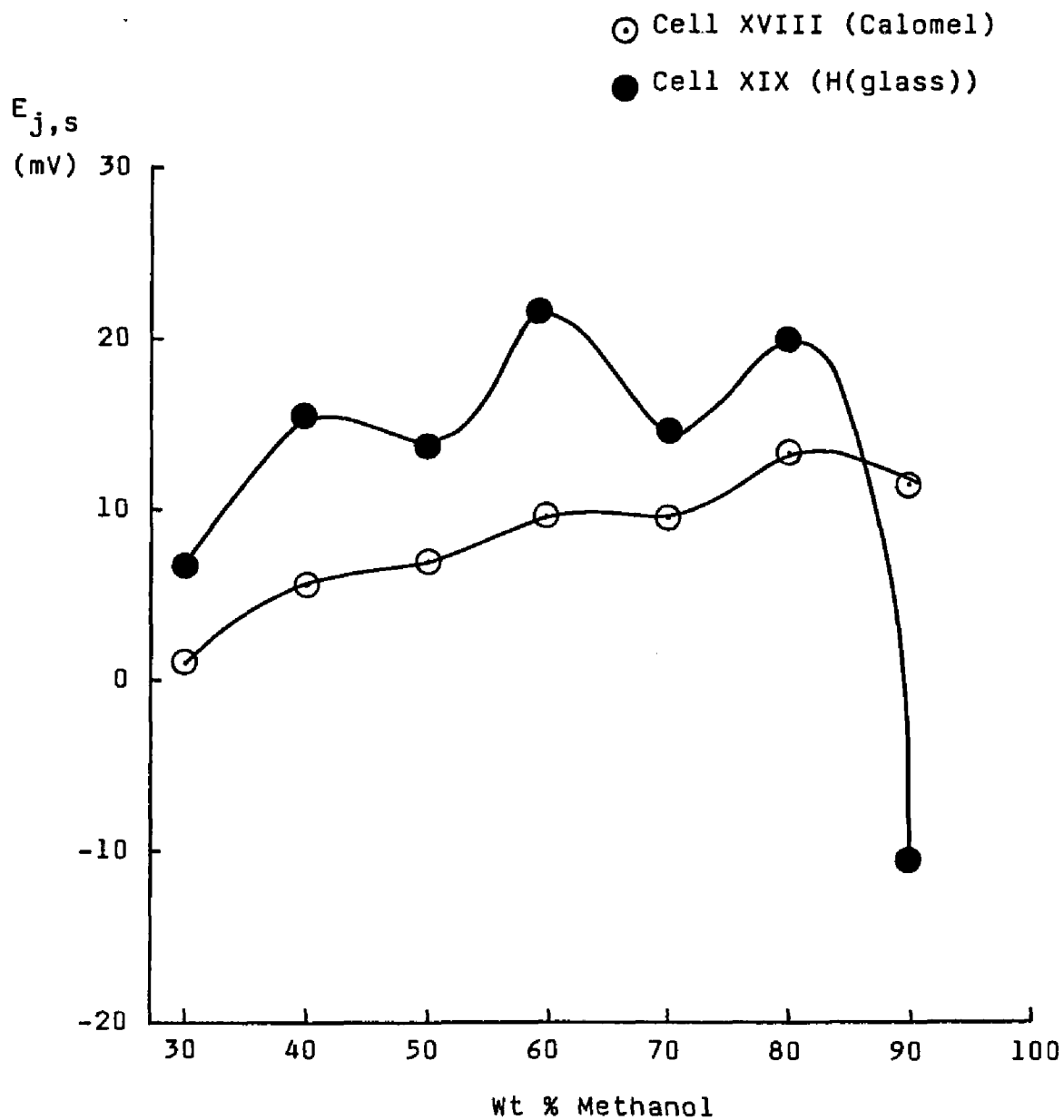


FIGURE 11

$E_{j,s}$ of Cells XVIII and XIX in Methanol-Water Solvents.

(Effect of Using H(glass) Electrodes Instead of Calomel Electrodes; HCl | HCl Junction.)



To illustrate this process, two equations have to be introduced. For simplicity's sake, we will omit the term accounting for differences in the conventional activities of the electrolyte MCl as well as the $E_{j,H}$ term. The concentrations of the electroactive species were adjusted to be equal in both half-cells, and even though calculations were performed to account for the very small differences in the actual concentrations, the results were small enough to be ignored in this discussion.

The first equation is a general expression for $E_{j,s}$ of a simple junction MCl | MCl using calomel electrodes:

$$E_{j,s} = E_{\text{exp}} + 59.16 t_M \log_m \gamma_{\text{MCl}} \quad (71)$$

The second equation is for the same $E_{j,s}$, only with glass electrodes:

$$E_{j,s} = E_{\text{exp}} - 59.16 t_{\text{Cl}} \log_m \gamma_{\text{MCl}} \quad (72)$$

Calculated $E_{j,s}$ values for NaCl solutions are represented in Figure 8. The top line corresponds to Equation 71, the bottom line, to Equation 72. The gap between them is not large (~7mV at most), and one way to narrow it would be to consider the value of t_+ and t_- used here. It has been a general practice to use transport numbers at infinite dilution, t_+^0 and t_-^0 . While the concentration dependence of transport numbers is very small, it is real. For a t^0 value which is less than 0.5, one can expect a decrease in its value as the concentration of the electrolyte increases.

When a t^0 is greater than 0.5, as is the case with t^0_+ , the opposite is true. Using transport numbers corrected for the concentration dependence will narrow the gap between the two lines in Figure 8 and Figure 10.

Figure 9 and 11 are for salt-bridge junctions. The general expressions for $E_{j,s}$ in such a junction are:

$$E_{j,s} = E_{\text{exp}} + 59.16 t_K \log_m \gamma_{\text{KCl}} \quad (73)$$

for calomel electrodes and

$$E_{j,s} = E_{\text{exp}} - 59.16 \log_m \gamma_{\text{MCl}} + 59.16 t_K \log_m \gamma_{\text{KCl}} \quad (74)$$

for glass electrodes.

It was found that the $E_{j,s}$ values obtained using calomel electrodes in both electrolytes (that is HCl and NaCl) are identical within experimental error (see Figure 13). This is, of course, expected from Equation 73. We can say that a system using calomel electrodes is a well-behaved system. The results obtained using glass electrodes are calculated by Equation 74 and illustrated by Figures 10 and 11. It can be seen by comparison with Figure 9 that the results for sodium glass electrodes are much closer to the calomel electrode results than the same results calculated for the hydrogen glass electrodes. One conclusion that might be drawn from this is that the calibration results for the H(glass) electrodes and/or the transfer activity coefficients of HCl (literature values) are not as good, as those determined for Na(glass) electrodes and NaCl, respectively.

It has been observed before that the solvent contribution to liquid-junction potential depends on the nature of the electrolyte crossing the boundary. Starting with Figure 12, we see that the presence of H^+ results in very low calculated $E_{j,s}$ values up to 80% MeOH. While the use of transport numbers corrected for concentration would narrow the gap between the results for HCl and NaCl, it would not be a large change. Additional evidence for the electrolyte contribution to $E_{j,s}$ can be seen wherever the salt-bridge effect is studied (Figures 16-19), since in each case the electrolyte on one side of the junction is replaced with satd. KCl. Unfortunately, the effect of KCl is combined with the effect of its high concentration and at present we don't have a method for separating those two factors. One thing clear is that the use of a salt bridge to eliminate a liquid junction potential between solutions in different solvents fails in the case of a junction between water and methanol-water solvents.

FIGURE 12

$E_{j,s}$ of Cells IX and XVI in Methanol-Water Solvents.

Effect of Changing Na^+ to H^+ in a Simple Junction; Calomel Electrodes Used.

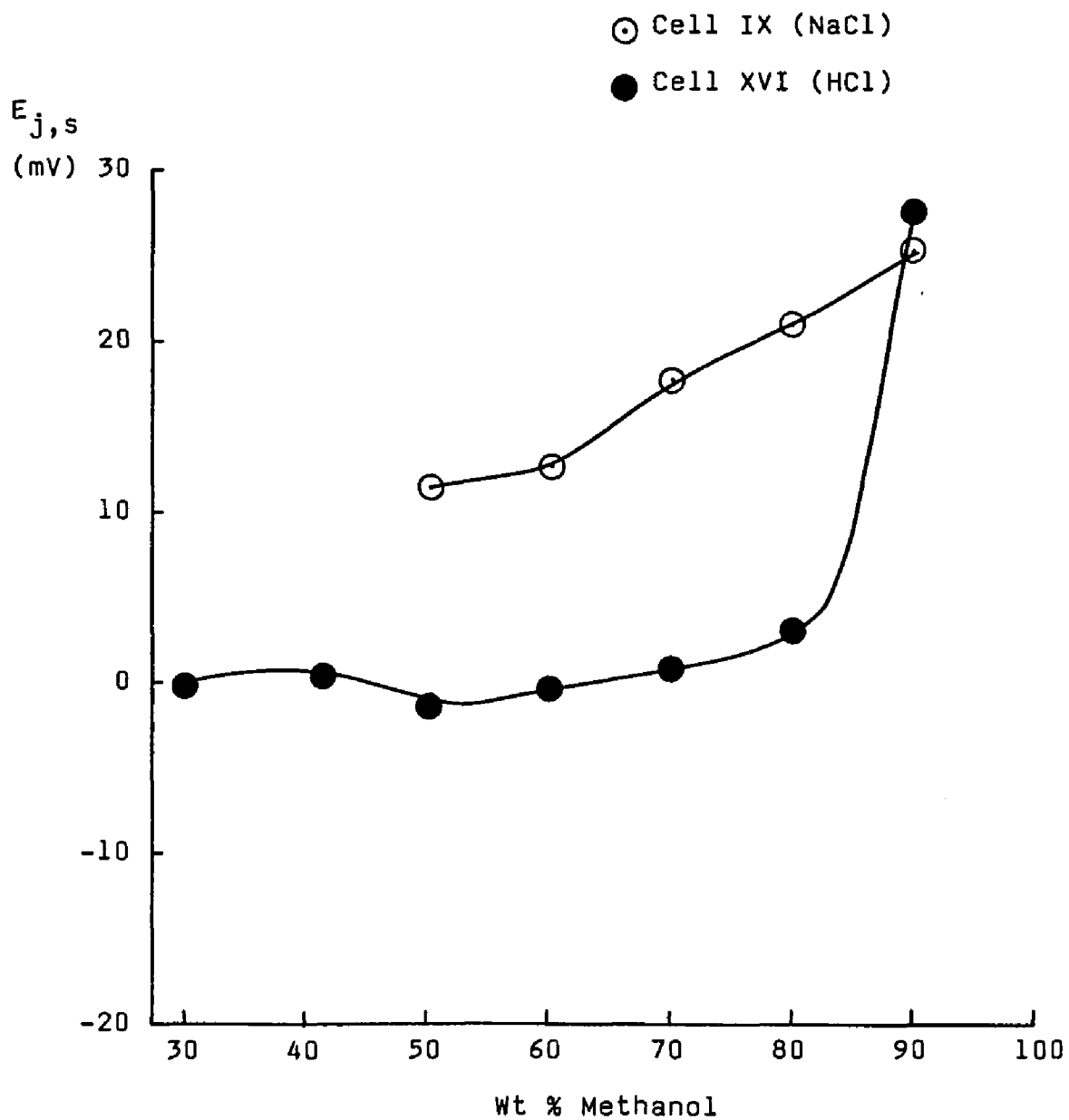


FIGURE 13

$E_{j,s}$ of Cells XI and XVIII in Methanol-Water Solvents.

Effect of Changing Na^+ to H^+ in a Salt-bridge Junction;
Calomel Electrodes Used.

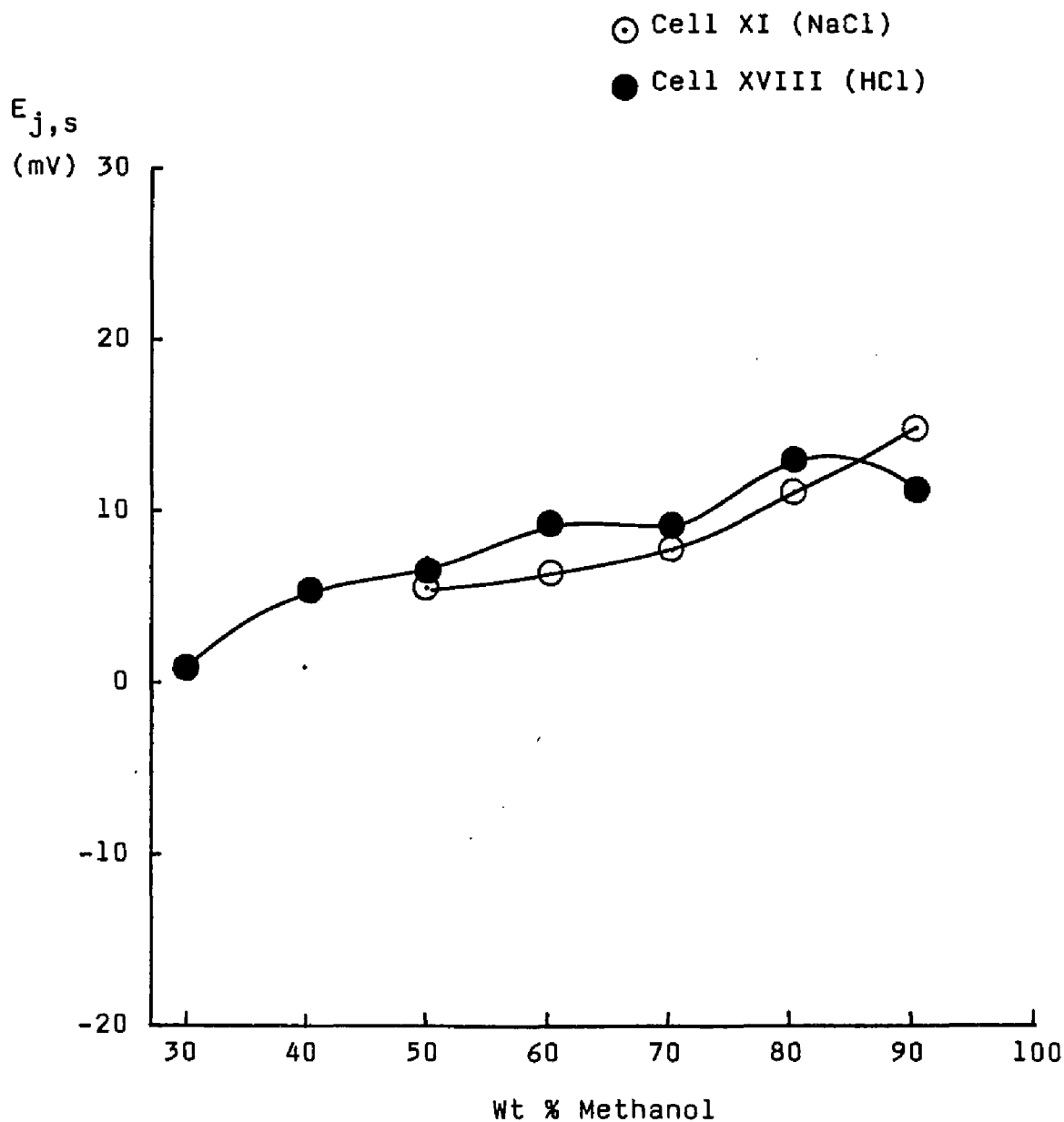


FIGURE 14

$E_{j,s}$ of Cells X and XVII in Methanol-Water Solvents.

Effect of Changing from Na^+ to H^+ in a Simple Junction;
Glass Electrodes Used.

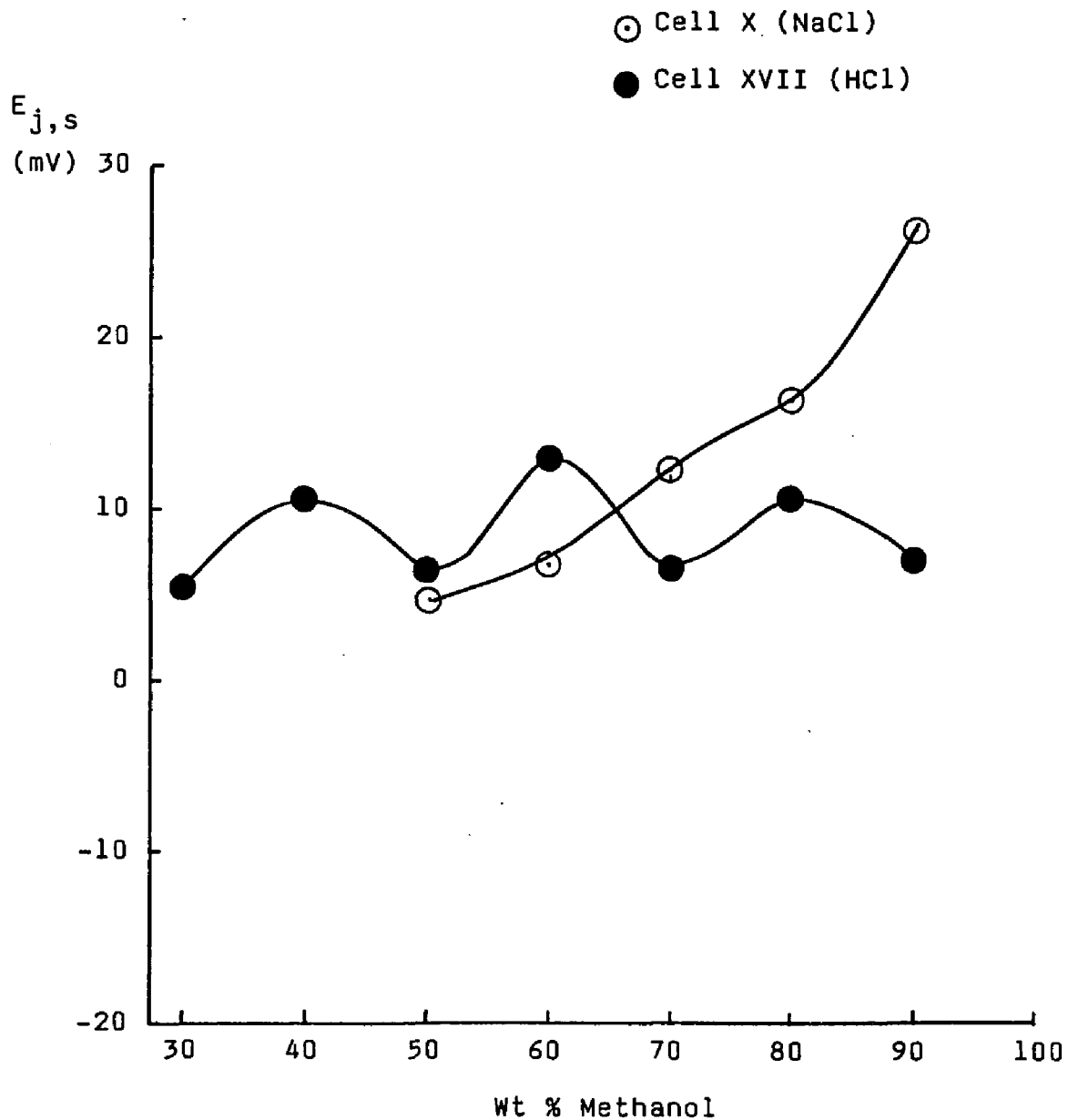


FIGURE 15

$E_{j,s}$ of Cells XII and XIX in Methanol-Water Solvents.

Effect of Changing from Na^+ to H^+ in a Salt-Bridge Junction;
Glass Electrodes Used.

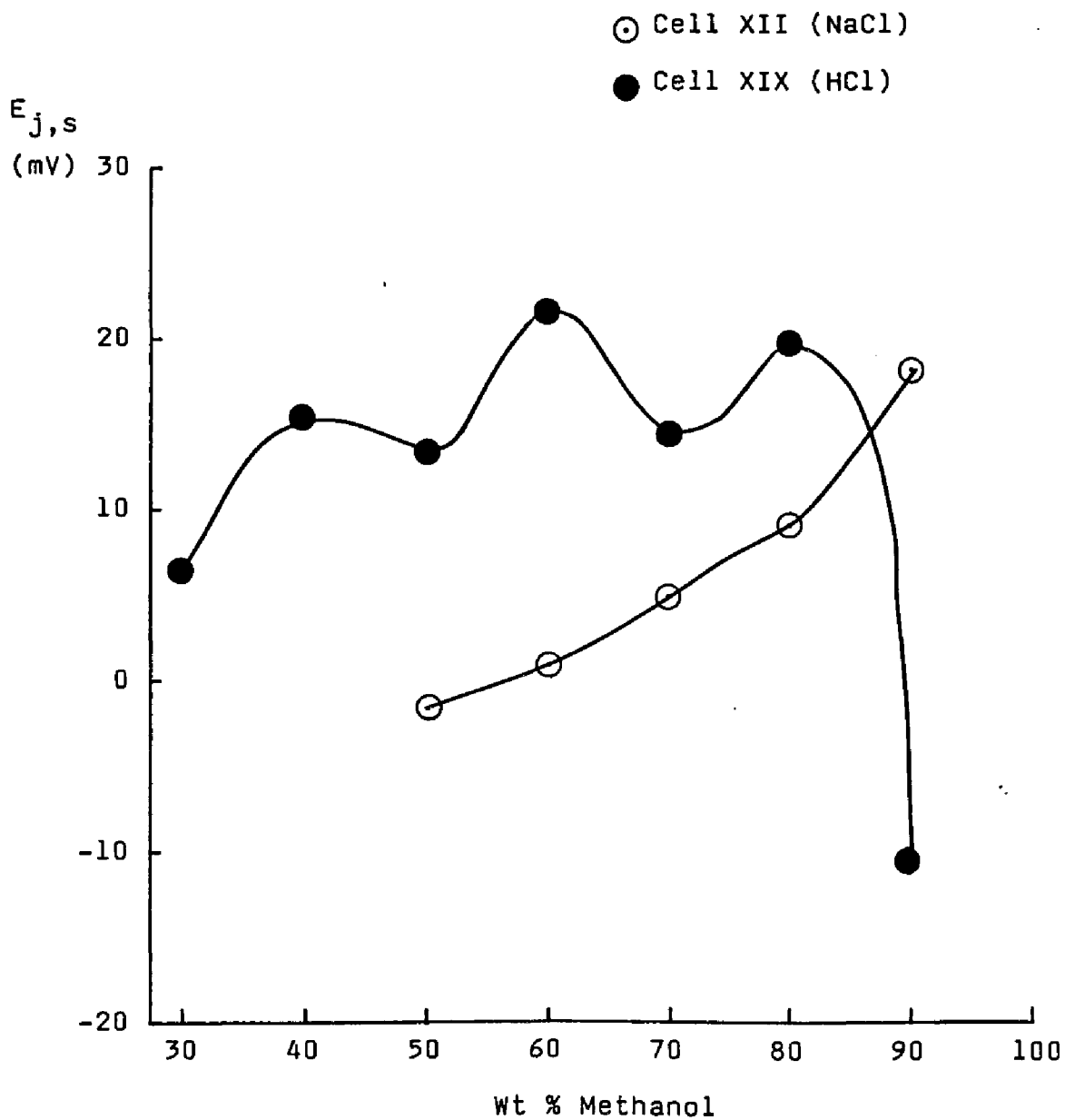


FIGURE 16

$E_{j,s}$ of Cells XI and IX in Methanol-Water Solvents.

Effect of Salt Bridge on NaCl | NaCl Junction; Calomel Electrodes Used.

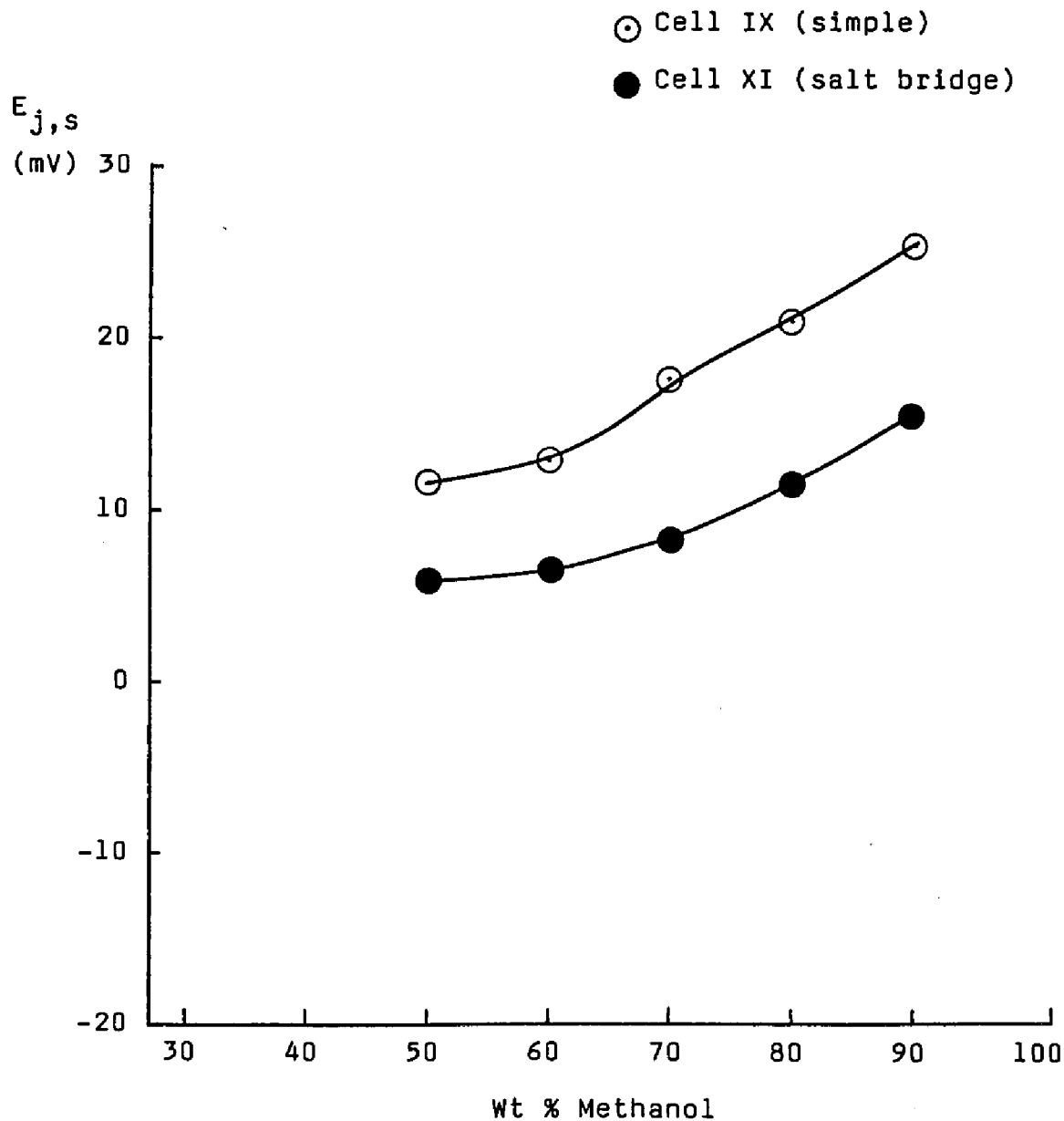


FIGURE 17

$E_{j,s}$ of Cells X and XII in Methanol-Water Solvents.

Effect of Salt Bridge on NaCl | NaCl Junction; Na(glass)
Electrodes Used.

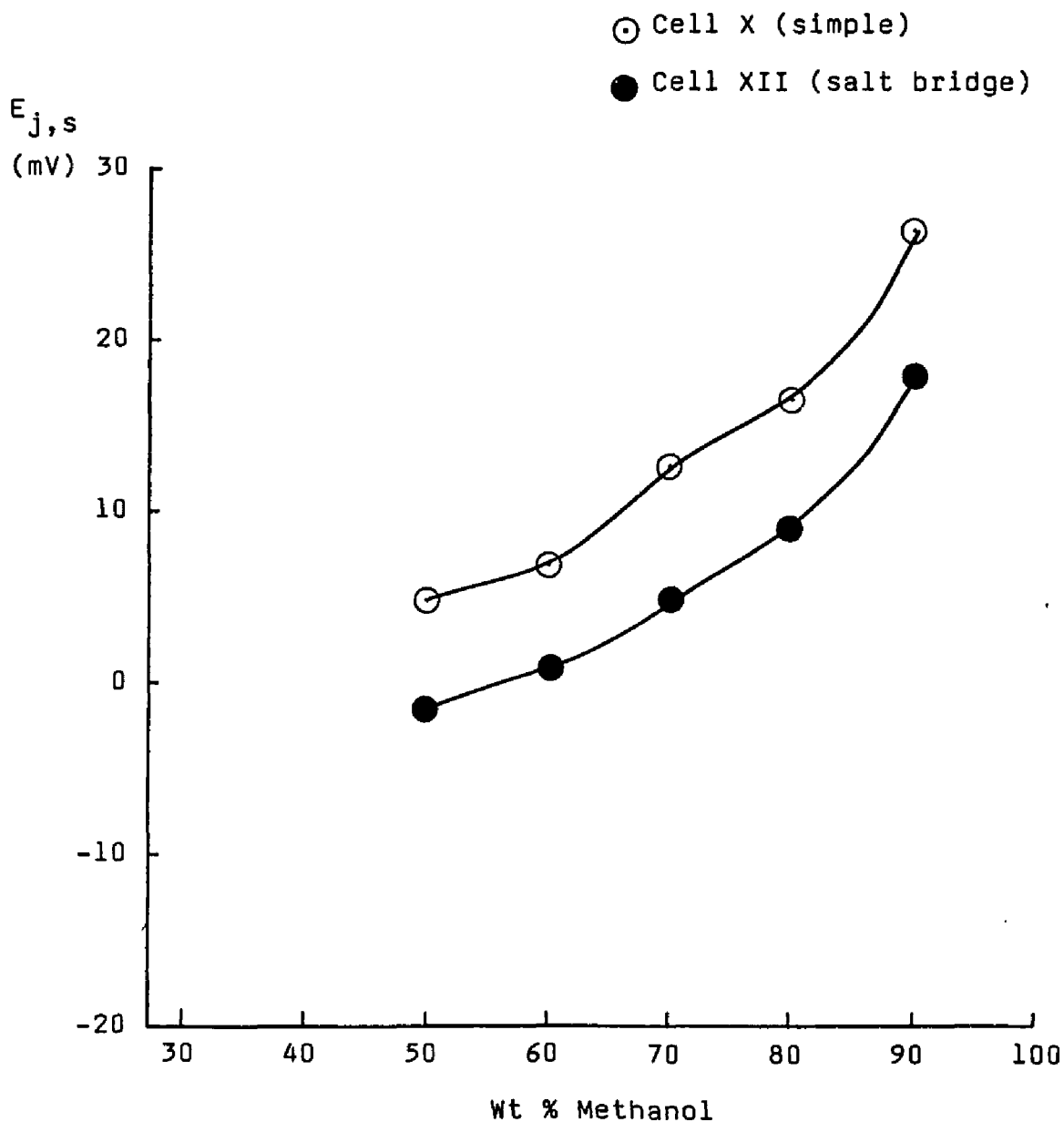


FIGURE 18

$E_{j,s}$ of Cells XVI and XVIII in Methanol-Water Solvents.

Effect of Salt Bridge on HCl | HCl Junction; Calomel Electrodes Used.

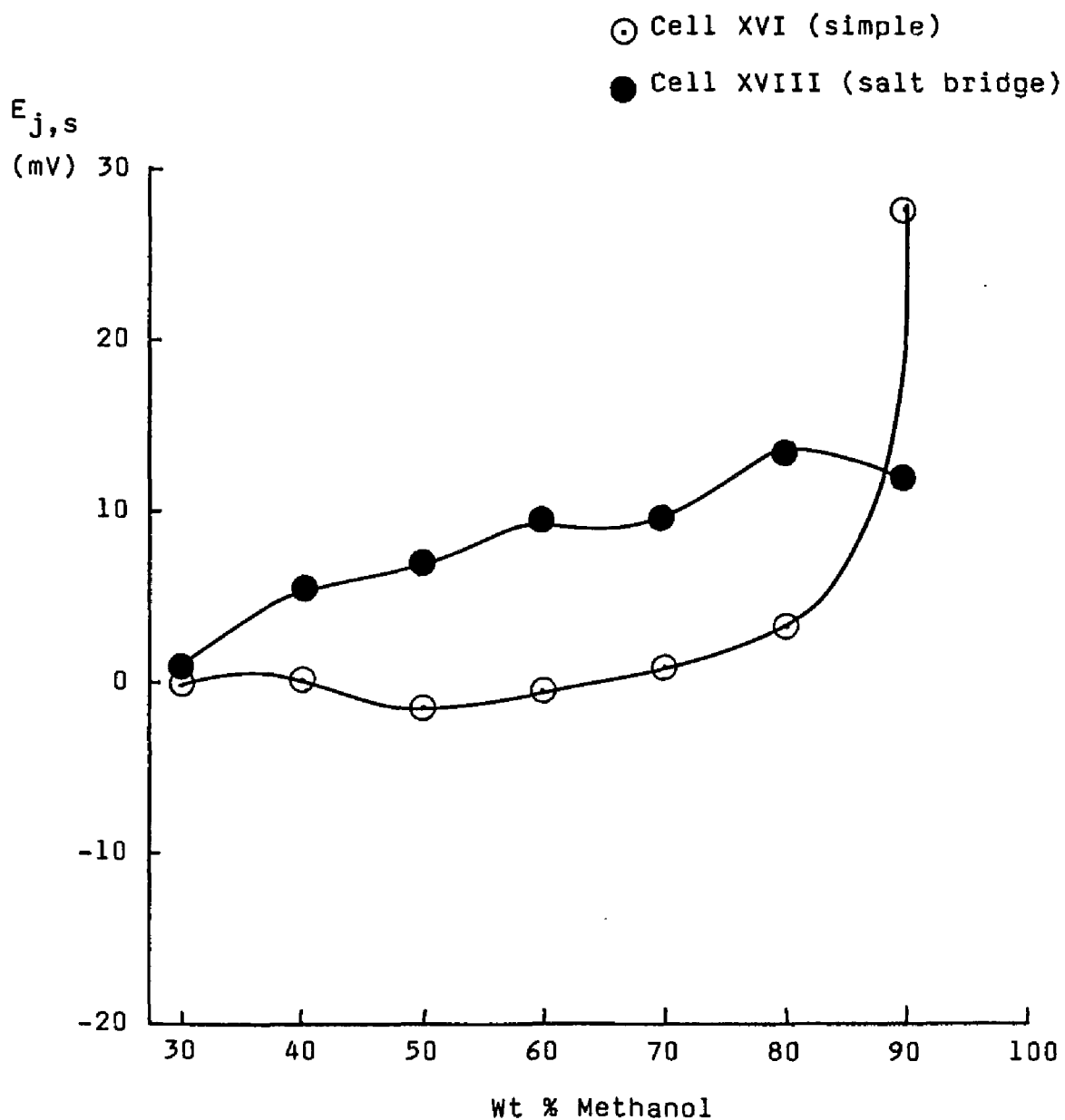
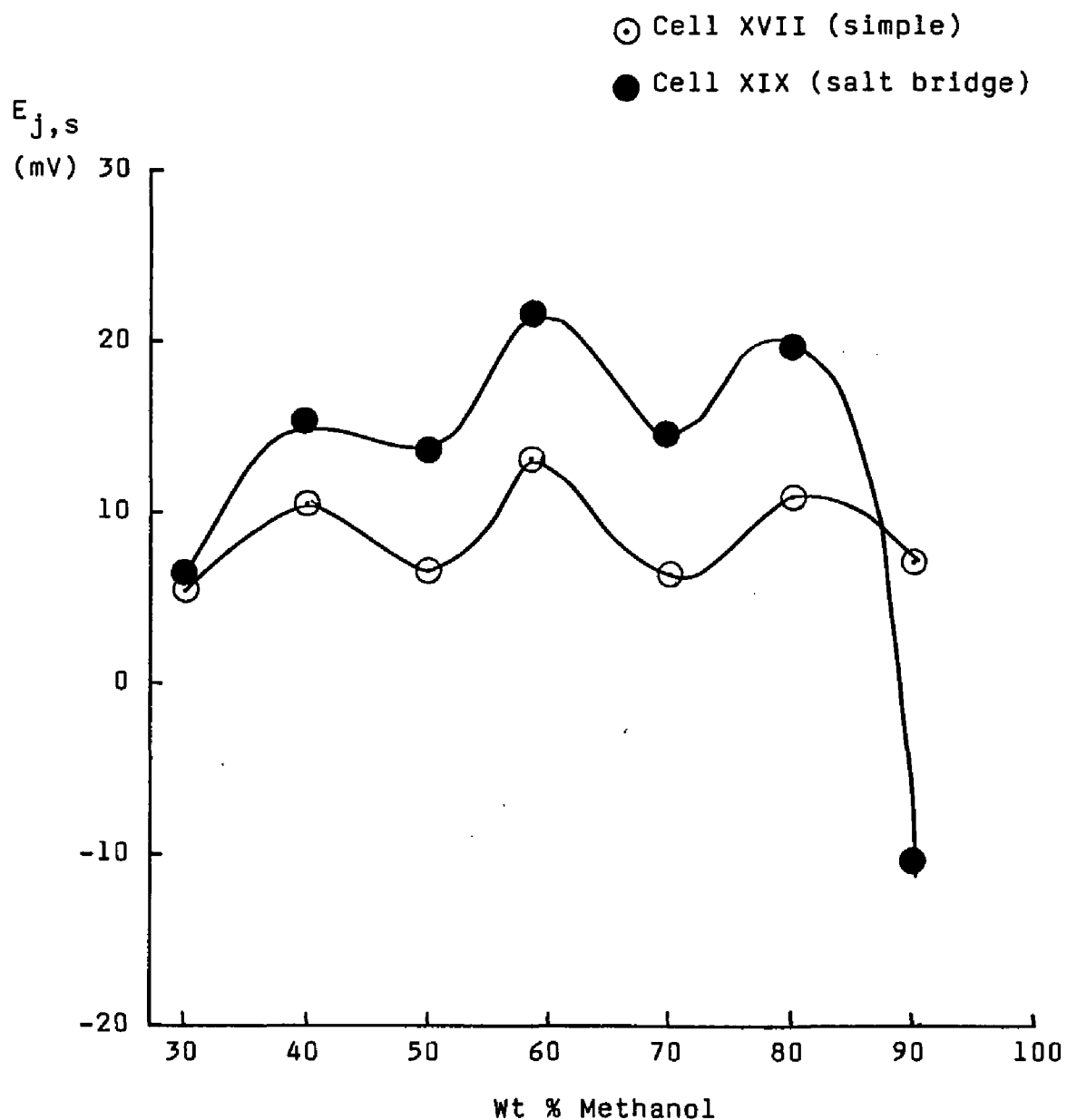


FIGURE 19

$E_{j,s}$ of Cells XVII and XIX in Methanol-Water Solvents.

Effect of Salt Bridge on HCl | HCl Junction; H(glass)
Electrodes Used.



Error analysis for $E_{j,s}$ calculations.

We may recall the general equation used to calculate $E_{j,s}$:

$$E_{j,s} = E_{\text{exp}} - E' - E_j \quad (57)$$

In order to estimate the uncertainty of a single $E_{j,s}$ determination, we must first examine the individual terms used in Equation 57. The number of significant figures reported for each value of E_{exp} depended on its stability, which was a function of the solvent, the electrolyte, and the type of junction formed. E.m.f. reported to 0.1mV implies that the measured voltage changed by less than 0.1mV in ten minutes. Of course, many cells were more stable than that, but some drifted considerably and that is reflected in e.m.f. values reported only to ± 1 mV. The uncertainty in E' is basically a function of the uncertainty in the value of $\log_m \gamma$ used to calculate E' . As it can be seen from Table 6, the transfer activity coefficients listed here are reported to two places after the decimal point, implying the uncertainty of ± 0.01 . Popovych (73) reports the results of error analysis for the estimation of transfer activity coefficients of the reference ion, BPh_4^- , in methanol-water solvents, which were listed with standard deviations ranging from 0.01 (lower % MeOH) to 0.03 for % MeOH greater than 50. Since the transfer activity coefficients of single ions were obtained by the method of successive subtractions using equations similar to Equations 38b, c, and d, the final uncertainty of the single

ion medium effect is at least equal to that of the reference ion, and will be increased by any significant contributions from the transfer activity coefficients of any other electrolytes used in the calculations. For example,

$$\log_m \gamma_{Cl} = \log_m \gamma_{KCl} - \log_m \gamma_{KBPh4} + \log_m \gamma_{BPh4} \quad (75)$$

In 90% MeOH, the standard deviation of $\log_m \gamma_{KBPh4}$ is ± 0.02 , for $\log_m \gamma_{KCl}$ it is assumed to be ± 0.05 (calculated by averaging $\log_m \gamma_{KCl}$ obtained by three independent methods), and for $\log_m \gamma_{BPh4}$ it is ± 0.03 . The uncertainty of the $\log_m \gamma_{Cl}$ is calculated using the formula for indeterminate errors, as described by Kolthoff, et al. (79) and is equal to ± 0.06 . The $\log_m \gamma_H$ was calculated from the known values of $\log_m \gamma_{HCl}$ (72) by subtracting $\log_m \gamma_{Cl}$. While the standard deviations of $\log_m \gamma_{HCl}$ have not been reported, the uncertainty in the $\log_m \gamma_H$ cannot be less than that of $\log_m \gamma_{Cl}$ used to calculate it. In conclusion, even though the transfer activity coefficients of single ions used here are reported to two places, the standard deviation of each is estimated to be on the average ± 0.06 , which corresponds to uncertainty of $\pm 3.5mV$ in the calculated value of E' . The uncertainties in $\log_m \gamma_K$ are lower, and for $\log_m \gamma_{Na}$ and $\log_m \gamma_H$ may be higher because of number of steps employed in the calculations of $\log_m \gamma$ for each single ion.

The uncertainty in the E'_j value depends mainly on the uncertainty of $E_{j,G}$, because $E_{j,G}$ is the largest contributor to E' . However, some of the transfer activity coefficients

used to calculate the value of $E_{j,G}$ are also used to calculate the value of E' and therefore the uncertainties in each are not independent of each other. In fact, one can rearrange every existing formulation for $E_{j,s}$ employed here and show that the complete equation for $E_{j,s}$ (using Cells IX-XII and XVI-XIX) is a function of the transfer activity coefficients for either one or at most two complete electrolytes. For example, using e.m.f. of Cell XVI, $E_{j,s}$ is calculated by:

$$E_{j,s} = E(\text{XVI}) + 59.16 t_H \log_m \gamma_{\text{HCl}} + 59.16(1 + 2t_H) \log \frac{s^{a+}}{w^{a+}} \quad (76)$$

while employing Cell XIX results in the following formulation for $E_{j,s}$:

$$E_{j,s} = E(\text{XIX}) - 59.16 \log_m \gamma_{\text{HCl}} + t_K 59.16 \log_m \gamma_{\text{KCl}} + (m_s \log_s a_H - m_w \log_w a_H) \quad (77)$$

Equations 76 and 77 are typical of the formulations used for either simple or salt-bridge junctions, respectively, and can be applied in the present discussion to all cells in methanol-water solvents studied here. The last term in Equation 76 and 77 is very small and can be ignored. Looking back at Equation 76, we see that the uncertainty in $E_{j,s}$ depends on the uncertainty in the e.m.f. value, which we already discussed, and on the product of the transport number of the cation of the electrolyte multiplied by the

transfer activity coefficient of that electrolyte. While the known values of t_H are reported to ± 0.0001 , such precision cannot be claimed for the interpolated values. Eventually those values will have to be confirmed experimentally and now only semiquantitative statements can be made. Assuming an uncertainty of ± 0.001 for t_H and an uncertainty of ± 0.01 in the value of $\log_m \text{HCl}$, we get a standard deviation of $\pm 0.5\text{mV}$ in the second term of Equation 76, applied to 90% MeOH. The same assumptions applied to values of t_{Na} and $\log_m \text{NaCl}$ result in a standard deviation of $\pm 0.3\text{mV}$ in 90% MeOH. Combining the standard deviations of the second and the third term of Equation 77 (where the uncertainty of $\log_m \text{KCl}$ is assumed to be ± 0.05 , and of t_K , ± 0.0001) results in an overall uncertainty of $\pm 1.5\text{mV}$.

The final conclusions regarding the uncertainty in the value of $E_{j,s}$ calculated in this study can be outlined as follows:

1. the uncertainty of a single $E_{j,s}$ determination usually does not exceed $\pm 2\text{mV}$, and can be much less.
2. when the liquid-liquid junction is formed several times, the scatter of the e.m.f. values measured is either comparable to, or exceeds the calculated uncertainty of a single determination, in which case it becomes the dominating factor in estimating the uncertainty of calculated $E_{j,s}$.

The relationship between $E_{j,s}$ and the concentration of the electrolyte.

Murray and Aikens (52) reported a value of $E_{j,s}$ equal to +18mV for a junction between saturated solutions of KCl in water and methanol. Alfenaar, et al. (50) calculated a value of 53mV for the same junction between very dilute solutions ($\sim 2.0 \times 10^{-5}$ mole fraction). Goldberg (48) obtained values of $E_{j,s}$ ranging from 2mV to 18mV for junctions between saturated solutions of NaCl in water and series of methanol-water solvents. Those values were considerably lower (by 15-25mV) than the values of $E_{j,s}$ obtained by him for a given junction using dilute ($3 \times 10^{-2}M$ and $3 \times 10^{-3}M$) solutions of NaCl. In this investigation, the concentrations of NaCl and HCl solutions ranged from 1×10^{-3} to 1×10^{-1} molar. At this time there is enough evidence to say that, at least for junctions made with strongly solvated ions, the value of $E_{j,s}$ is inversely related to the concentration of the electrolyte forming the interface between the two solvents. Unfortunately, none of the data available is good enough for quantitative analysis of this phenomenon. Goldberg (48) varied the concentration of NaCl from saturated NaCl to $3 \times 10^{-2}M$ and then to $3 \times 10^{-3}M$ NaCl. While this investigation reports $E_{j,s}$ values obtained for one more concentration (that is for $1 \times 10^{-1}M$ NaCl), the improved formulations and data used to calculate $E_{j,s}$ values resulted in smaller variations of those values for different NaCl concentrations. While the trend of increased $E_{j,s}$ with

decreasing $c_{\text{electrolyte}}$ is definitely observable, in some cases it seems to vanish (in 50% MeOH), and once it reverses, in 70% MeOH, Cell XI. Curiously, the same reversal occurs with Goldberg data. Be that as it may, one line of thought may be fruitful. Staverman's equation (Equation 8) implies that the transport of uncharged species (in this case, the two solvents) contributes to the liquid-junction potential E_j . That contribution can be formally expressed as a function of the free energy changes for both solvents

$$E_{j,s} = - \sum_i \int_L^R t_i^r dG_i \quad (78)$$

where the summation refers to all solvents i crossing the boundary. In theory, the integration of Equation 78 can be accomplished by splitting the free energy function for each solvent according to Equation 11

$$G_i = G_i^0 + RT \ln a_i \quad (11)$$

While the integration of dG_i^0 would result in a value dependent only on the identity of the two solvents forming a junction, the results of integration over the $RT \ln a_i$ would have to depend on the conventional activities of the species i . In dilute solutions, the activity of the solvent is usually assigned the value of one (or not considered at all). However, according to the Gibbs-Duhem equation, which

states that

$$\sum_{i=1}^r x_i dG_i = 0 \quad (79)$$

where x is the mole fraction of component $\underline{i}$, for a two-component system, as the activity of one component increases (as is the case when the NaCl concentration approaches saturation), the activity of the other component must decrease. This would correlate with the decreasing value of $E_{j,s}$ as the electrolyte activity increases and the solvent activity decreases. An investigation into an area of thermodynamics of solutions with emphasis on the effect of the electrolyte on the solvent may be very fruitful.

A Comparison of $E_{j,s}$ Values Obtained in This Study with the Literature Values.

Bates, et al. and de Ligny, et al.

Bates, et al. (80) studied the e.m.f. of cells in which a liquid junction was formed between a saturated KCl solution in H_2O and dilute solutions of hydrogen ions (in buffers) in methanol-water solvents. From the experimental data, a value of δ was calculated for each methanol-water solvent, where δ was defined by

$$\delta \equiv E_j - \log_m \gamma_H \quad (80)$$

where E_j was in pH units. The liquid-junction potential E_j for this interface can be calculated using Equation 56, if we assume that the contributions to E_j from the buffer constituents can be ignored, relative to that of the saturated KCl. Since the transfer activity coefficients for hydrogen ion are also known or can be calculated (73), we have access to $E_{j,s}$ values via the formulation

$$E_{j,s} = \delta + \log_m \gamma_H - E_j' \quad (81)$$

The values of δ reported by Bates (80) were combined with the δ values calculated from the data of de Ligny, et al. (81), for the whole range of methanol-water solvents, and the corresponding $E_{j,s}$ values were calculated. The results are shown in Table 19 and Figure 20. While the individual terms are on molal scale, the $E_{j,s}$ values are independent of

the scale and can be compared directly with others. In Figure 20, the $E_{j,s}$ values from three investigators (Bates, de Ligny and this author) are compared. Even though there is a general trend among the $E_{j,s}$ values of first increasing, and then rapidly decreasing with the increasing methanol content, the individual values are rather scattered. The results obtained by Bates, et al. do not correlate very well with the results based on de Ligny, et al. data, even though the values themselves follow a smooth curve, when combined on the same graph (80). This last fact indicates that perhaps the formulation for E_j' (including the value of $\log_m \gamma_H$) is at fault. The assumption that only KCl contributes to the liquid-junction potential may be of questionable value in case of Bates's and de Ligny's data: an analysis of our own results shows that, in general, a junction involving the very mobile hydrogen ions is rather difficult to interpret.

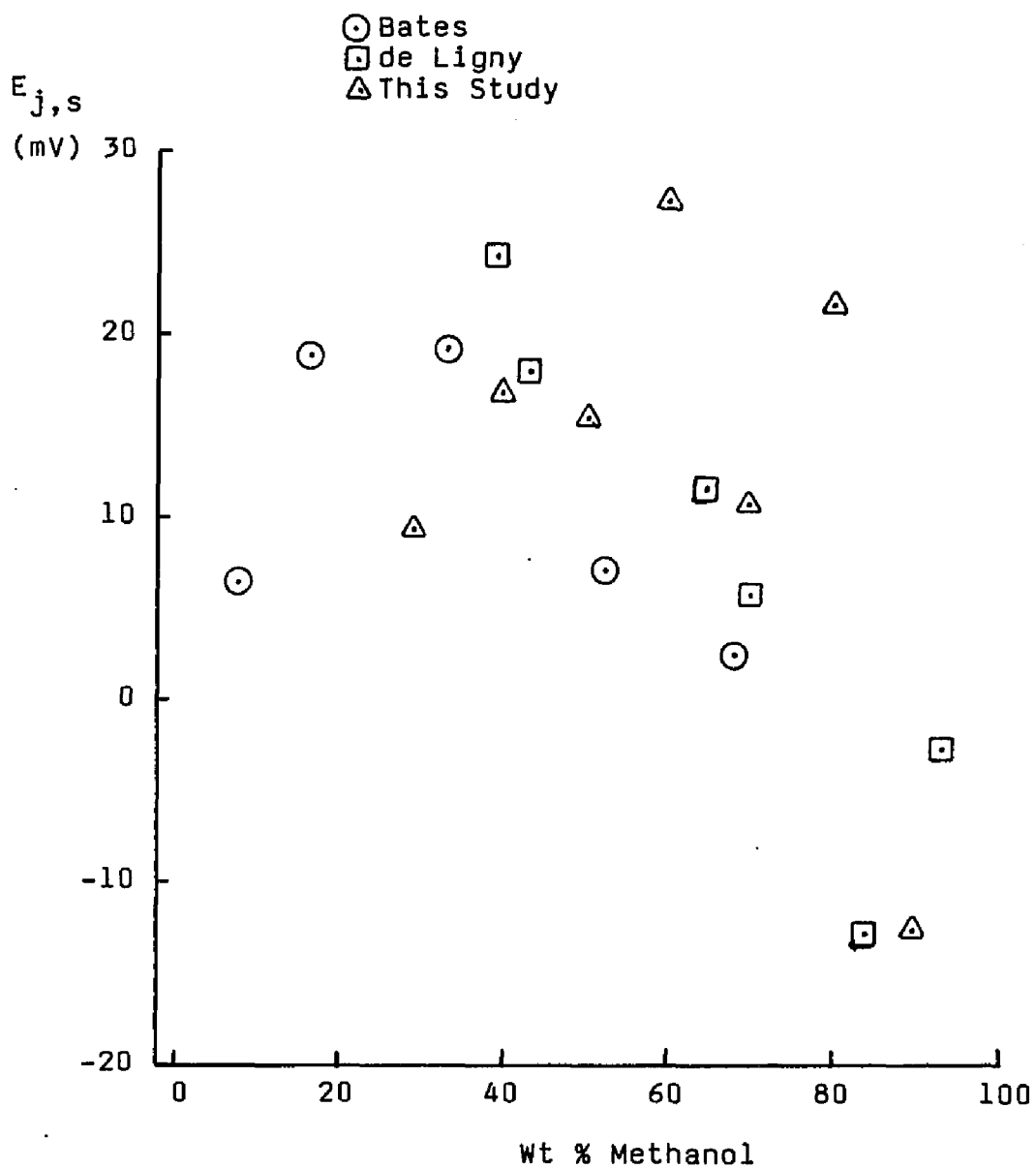
TABLE 19

$E_{j,s}$ Values Calculated from Data of Bates (80) and de Ligny (81) in Methanol-Water Solvents.

Wt % MeOH	δ (mV)	E_j	E'_j	$E_{j,s}$
<u>Bates</u>				
8.1	0.1	3.2	-3.3	6.5
16.3	0.2	9.7	-9.4	19.1
33.3	3.0	7.0	-12.4	19.4
52.1	7.7	-0.2	-7.5	7.2
68.1	7.2	-3.2	-5.9	2.7
<u>de Ligny</u>				
39.1	9.1	12.0	-12.4	24.4
43.3	8.3	7.1	-11.0	18.1
64.2	13.2	4.0	-7.7	11.7
70.0	11.4	1.1	-4.9	6.0
84.2	8.7	10.3	2.2	-12.5
94.2	46.0	10.4	12.9	-2.6
100	133.8	-34.6	22.3	-56.9

FIGURE 20

$E_{j,s}$ Values Obtained by Bates (80), de Ligny (81) and in This Study (Cell XIX) in Methanol-Water Solvents.



Goldberg.

$E_{j,s}$ values for interfaces between NaCl solutions in water and methanol-water solvents, with and without an aqueous KCl salt bridge were determined first by Goldberg (48) and these are listed in Table 20. A direct comparison with the results of this author's investigation of the same system, which are listed in Table 17 shows that, while the general trends are obviously the same, values listed in Table 17 are systematically lower than those calculated by Goldberg. This difference is attributed by this author to the fact that we paid greater attention to the details of the calculations, thus supporting the statement, that at least part of the previously reported $E_{j,s}$ values can be attributed to improper or inadequate formulations. Goldberg simplified his calculations by assuming that $t_{Na} = t_{Cl} = 0.5$ in all solvents, where in fact t_{Na}^o changes from 0.396 in H_2O to 0.463 in MeOH. He also assumed the same equality for transport numbers of K^+ and Cl^- in KCl, while we found that $t_K = 0.4854$ for a saturated solution of KCl in H_2O . Table 10 illustrates the effect of using the two values of t_K on the calculated value of E_j^1 . The sodium glass electrodes used by Goldberg were assumed to have a perfect Nernstian response in all methanol-water solvents, which also introduced an error. The last, albeit rather small improvement, has to do with using better values for transfer activity coefficients of KCl, which became available through the work done in this laboratory, both experimental and in terms of

recalculations, the results of which were published in 1984 by Popovych (73).

TABLE 20

$E_{j,s}$ Values Determined by Goldberg (40) Using Cells IX-XII
in Methanol-Water Solvents.

Wt % MeOH	C_{NaCl}	IX	X	XI	XII
90	sat	14	18	8	16
	3×10^{-2}	40	37	23	16
	3×10^{-3}	45	45	28	24
80	sat	7	12	10	13
	3×10^{-2}	32	30	14	14
	3×10^{-3}	39	36	15	20
70	sat	7	11	2	7
	3×10^{-2}	26	26	10	11
	3×10^{-3}	32	32	5	17
50	sat	2	7	7	8
	3×10^{-2}	21	23	7	11
	3×10^{-3}	20	26	5	13

A New Formulation for the Liquid-Junction Potential at the Interface of Two Solvents.

The ion constituents of the two solutions participating in the formation of a liquid-liquid junction diffuse across the boundary because of the presence of a chemical potential gradient. That chemical potential gradient has two components: one resulting from the concentration differences on both sides of the junction, and the second resulting from the changes in the standard free energy of solvation of each ion with the changing solvent medium across the junction. The concentration-gradient contribution to the E_j , $E_{j,H}$, is usually calculated by the Henderson equation (9). In this investigation, two sets of concentrations were used, both chosen to render the value of $E_{j,H}$ as small as possible. In the case of a simple junction, the same electrolyte was present in both end solutions at equal concentrations; in the case of a salt-bridge junction, the highly concentrated salt-bridge electrolyte KCl dominated the diffusion process and the almost equal mobilities of K^+ and Cl^- ions resulted in a negligible value for the $E_{j,H}$.

None of these strategies can minimize the second component of the chemical-potential gradient contribution to E_j . That component, $E_{j,G}$, for a single ion i has been calculated previously from the Staverman equation

$$E_{j,G}^{(i)} = - \frac{1}{F} \int_1^2 \frac{t_i}{z_i} dG_i^{\circ} \quad (82)$$

which can be solved if t_i is assumed to remain constant across the junction and therefore can be placed outside the integral. In that simplified case,

$$E_{j,G(i)} = - \frac{1}{F} \frac{t_i}{z_i} \int_1^2 dG_i^o \quad (83)$$

Equation 83 involves a function G_i^o which relates the solvation energy of the ion i to the composition of the solvent in the diffusion layer, as it changes from S_1 to S_2 . It may be tempting to investigate that relationship in hope of improving the solution to the integral present in Equation 83. That integral, however, is of the derivative of G_i^o , dG_i^o . Evaluating the integral of dG_i^o means simply reversing the process of taking a derivative (in effect, the two operations, derivation and integration, cancel each other out). In the end, we are left with the function G_i^o to be evaluated at the limits of integration, according to the rules for calculating a definite integral

$$E_{j,G(i)} = - \frac{t_i}{F z_i} G_i^o \bigg|_{S_1}^{S_2} \quad (84)$$

which becomes

$$E_{j,G(i)} = - \frac{t_i}{F z_i} ({}_2G_i^o - {}_1G_i^o) \quad (85)$$

The term in parenthesis is the transfer free energy of ion

i , ${}^1\Delta^2G_t^0(1)$ and is a function only of the end solutions (limits of integration) and not of the intermediate mixtures.

Equation 82 has always been solved by placing t_i outside the integral. The assumption that t_i is independent of the changing solvent composition in the diffusion layer has been disproved experimentally. The value of t_{Na}^0 changes by ~16% from water to methanol, while the value of t_H^0 not only changes by ~11%, but also goes through a very pronounced minimum (~30% below the value of the t_H^0 in water) near 97% MeOH. Figures 5 and 6 illustrate the relationship between the values of t_i^0 for Na^+ and H^+ ions and the methanol-water solvent composition. We would like to mention here that the use of limiting transport numbers t_i^0 instead of t_i should not contribute a large uncertainty in the final calculations, since the variation of t_i with concentration is very small (1-2% for the range of concentrations used in this study).

The t_i dependence on solvent composition has not gone unnoticed. The only method employed so far to account for that variation has been to use the average t_i value for a given pair of solvents (48, 49).

I propose a new formulation for $E_{j,G}$, which accounts for the dependence of t_i on solvent composition in an analytical way. In this new formulation, it is assumed that the composition of the solvent in the diffusion layer changes from S_1 to S_2 in a single-valued manner. This assumption is

similar in kind to the one made by Henderson (9) regarding the variation in the concentration of an ion constituent i diffusing from one side of the boundary to the other. Also, the relationship between the transport number t_i and the solvent composition is described in this formulation by using some function $t_i(S)$. (For visual simplification the subscript "o" referring to limiting transport numbers is omitted in the present discussion.) With these considerations in mind we can write for a single ion:

$$E_{j,G(i)} = - \frac{1}{F} \int_1^2 \frac{t_i(S)}{z_i} \frac{dG_i^o(S)}{dS} dS \quad (86)$$

where dS denotes an infinitesimal change in the composition of the solvent S and the limits of integration, 1 and 2, refer to solvents S_1 and S_2 , respectively. Utilizing a general formula for the integral

$$u dv = d(uv) - v du \quad (87)$$

Equation 86 can be rewritten as

$$\begin{aligned} E_{j,G} = & - \frac{1}{F z_i} \int_1^2 \frac{d[t_i(S) \times G_i^o(S)]}{dS} dS \\ & + \frac{1}{F z_i} \int_1^2 G_i^o(S) \frac{dt_i(S)}{dS} dS \end{aligned} \quad (88)$$

The first term of this equation has an exact solution:

$$\begin{aligned}
& - \frac{1}{F z_i} \int_1^2 \frac{d[t_i(S) \times G_i^0(S)]}{dS} dS = \\
& = - \frac{1}{F z_i} \times t_i(S) \times G_i^0(S) \Big|_1^2 \quad (89)
\end{aligned}$$

which can be calculated if the solvation energies and the transport numbers of the ion i are known in both end solvents.

The second term of Equation 88 requires knowledge of the two functions, $G_i^0(S)$ and $t_i(S)$, which generally are not available. It is possible, however, to gather enough experimental data for a graphical integration of the second term of Equation 88. Specifically, we have detailed knowledge of the transfer free energies of H^+ , Na^+ , and Cl^- ions between water and methanol-water solvent. Furthermore, Rosseinsky (82) reported the hydration energies of several ions using the gas-phase hydrogen ion in its standard state as the reference. Alfenaar, et al. (83) estimated the hydration energy of H^+ ion to be -253 kcal/g ion. That value was combined with Rosseinsky's data for other ions and converted to molar scale. The results are given in Table 21. The last column represents the molar hydration energy of each ion converted to the logarithmic scale.

TABLE 21

Energies of Hydration for H^+ , Na^+ , K^+ , and Cl^- Ions
(Molar Scale, $25^\circ C$).

Ion	ΔG_h° (molal)	ΔG_h° (molar)	ΔG_h°
	kcal/mole	kcal/mole	1.364
H^+	-253	-252.2	-185.0
Na^+	-90.7	-90.4	-66.3
K^+	-73.1	-72.9	-53.4
Cl^-	-83.3	-83.1	-60.9

Once the hydration energy of the ion i is known, the energy of solvation of that ion in any other solvent S can be calculated via the relationship

$$G_i^0(S) = G_i^0(H_2O) + {}^w\Delta^S G_t^0(i) \quad (90)$$

Since we have access to transfer free energies of the relevant single ions determined at 10% intervals for methanol-water solvents (73), large-scale graphs can be used to interpolate these values to any solvent composition.

Limiting transport numbers have been reported only for three solvents relevant to this discussion: water, methanol, and 64% MeOH-H₂O. I have already discussed the interpolation procedure used to obtain the transport numbers of Na⁺ in NaCl and of H⁺ in HCl. While the interpolated t_{Na}^0 values can be compared with the t_{Na} values for 0.05m solutions obtained by Longsworth (76), such a procedure is not available for the confirmation of the minimum in the $t_H^0(S)$ function, since there are no data for t_H at any concentration of HCl in the 90-99% range of methanol-water solvents. There is a need for experimental confirmation of the transport numbers used here, possibly through a detailed study of the limiting equivalent conductances of Na⁺ and Cl⁻ ions across the whole range of methanol-water solvents. In view of this limitation, the $E_{j,G}$ values calculated partly by graphical integration of Equation 88 have to be considered as tentative estimations only, subject to verification once all of the t_i values are confirmed experimentally.

The $E_{j,G}$ values calculated using Equation 88 for the NaCl | NaCl junction as well as for the HCl | HCl junction are presented in Table 22. The $E_{j,G}$ values calculated on the basis of the new formulation are compared to those obtained by using average transport numbers, that is, with $\bar{t}_i = 1/2(t_{i1} + t_{i2})$. The results shows that for a smooth, well-behaved $t_i(S)$ function, the $E_{j,G}$ values calculated by both methods are very similar, as illustrated by the results for the NaCl | NaCl junction. However, this is not the case for the HCl | HCl junction. For the solvent region in which t_H changes slowly, and fairly uniformly, that is between water and ~80% MeOH (see Figure 7), the average $\bar{t}_H$ can be used safely. Above 80% MeOH, however, the differences between the two methods become more pronounced.

In conclusion, the new formulation for the $E_{j,G}$ calculation of liquid-junction potential at the interface of two solvents can be applied to any system for which there are sufficient data relating solvation energies and transport numbers of the ions in the diffusion layer to the varying composition of the solvent in that layer. The integration approach is of particular importance for any system in which the $t_i^0(S)$ function goes through a minimum or a maximum.

TABLE 22

$E_{j,G}$ Values for NaCl|NaCl and HCl|HCl Junctions Calculated Using $\bar{t}_i$ (Column A) and by Graphic Integration (Column B).

Wt % MeOH	NaCl NaCl		HCl HCl	
	A	B	A	B
100	39.7	38.1	-51.2	52.7
95			-8.6	-13.7
90	24.8	24.7	9.5	4.5
80	13.5	13.2	26.5	28.4
70	5.6	5.1	21.5	22.3
60	1.6	0.9	16.3	17.3
50	-1.2	-0.6	11.4	12.5
40	-7.3	-6.6	1.4	2.9
30	-8.2	-8.3	-2.4	-1.3
20	-12.2	-12.6	-8.9	-6.1
10	-4.8	-3.4	-3.6	-2.0

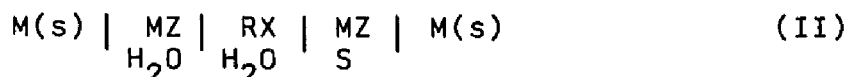
Studies in Dipolar Aprotic Solvents.

A New Method for the Estimation of Transfer Activity Coefficients of Single Ions.

E.m.f. cells and the general equation used to obtain transfer activity coefficients of single ions.

Introductory Remarks

The only experimental method which, in principle, can provide direct estimates of the transfer activity coefficients of single ions is potentiometry using e.m.f. cells with liquid junction. Historically, Cell II was used, composed of the same metal electrode M in equilibrium with its ions M^+ in water and the nonaqueous solvent S , with a solution of a salt-bridge electrolyte RX inserted between the two end solutions:



We have shown before, that if the activity of M^+ ions is adjusted to be equal in the two solvents, the potential of Cell II maybe expressed by:

$$E^0(II) = 59.16 \log_m \gamma_H + E_j \quad (40)$$

where the potentials are in millivolts. In principle, the potential of Cell II provides a direct measure of $\log_m \gamma_M$, if a condition of negligible or calculable E_j is met. This method can be applied to estimate the transfer activity

coefficient of any ion for which stable electrodes reversible to it exist in both solvents of interest.

The e.m.f. of Cell II with liquid junction between two different solvents can be used to estimate the ΔG_t° of ions other than the ion to which the electrode responds. Preferably, the ion of interest should be a constituent of the salt-bridge electrolyte RX, which normally makes the largest contribution to E_j . For Cell II, the liquid-junction potential is given by

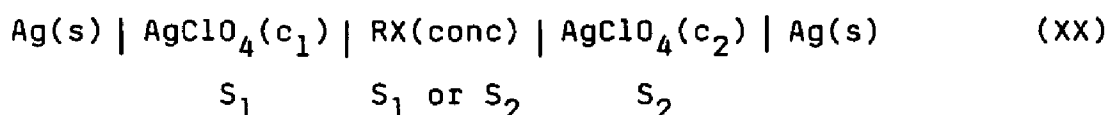
$$E_j = - \frac{1}{F} [t_M \Delta G_t^\circ(M) - t_Z \Delta G_t^\circ(Z) + t_R \Delta G_t^\circ(R) - t_X \Delta G_t^\circ(X)] + E_{j,s} \quad (91)$$

In Equation 91, the t 's and the ΔG_t° 's are respectively the Hittorf transport numbers and the transfer free energies of the ions, M^+ , Z^- , R^+ , and X^- . The transport numbers are assumed to be solvent-independent. If $E_{j,s}$, the contribution of solvent molecules to E_j , is small enough so that it can be neglected, then Equation 91 combined with Equation 40 will result in an expression which can be used to calculate a value for transfer activity coefficient of one of the ions in RX, provided that the appropriate transfer numbers and the transfer activity coefficients of the other three ions present in Equation 91 are known. If the concentration of RX is high enough relative to MZ, the quantities t_M and t_Z will approach zero, the E_j will be effectively accounted for by the salt-bridge electrolyte alone and the reliability of Equation of 91 will be increased. This acquires special

significance if we note that the most common method of determining the transfer activity coefficients of electrolytes is based on the ratio of their thermodynamic solubility products in water and the given nonaqueous solvent. This calculation method works best for slightly soluble salts, but becomes less reliable as the electrolyte solubility increases, since the high and uncertain corrections for activity coefficients and for ionic association, as well as the tendency of very soluble electrolytes to form crystal solvates, all introduce a potential error in the calculation. The fact that the new method of estimating transfer activity coefficients of single ions, outlined in this introduction, is uniquely suited for ions of appreciably soluble electrolytes as well as those for which no reversible electrodes exist underscores its practical utility.

This investigation

In this investigation, the following cell was used:



The AgClO_4 solution concentrations, c_1 and c_2 , were kept approximately equal in both half-cells. Measurements were taken with 1×10^{-2} , 1×10^{-3} , and 1×10^{-4} M solutions of AgClO_4 . Solvent pairs, S_1 and S_2 , were chosen from the following dipolar aprotic solvents: acetonitrile (MeCN), dimethylsulfoxide (DMSO), propylene carbonate (PC), and N,N'-dimethyl-

formamide (DMF). For every possible pair of solvents, a choice had to be made regarding the solvent for the salt-bridge solution. In order to do that, we looked carefully at the nature of the junction which would be formed between S_1 and S_2 . The ions crossing the boundary would be the ions of the salt-bridge electrolyte, RX as well as $AgClO_4$. The liquid-junction potential formed at the interface of solvents S_1 and S_2 depends partially on the profile of the chemical-potential gradient of the Ag^+ and ClO_4^- ions. The negatively charged ClO_4^- ion does not experience dramatic changes in its solvation energies in the solvents used here, but the Ag^+ ion is solvated quite strongly and a change of the solvent may result in a very large transfer free energy (20). In order to explain the origin of $E_{j,s}$, Murray and Aikens (52) have suggested that solvent molecules contribute to the E_j via migration of solvated ions across the boundary between the two solvents. This author suggested earlier that the $E_{j,s}$ component of E_j consists of two parts: one which depends solely on the interactions between the two solvents, and the second, which depends on the interactions of the ions with the molecules of each solvent. In the case of the interface between two dipolar aprotic solvents, we can make a case for the first component of $E_{j,s}$ to be negligible, and the rationale for this will be discussed later. Since the second component relates to the nature of each ion crossing the boundary between the two solvents as well as the profile of the chemical-potential change for each ion,

there is only one approach which would minimize that component for a junction between two solvents S_1 and S_2 with Ag^+ ions present in one of the solvents. This approach, which has been suggested by Alexander, Parker, Sharp, and Waghorne (25), is simply a selection (between S_1 and S_2) of that solvent for a salt-bridge solution which is the weaker solvator of the two for Ag^+ ions, signified by a less negative value of $\log_m \gamma_{Ag}$, when some third solvent is used as the reference. Table 23 lists the transfer activity coefficients of Ag^+ used in this investigation (water is the reference solvent). Medium effects of ClO_4 are also included. The transfer activity coefficients for Ag^+ have been compiled by Cox, et al. (85), but we decided to use updated results based on solubility products of $AgBPh_4$ in the solvents of interest, reported and critically evaluated by Popovych (84).

There were originally four salt-bridge electrolytes chosen for this study: tetramethylammonium perchlorate (Me_4NClO_4), tetraethylammonium perchlorate (Et_4NClO_4), tetrapropylammonium perchlorate (Pr_4NClO_4), and tetra-n-butylammonium perchlorate (Bu_4NClO_4). For reasons which will be explained later, another set of electrolytes was included, in which the perchlorate ion, ClO_4^- , was replaced by the picrate ion, Pi^- . The actual concentration of a given salt-bridge solution depended on the nature of the electrolyte and of the solvent, but it never was less than 0.1M, and in

TABLE 23

Transfer Activity Coefficients of Ag^+ and ClO_4^- Ions
Between Water and Selected Dipolar Aprotic Solvents (Molar
Scale, 25°C).

Solvent	$\log_m \gamma_{\text{Ag}}(84)$	$\log_m \gamma_{\text{ClO}_4}(85)$
MeCN	-3.88	0.81
DMSO	-6.15	-0.22
DMF	-3.03	0.07
PC	1.83	-0.3*

*from solubility of KClO_4 in PC and H_2O (48).

some cases exceeded 0.4M. In general, the solubility of the salts increased with the size of the alkyl group.

The formulation for the e.m.f. of Cell XX consists of three terms, E' , $E_{j,G}$ and $E_{j,H}$. For the purposes of this study, $E_{j,s}$, the solvent contribution to liquid-junction potential E_j , is assumed to be negligible.

E' is a term accounting for the difference between the electrode potentials:

$$E' = 59.16 \log_m \gamma_{Ag} + 59.16 \log \frac{{}_2a_{Ag}}{{}_1a_{Ag}} \quad (92)$$

where the transfer activity coefficient of the Ag^+ ion, $\log_m \gamma_{Ag}$, pertains to the transfer from S_1 (reference solvent) to S_2 , and ${}_1a_{Ag}$ and ${}_2a_{Ag}$ are the conventional activities of Ag^+ in both solvents.

The $E_{j,G}$ term accounts for the contributions of medium effects and transport numbers of all the ions present in the diffusion layer. In the case of a junction between solutions of $RClO_4$ and $AgClO_4$, $E_{j,G}$ is equal to

$$E_{j,G} = - 59.16(t_{Ag} \log_m \gamma_{Ag} + t_R \log_m \gamma_R - t_{ClO_4} \log_m \gamma_{ClO_4}) \quad (93)$$

where $t_{Ag} + t_R + t_{ClO_4} = 1$. For junctions between solutions of RPI and $AgClO_4$, $E_{j,G}$ is equal to

$$E_{j,G} = - 59.16(t_{Ag} \log_m \gamma_{Ag} + t_R \log_m \gamma_R - t_{PI} \log_m \gamma_{PI} - t_{ClO_4} \log_m \gamma_{ClO_4}) \quad (94)$$

where $t_{Ag} + t_R + t_{Pi} + t_{ClO_4} = 1$. The transport numbers used here are the average transport numbers between the two solvents, S_1 and S_2 . The formulation for $E_{j,G}$ used here does not take into account any nonlinear variations of t_i with the composition of the solvent in the transition layer. At this time, there are no data available which could prove (or disprove) that the simplified formulation is satisfactory for the ions and solvent pairs used here. If any such data become available in the future, their application to this new method of estimating transfer activity coefficients of single ions will only improve the accuracy of such values, and in no way detract from the validity of the new method.

The last term in the formulation of the e.m.f. of Cell XX is the term $E_{j,H}$, which is the result of applying the Henderson equation (9) to a junction with a salt-bridge. The expression for $E_{j,H}$ used here is based on the derivation found in Appendix 1:

$$E_{j,H} = -59.16(t_R - t_X) \log \frac{2^{a_{AgClO_4}}}{1^{a_{AgClO_4}}} \quad (95)$$

where t_R is the average transport number of the tetraalkylammonium cation, t_X is the average transport number of the corresponding anion of the salt-bridge electrolyte RX (in this case, ClO_4^- or Pi^- ion), and the a_{AgClO_4} is the conventional mean ionic activity of $AgClO_4$ in either solvent.

A slightly different formulation was used by Goldberg (48,49) in which the term $(t_R - t_X)$ was replaced by $(t_M - t_Z)$, where MZ refers to the electrolyte MZ present in both half-cells. While Goldberg's formulation was also derived from the Henderson equation as applied to the two junctions present when a salt bridge is interposed between two dilute solutions, the approximations made in his derivation seem less generally valid than those employed in Appendix 1. Furthermore, the formulation represented by Equation 95 is also supported by other workers (53, 86). It is easily seen that both formulations can have a minimal impact when the activities of the electroactive electrolyte are chosen to be equal in both solvents, because in that case $E_{j,H} = 0$. In practice, those activities may differ by several percent and that difference contributes to the liquid-junction potential E_j and should be calculated. All the results reported in this investigation are based on the expression for $E_{j,H}$ based on Equation 95.

When the measured e.m.f. of Cell XX is combined with the equations for E' , $E_{j,H}$, and $E_{j,G}$, the resulting expression can then be rearranged in terms of all the known quantities and solved for either $\log_m \gamma_R$ or $\log_m \gamma_X$, whichever is the unknown quantity. When the salt-bridge electrolyte was RClO_4 , the following equation has been used to calculate $\log_m \gamma_R$:

$$\log_m \gamma_R = \frac{1-t_{Ag}}{t_R} \log_m \gamma_{Ag} - \frac{E(XX)'}{59.16 t_R} - \frac{t_R-t_{ClO4}}{t_R} \log \frac{2^{a+}}{1^{a+}} + \frac{t_{ClO4}}{t_R} \log_m \gamma_{ClO4} \quad (96)$$

where $E(XX)'$ is the experimental e.m.f. of Cell XX corrected for Nernstian response of the silver electrodes:

$$E(XX)' = E(XX) - 59.16 \log \frac{2^{a_{Ag}}}{1^{a_{Ag}}} \quad (97)$$

E.m.f. measurements of Cell XX with RPi as a salt-bridge electrolyte were used to calculate $\log_m \gamma_{Pi}$, since the values of $\log_m \gamma_R$ were now available:

$$\begin{aligned} \log_m \gamma_{Pi} &= \frac{t_{Ag}-1}{59.16 t_{Pi}} \log_m \gamma_{Ag} + \frac{E(XX)'}{59.16 t_{Pi}} \\ &+ \frac{t_R-t_{Pi}}{59.16 t_{Pi}} \log \frac{2^{a+}}{1^{a+}} - \frac{t_{ClO4}}{t_{Pi}} \log_m \gamma_{ClO4} \\ &+ \frac{t_R}{t_{Pi}} \log_m \gamma_R \end{aligned} \quad (98)$$

Calculated Results.

In order to use Equations 96 and 97 to calculate $\log_m \gamma_R$ or $\log_m \gamma_{Pi}$, respectively, the following sets of data had to be available:

a) Transfer activity coefficients of Ag^+ and ClO_4^- ions between all the solvent pairs studied here.

b) Transport numbers of all the ions present in the diffusion layer.

c) Conventional activities of AgClO_4 solutions in MeCN, DMSO, DMF, and PC.

The $\log_m \gamma_{\text{Ag}}$ and $\log_m \gamma_{\text{ClO}_4}$ values used here were already discussed and are given in Table 23. To convert the values found in Table 23 to reference solvents other than H_2O , the following expression was used:

$$\log_m^1 \gamma^2 = \log_m^W \gamma^2 - \log_m^W \gamma^1 \quad (99)$$

The $\log_m \gamma_R$ values obtained by using Equation 95 were subsequently used in Equation 96 to calculate $\log_m \gamma_{Pi}$.

Transport numbers.

Transport numbers were calculated for each transition layer, one for the $\text{AgClO}_4(\text{S}_1) \text{RX}(\text{S}_1)$ junction, the other for the $\text{RX}(\text{S}_1) \text{AgClO}_4(\text{S}_2)$ junction, using the following expression for the transport number t_i of a given ion i :

$$t_i = \frac{c_i \lambda_i^0}{\sum_i c_i \lambda_i^0} \quad (100)$$

The t_i value finally used in Equations 96 and 97 was obtained by averaging the values calculated for the two junctions. It is important to realize that these calculations treat the whole transition layer between the two solutions as a homogenous mixture of the two solutions, but at the same time some account of the different solvents is taken when the t_i values are chosen. For the $RX(S_1) | AgClO_4(S_2)$ junction, the λ_R^0 and λ_X^0 values are for solvent S_1 , while the λ_{Ag}^0 and $\lambda_{ClO_4}^0$ are for solvent S_2 . These approximations gain in validity as the concentration of $AgClO_4$ decreases, until the contributions from Ag^+ and ClO_4^- can be neglected completely. The ratio of concentrations of RX to $AgClO_4$ at which that happens depends to some degree on the values of the limiting equivalent conductances of all the ions included in the calculation, but in general the 100 to 1 ratio has been accepted as sufficient to render the contribution of Ag^+ and ClO_4^- ions negligible.

Table 24 illustrates the effect of ignoring the presence of $AgClO_4$ in $\log_m \gamma_R$ calculations for a number of R^+ ions and a number of solvent pairs. The ratio of the salt-bridge electrolyte concentration to the concentration of $AgClO_4$ is given only to two significant figures. The $\log_m \gamma_R$ values are given here only for selected cases for purposes of discussion and do not represent the final values. The complete list of e.m.f. measurements, calculated E_j^0 and all of the final $\log_m \gamma_R$ values is given later in Tables 34-37. In order to evaluate the results presented in Table 24, it

was necessary to first know the limiting equivalent conductances λ^0 of all the ions included in this study. Table 25 lists the λ^0 values of Ag^+ , ClO_4^- , Pi^- , Me_4N^+ , Et_4N^+ , Pr_4N^+ , and Bu_4N^+ ions in the four solvents used here.

It was mentioned earlier that the choice of solvent for the salt-bridge solution was not arbitrary, but had to do with its ability to solvate Ag^+ ions. Eventually, the e.m.f. measurements were always taken using the weaker solvating solvent as the reference, and therefore the salt bridge contained the same solvent. Thus, the interface between two different solvents, S_1 and S_2 , was present at the second junction of Cell XX. When the transfer activity coefficients of R^+ ions are denoted by the symbol ${}^1_m\gamma_R^2$, the RClO_4 electrolyte was present in the solvent S_1 , and AgClO_4 was present in solvent S_2 . With that in mind we can now look at Tables 24 and 25.

TABLE 24

Transfer Activity Coefficients of R⁺ Ions Calculated Using the Complete Equation 96 (Column A) and the Simplified Equation 96 (Column B).

R ⁺	$\frac{c(\text{RClO}_4)}{c(\text{AgClO}_4)}$			$\frac{c(\text{RClO}_4)}{c(\text{AgClO}_4)}$		
		A	B		A	B
		$\log^{\text{DMF}}_{\text{m R}} \gamma^{\text{MeCN}}$			$\log^{\text{MeCN}}_{\text{m R}} \gamma^{\text{DMSO}}$	
Me ₄ N ⁺	11	1.68	1.32	10	-0.89	-0.96
	110	0.98	0.95	100	-0.65	-0.66
	1100	0.44	0.44	1000	-0.52	-0.52
Et ₄ N ⁺	40	1.29	1.20	33	-0.60	-0.64
	400	0.86	0.85	330	-0.31	-0.31
	4000	0.65	0.65	3300	-0.12	-0.12
Pr ₄ N ⁺	40	1.51	1.41	40	-0.34	-0.39
	400	1.06	1.05	400	-0.01	-0.01
	4000	0.61	0.61	4000	-0.39	-0.39
Bu ₄ N ⁺	40	1.75	1.63	45	-0.38	-0.42
	400	1.29	1.28	450	-0.05	-0.06
	4000	0.87	1.87	4500	+0.46	+0.46
		$\log^{\text{PC}}_{\text{m R}} \gamma^{\text{MeCN}}$			$\log^{\text{PC}}_{\text{m R}} \gamma^{\text{DMSO}}$	
Me ₄ N ⁺	10	7.31	4.09	10	4.40	3.14
	100	3.75	3.40	100	3.18	3.05
				1000	1.19	1.18

TABLE 24 (con't.)

R^+	$\frac{c(RClO_4)}{c(AgClO_4)}$			$\frac{c(RClO_4)}{c(AgClO_4)}$		
		A	B		A	B
		$\log_{mR}^{PC, MeCN}$			$\log_{mR}^{PC, DMSO}$	
Et_4N^+	10	8.34	4.23	10	4.80	3.47
	100	4.66	4.25	100	3.55	3.41
	1000	3.42	3.38			
Pr_4N^+	47	5.96	4.94	47	4.92	4.49
	470	5.27	4.59	470	4.56	4.52
Bu_4N^+	44	7.04	5.76	44	5.64	5.15
	440	4.19	4.07	440	5.19	5.14

TABLE 25

Limiting Equivalent Conductances of Ions in Dipolar Aprotic Solvents (25°C).

Ion	Solvent			
	MeCN	DMSO	DMF	PC
Ag ⁺	8.60 ^(b)	15.9 ^(d)	35.2 ^(d)	10.8(g)
ClO ₄ ⁻	103.65 ^(a)	24.6 ^(d)	52.4 ^(d)	18.43 ^(a)
PI ⁻	77.32 ^(e)	17.3 ^(e)	35.5 ^(e)	12.7 ^(f)
Me ₄ N ⁺	94.54 ^(a)	18.6 ^(c)	39.1 ^(d)	14.17 ^(a)
Et ₄ N ⁺	85.21 ^(a)	17.06 ^(c)	35.4 ^(b)	13.19 ^(a)
Pr ₄ N ⁺	70.20 ^(a)	13.4 ^(c)	29.0 ^(d)	10.47 ^(a)
Bu ₄ N ⁺	61.49 ^(a)	11.59 ^(c)	25.4 ^(d)	9.00 ^(a)

(a) Found in ref. (87).

(b) Found in ref. (88).

(c) Found in ref. (89).

(d) Found in ref. (75).

(e) Found in ref. (25).

(f) Found in ref. (48).

(g) Calculated using Walden product in MeOH.

The simplification of Equation 96 consisted of ignoring the presence of AgClO_4 in the diffusion layer and assuming that only R^+ and ClO_4^- ions carried the current across the junction. We see that this type of approximation can be used for $c(\text{RClO}_4)/c(\text{AgClO}_4) \geq 100$, as evidenced by the $\log_m \gamma_R$ values calculated both ways for the $\text{DMF}|\text{MeCN}$ and $\text{MeCN}|\text{DMSO}$ interfaces. However, this approximation requires higher $c(\text{RClO}_4)/c(\text{AgClO}_4)$ ratios when applied to cases where the salt-bridge solvent was PC. Even though we don't have data (due to solution decomposition) for more dilute solutions of AgClO_4 (specifically, $1 \times 10^{-4} \text{M}$), it is easily seen from the calculated values of $\log_m^{\text{PC, MeCN}} \gamma_R$ and $\log_m^{\text{PC, DMSO}} \gamma_R$ that ignoring the presence of AgClO_4 in the diffusion layer produces results that are still significantly different from those obtained by using the complete Equation 96 at $c(\text{RClO}_4)/c(\text{AgClO}_4)$ ratios of 100. The reason for this becomes apparent when the relative values of the limiting equivalent conductances of all the ions are considered. In the PC they are very low, ranging from 9 to 18, whereas in MeCN they are much higher, ranging from 62 to 104. Each species crossing a junction carries an amount of current related to the product of its concentration and its mobility (here approximated by λ^0), and in systems where mobilities do not change drastically from solvent to solvent as is the case with the DMF MeCN, only relative concentrations need be considered when deciding the importance of a given ion in the current-carrying process. When two solvents with very

different properties are paired, such as PC and MeCN, both concentrations and mobilities have to be considered.

The transport numbers averaged over both junctions and then used in the calculations are listed in Tables 26-29 for RC10_4 and Tables 30-33, for RPi. The value of t_R , calculated for the case of negligible contribution of AgClO_4 , is included (as t_R') for comparison. Obviously, as the $c(\text{AgClO}_4)$ decreases, the value of t_R approaches t_R' and t_{ClO_4} approaches the value of $1 - t_R'$. The I.D. # is used to correlate the calculated t_i values with the concentrations of the solutions, which are included in Tables 34-37 for RC10_4 electrolytes and Tables 41-44 for RPi electrolytes. As mentioned before, the first solvent of every solvent pair, S_1 , represents the salt-bridge solution, as well as the solution of AgClO_4 in the left half-cell, whereas the second solvent, S_2 , refers to the solution of AgClO_4 in the right half-cell.

TABLE 26

Transport Numbers of Ag^+ , ClO_4^- , and Me_4N^+ Calculated for Various Solvent Pairs.

ID #	$\sim^{\text{C}}\text{Me}_4\text{NClO}_4$	$\sim^{\text{C}}\text{AgClO}_4$	t_{Ag}	t_{ClO_4}	$t_{\text{Me}_4\text{N}}$
	$S_1 = \text{MeCN}$	$S_2 = \text{DMSO}$			$t_{\text{Me}_4\text{N}}^i = 0.4770$
1.	0.1	1×10^{-2}	0.0228	0.5248	0.4524
2.	0.1	1×10^{-2}	0.0276	0.5252	0.4472
3.	0.1	1×10^{-3}	0.0024	0.5233	0.4744
4.	0.1	1×10^{-3}	0.0030	0.5232	0.4738
5.	0.1	1×10^{-4}	0.0002	0.5230	0.4768
6.	0.1	1×10^{-4}	0.0003	0.5230	0.4767
	$S_1 = \text{DMF}$	$S_2 = \text{DMSO}$			$t_{\text{Me}_4\text{N}}^i = 0.4273$
1.	0.1	1×10^{-2}	0.0237	0.5744	0.4018
2.	0.1	1×10^{-2}	0.0276	0.5747	0.3978
3.	0.1	1×10^{-3}	0.0025	0.5728	0.4246
4.	0.1	1×10^{-3}	0.0030	0.5729	0.4242
5.	0.1	1×10^{-4}	0.0002	0.5727	0.4270
6.	0.1	1×10^{-4}	0.0003	0.5727	0.4270

TABLE 26 (con't.)

ID #	$\sim^C\text{Me}_4\text{NC104}$	$\sim^C\text{AgC104}$	t_{Ag}	t_{C104}	t_{Me4N}
	$S_1 = \text{DMF}$	$S_2 = \text{MeCN}$			$t'_{\text{Me4N}} = 0.4273$
1.	0.10	1×10^{-2}	0.0529	0.5716	0.3755
2.	0.10	1×10^{-2}	0.0607	0.5713	0.3680
3.	0.10	1×10^{-3}	0.0060	0.5725	0.4214
4.	0.10	1×10^{-3}	0.0070	0.5725	0.4204
5.	0.10	1×10^{-4}	0.0006	0.5727	0.4267
6.	0.10	1×10^{-4}	0.0007	0.5727	0.4266
	$S_1 = \text{PC}$	$S_2 = \text{DMF}$			$t'_{\text{Me4N}} = 0.4347$
1.	0.10	1×10^{-2}	0.0595	0.5717	0.3689
2.	0.10	1×10^{-3}	0.0071	0.5661	0.4268
3.	0.10	1×10^{-4}	0.0007	0.5654	0.4339
	$S_1 = \text{PC}$	$S_2 = \text{DMSO}$			$t'_{\text{Me4N}} = 0.4347$
1.	0.10	1×10^{-2}	0.0419	0.5709	0.3872
2.	0.10	1×10^{-3}	0.0047	0.5659	0.4293
3.	0.10	1×10^{-4}	0.0005	0.5654	0.4341
	$S_1 = \text{PC}$	$S_2 = \text{MeCN}$			$t'_{\text{Me4N}} = 0.4347$
1.	0.10	1×10^{-2}	0.1086	0.5654	0.3267
2.	0.10	1×10^{-2}	0.1064	0.5643	0.3294
3.	0.10	1×10^{-3}	0.0162	0.5651	0.4187
4.	0.10	1×10^{-3}	0.0159	0.5650	0.4190

TABLE 27

Transport Numbers of Ag^+ , ClO_4^- , and Et_4N^+ Calculated for Various Solvent Pairs.

ID #	$\sim^c\text{Et}_4\text{NClO}_4$	$\sim^c\text{AgClO}_4$	t_{Ag}	t_{ClO_4}	$t_{\text{Et}_4\text{N}}$
$S_1 = \text{MeCN}$		$S_2 = \text{DMSO}$	$t'_{\text{Et}_4\text{N}} = 0.4512$		
1.	0.1	1×10^{-2}	0.0241	0.5493	0.4266
2.	0.16	1×10^{-2}	0.0183	0.5492	0.4325
3.	0.31	1×10^{-2}	0.0099	0.5490	0.4410
4.	0.1	1×10^{-3}	0.0026	0.5489	0.4485
5.	0.16	1×10^{-3}	0.0019	0.5489	0.4492
6.	0.31	1×10^{-3}	0.0001	0.5488	0.4501
7.	0.1	1×10^{-4}	0.0003	0.5488	0.4509
8.	0.31	1×10^{-4}	0.0000	0.5488	0.4511
$S_1 = \text{DMF}$		$S_2 = \text{DMSO}$	$t'_{\text{Et}_4\text{N}} = 0.4032$		
1.	0.12	1×10^{-2}	0.0239	0.5971	0.3790
2.	0.41	1×10^{-2}	0.0076	0.5969	0.3956
3.	0.12	1×10^{-3}	0.0025	0.5968	0.4006
4.	0.41	1×10^{-3}	0.0008	0.5968	0.4024
5.	0.12	1×10^{-4}	0.0002	0.5968	0.4029
6.	0.41	1×10^{-4}	0.0001	0.5968	0.4031

TABLE 27 (con't.)

ID #	$\sim^c\text{Et4NC104}$	$\sim^c\text{AgC104}$	t_{Ag}	t_{C104}	t_{Et4N}
	$S_1 = \text{DMF}$	$S_2 = \text{MeCN}$			$t_{\text{Et4N}}^i = 0.4032$
1.	0.12	1×10^{-2}	0.0506	0.5932	0.3562
2.	0.41	1×10^{-2}	0.0180	0.5954	0.3866
3.	0.12	1×10^{-3}	0.0057	0.5964	0.3979
4.	0.41	1×10^{-3}	0.0019	0.5967	0.4015
5.	0.12	1×10^{-4}	0.0006	0.5968	0.4027
6.	0.41	1×10^{-4}	0.0002	0.5968	0.4030
	$S_1 = \text{PC}$	$S_2 = \text{DMF}$			$t_{\text{Et4N}}^i = 0.4171$
1.	0.10	1×10^{-2}	0.0587	0.5864	0.3549
2.	0.10	1×10^{-3}	0.0071	0.5833	0.4097
	$S_1 = \text{PC}$	$S_2 = \text{DMSO}$			$t_{\text{Et4N}}^i = 0.4171$
1.	0.10	1×10^{-2}	0.0417	0.5864	0.3718
2.	0.10	1×10^{-3}	0.0047	0.5832	0.4121
	$S_1 = \text{PC}$	$S_2 = \text{MeCN}$			$t_{\text{Et4N}}^i = 0.4171$
1.	0.10	1×10^{-2}	0.1139	0.5781	0.3080
2.	0.10	1×10^{-3}	0.0171	0.5820	0.4010
3.	0.10	1×10^{-4}	0.0018	0.5820	0.4154

TABLE 28

Transport Numbers of Ag^+ , ClO_4^- , and Pr_4N^+ Calculated for Various Solvent Pairs.

ID #	$\sim\text{C}_{\text{Pr}_4\text{NClO}_4}$	$\sim\text{C}_{\text{AgClO}_4}$	t_{Ag}	t_{ClO_4}	$t_{\text{Pr}_4\text{N}}$
$S_1 = \text{MeCN}$		$S_2 = \text{DMSO}$		$t'_{\text{Pr}_4\text{N}} = 0.4038$	
1.	0.20	1×10^{-2}	0.0135	0.5950	0.3915
2.	0.20	1×10^{-2}	0.0136	0.5950	0.3914
3.	0.40	1×10^{-2}	0.0085	0.5955	0.3961
4.	0.20	1×10^{-3}	0.0014	0.5961	0.4025
5.	0.20	1×10^{-3}	0.0014	0.5961	0.4025
6.	0.40	1×10^{-3}	0.0009	0.5961	0.4030
7.	0.20	1×10^{-4}	0.0001	0.5962	0.4037
8.	0.20	1×10^{-4}	0.0001	0.5962	0.4037
9.	0.40	1×10^{-4}	0.0001	0.5962	0.4037
$S_1 = \text{DMF}$		$S_2 = \text{DMSO}$		$t'_{\text{Pr}_4\text{N}} = 0.3563$	
1.	0.18	1×10^{-2}	0.0174	0.6418	0.3407
2.	0.44	1×10^{-2}	0.0075	0.6430	0.3496
3.	0.18	1×10^{-3}	0.0018	0.6435	0.3546
4.	0.44	1×10^{-3}	0.0008	0.6436	0.3556
5.	0.18	1×10^{-4}	0.0002	0.6437	0.3561
6.	0.44	1×10^{-4}	0.0001	0.6437	0.3562

TABLE 28 (con't.)

ID #	$\sim^c\text{Pr4NC104}$	$\sim^c\text{AgCl04}$	t_{Ag}	t_{Cl04}	t_{Pr4N}
	$S_1 = \text{DMF}$	$S_2 = \text{MeCN}$			$t'_{\text{Pr4N}} = 0.3563$
1.	0.18	1×10^{-2}	0.0375	0.6370	0.3256
2.	0.44	1×10^{-2}	0.0180	0.6404	0.3416
3.	0.18	1×10^{-3}	0.0041	0.6430	0.3529
4.	0.44	1×10^{-3}	0.0019	0.6434	0.3547
5.	0.18	1×10^{-4}	0.0004	0.6437	0.3559
6.	0.44	1×10^{-4}	0.0002	0.6437	0.3561
	$S_1 = \text{PC}$	$S_2 = \text{DMF}$			$t'_{\text{Pr4N}} = 0.3623$
1.	0.47	1×10^{-2}	0.0160	0.6364	0.3475
	$S_1 = \text{PC}$	$S_2 = \text{DMSO}$			$t'_{\text{Pr4N}} = 0.3623$
1.	0.47	1×10^{-2}	0.0124	0.6371	0.3505
2.	0.47	1×10^{-3}	0.0013	0.6376	0.3611
	$S_1 = \text{PC}$	$S_2 = \text{MeCN}$			$t'_{\text{Pr4N}} = 0.3623$
1.	0.47	1×10^{-2}	0.0357	0.6313	0.3331
2.	0.47	1×10^{-3}	0.0040	0.6370	0.3590

TABLE 29

Transport Numbers of Ag^+ , ClO_4^- , and Bu_4N^+ Calculated for Various Solvent Pairs.

ID #	$\sim^c\text{Bu}_4\text{NClO}_4$	$\sim^c\text{AgClO}_4$	t_{Ag}	t_{ClO_4}	$t_{\text{Bu}_4\text{N}}$
	$S_1 = \text{MeCN}$	$S_2 = \text{DMSO}$			$t_{\text{Bu}_4\text{N}}^i = 0.3724$
1.	0.20	1×10^{-2}	0.0143	0.6254	0.3603
2.	0.45	1×10^{-2}	0.0079	0.6264	0.3657
3.	0.20	1×10^{-3}	0.0015	0.6274	0.3711
4.	0.45	1×10^{-3}	0.0008	0.6275	0.3717
5.	0.20	1×10^{-4}	0.0001	0.6276	0.3722
6.	0.45	1×10^{-4}	0.0001	0.6276	0.3723
	$S_1 = \text{DMF}$	$S_2 = \text{DMSO}$			$t_{\text{Bu}_4\text{N}}^i = 0.3265$
1.	0.22	1×10^{-2}	0.0150	0.6709	0.3141
2.	0.44	1×10^{-2}	0.0078	0.6721	0.3201
3.	0.22	1×10^{-3}	0.0013	0.6733	0.3253
4.	0.44	1×10^{-3}	0.0008	0.6734	0.3259
5.	0.22	1×10^{-4}	0.0000	0.6735	0.3265
	$S_1 = \text{DMF}$	$S_2 = \text{MeCN}$			$t_{\text{Bu}_4\text{N}}^i = 0.3265$
1.	0.22	1×10^{-2}	0.0323	0.6655	0.3023
2.	0.44	1×10^{-2}	0.0188	0.6687	0.3125
3.	0.22	1×10^{-3}	0.0035	0.6727	0.3239
4.	0.44	1×10^{-3}	0.0020	0.6730	0.3250
5.	0.22	1×10^{-4}	0.0004	0.6734	0.3262
6.	0.44	1×10^{-4}	0.0002	0.6735	0.3263

TABLE 29 (con't.)

ID #	$\sim^c\text{Bu}_4\text{NC104}$	$\sim^c\text{AgC104}$	t_{Ag}	t_{C104}	t_{Bu4N}
	$S_1 = \text{PC}$	$S_2 = \text{DMF}$			$t'_{\text{Bu4N}} = 0.3281$
1.	0.68	1×10^{-2}	0.0130	0.6697	0.3172
2.	0.68	1×10^{-3}	0.0013	0.6717	0.3270
	$S_1 = \text{PC}$	$S_2 = \text{DMSO}$			$t'_{\text{Bu4N}} = 0.3281$
1.	0.44	1×10^{-2}	0.0124	0.6701	0.3175
2.	0.44	1×10^{-3}	0.0013	0.6717	0.3270
	$S_1 = \text{PC}$	$S_2 = \text{MeCN}$			$t'_{\text{Bu4N}} = 0.3281$
1.	0.44	1×10^{-2}	0.0393	0.6617	0.2990
2.	0.44	1×10^{-3}	0.0045	0.6707	0.3248

TABLE 30

Transport Numbers of Ag^+ , ClO_4^- , Me_4N^+ , and Pi^-
Calculated for Various Solvent Pairs.

ID #	$\sim^c\text{Me}_4\text{N}^+\text{Pi}^-$	$\sim^c\text{AgClO}_4$	t_{Ag}	t_{ClO_4}	$t_{\text{Me}_4\text{N}}$	t_{Pi}
	$S_1 = \text{MeCN}$	$S_2 = \text{DMSO}$			$t'_{\text{Me}_4\text{N}} = 0.5501$	
1.	0.1	1×10^{-2}	0.0251	0.0316	0.5189	0.4244
2.	0.1	1×10^{-3}	0.0027	0.0034	0.5467	0.4471
3.	0.1	1×10^{-4}	0.0003	0.0003	0.5498	0.4496
	$S_1 = \text{DMF}$	$S_2 = \text{DMSO}$			$t'_{\text{Me}_4\text{N}} = 0.5104$	
1.	0.14	1×10^{-2}	0.0272	0.0409	0.4757	0.4562
2.	0.14	1×10^{-3}	0.0029	0.0044	0.5067	0.4860
3.	0.14	1×10^{-4}	0.0003	0.0004	0.5101	0.4892
	$S_1 = \text{DMF}$	$S_2 = \text{MeCN}$			$t'_{\text{Me}_4\text{N}} = 0.5104$	
1.	0.14	1×10^{-2}	0.0572	0.0741	0.4434	0.4253
2.	0.14	1×10^{-3}	0.0066	0.0085	0.5027	0.4822
3.	0.14	1×10^{-4}	0.0007	0.0009	0.5097	0.4888
	$S_1 = \text{PC}$	$S_2 = \text{DMF}$			$t'_{\text{Me}_4\text{N}} = 0.5274$	
1.	0.12	1×10^{-2}	0.0584	0.0903	0.4490	0.4024
2.	0.12	1×10^{-3}	0.0070	0.0107	0.5180	0.4643
3.	0.12	1×10^{-4}	0.0007	0.0011	0.5264	0.4718

TABLE 30 (con't.)

ID #	$\sim^c\text{Me}_4\text{NP1}$	$\sim^c\text{AgClO}_4$	t_{Ag}	t_{ClO_4}	$t_{\text{Me}_4\text{N}}$	t_{P1}
	$S_1 = \text{PC}$	$S_2 = \text{DMSO}$			$t'_{\text{Me}_4\text{N}} = 0.5274$	
1.	0.13	1×10^{-2}	0.0411	0.0660	0.4709	0.4220
2.	0.13	1×10^{-3}	0.0046	0.0073	0.5211	0.4670
3.	0.13	1×10^{-4}	0.0005	0.0007	0.5267	0.4721
	$S_1 = \text{PC}$	$S_2 = \text{MeCN}$			$t'_{\text{Me}_4\text{N}} = 0.5247$	
1.	0.13	1×10^{-2}	0.1070	0.1376	0.3984	0.3570
2.	0.13	1×10^{-2}	0.1048	0.1338	0.4015	0.3599
3.	0.13	1×10^{-3}	0.0158	0.0200	0.5084	0.4557
4.	0.13	1×10^{-3}	0.0156	0.0196	0.5088	0.4560

TABLE 31

Transport Numbers of Ag^+ , ClO_4^- , and Et_4N^+ , and Pi^- Calculated for Various Solvent Pairs.

ID #	$\sim^c\text{Et}_4\text{N}^+\text{Pi}^-$	$\sim^c\text{AgClO}_4$	t_{Ag}	t_{ClO_4}	$t_{\text{Et}_4\text{N}}$	t_{Pi}
	$S_1 = \text{MeCN}$	$S_2 = \text{DMSO}$			$t_{\text{Et}_4\text{N}}^i = 0.5243$	
1.	0.13	1×10^{-2}	0.0212	0.0268	0.4991	0.4529
2.	0.13	1×10^{-3}	0.0023	0.0028	0.5216	0.4733
3.	0.13	1×10^{-4}	0.0002	0.0003	0.5240	0.4755
	$S_1 = \text{DMF}$	$S_2 = \text{DMSO}$			$t_{\text{Et}_4\text{N}}^i = 0.4856$	
1.	0.16	1×10^{-2}	0.0244	0.0368	0.4558	0.4829
2.	0.16	1×10^{-3}	0.0026	0.0039	0.4824	0.5111
3.	0.16	1×10^{-4}	0.0003	0.0004	0.4853	0.5141
	$S_1 = \text{DMF}$	$S_2 = \text{DMSO}$			$t_{\text{Et}_4\text{N}}^i = 0.4856$	
1.	0.16	1×10^{-2}	0.0529	0.0683	0.4267	0.4520
2.	0.16	1×10^{-3}	0.0060	0.0078	0.4789	0.5073
3.	0.16	1×10^{-4}	0.0006	0.0008	0.4849	0.5137
	$S_1 = \text{PC}$	$S_2 = \text{DMF}$			$t_{\text{Et}_4\text{N}}^i = 0.5095$	
1.	0.17	1×10^{-2}	0.0438	0.0674	0.4528	0.4360
2.	0.17	1×10^{-3}	0.0050	0.0077	0.5030	0.4843

TABLE 31 (con't.)

ID #	$\sim^c_{\text{Et4Npi}}$	$\sim^c_{\text{AgClO4}}$	t_{Ag}	t_{ClO4}	t_{Et4N}	t_{pi}
	$S_1 = \text{PC}$	$S_2 = \text{DMSO}$			$t'_{\text{Et4N}} = 0.5095$	
1.	0.21	1×10^{-2}	0.0254	0.0408	0.4757	0.4581
2.	0.21	1×10^{-3}	0.0027	0.0044	0.5059	0.4871
	$S_1 = \text{PC}$	$S_2 = \text{MeCN}$			$t'_{\text{Et4N}} = 0.5095$	
1.	0.21	1×10^{-2}	0.0779	0.1002	0.4188	0.4032
2.	0.21	1×10^{-3}	0.0101	0.0129	0.4977	0.4792
3.	0.21	1×10^{-4}	0.0011	0.0013	0.5083	0.4894

TABLE 32

Transport Numbers of Ag^+ , ClO_4^- , and Pr_4N^+ , and Pi^- Calculated for Various Solvent Pairs.

ID #	$\sim^c\text{Pr}_4\text{N}^+\text{Pi}^-$	$\sim^c\text{AgClO}_4$	t_{Ag}	t_{ClO_4}	$t_{\text{Pr}_4\text{N}}$	t_{Pi}
	$S_1 = \text{MeCN}$	$S_2 = \text{DMSO}$			$t'_{\text{Pr}_4\text{N}} = 0.4759$	
1.	0.16	1×10^{-2}	0.0191	0.0241	0.4553	0.5015
2.	0.16	1×10^{-2}	0.0232	0.0294	0.4508	0.4966
3.	0.15	1×10^{-2}	0.0246	0.0311	0.4493	0.4949
4.	0.16	1×10^{-3}	0.0020	0.0026	0.4737	0.5217
5.	0.16	1×10^{-3}	0.0025	0.0031	0.4732	0.5212
6.	0.15	1×10^{-3}	0.0027	0.0033	0.4730	0.5210
7.	0.15	1×10^{-4}	0.0003	0.0003	0.4756	0.5238
	$S_1 = \text{DMF}$	$S_2 = \text{DMSO}$			$t'_{\text{Pr}_4\text{N}} = 0.4361$	
1.	0.13	1×10^{-2}	0.0315	0.0476	0.4016	0.5194
2.	0.13	1×10^{-3}	0.0032	0.0052	0.4324	0.5591
3.	0.13	1×10^{-4}	0.0003	0.0005	0.4357	0.5635
	$S_1 = \text{DMF}$	$S_2 = \text{MeCN}$			$t'_{\text{Pr}_4\text{N}} = 0.4361$	
1.	0.13	1×10^{-2}	0.0668	0.0864	0.3693	0.4775
2.	0.13	1×10^{-3}	0.0079	0.0102	0.4282	0.5537
3.	0.13	1×10^{-4}	0.0008	0.0010	0.4353	0.5629
	$S_1 = \text{PC}$	$S_2 = \text{DMF}$			$t'_{\text{Pr}_4\text{N}} = 0.4519$	
1.	0.30	1×10^{-2}	0.0300	0.0464	0.4174	0.5063
2.	0.30	1×10^{-3}	0.0033	0.0051	0.4481	0.5436

TABLE 32 (con't.)

ID #	$\sim^C\text{Pr}_4\text{N}^+\text{Pi}^-$	$\sim^C\text{AgClO}_4$	t_{Ag}	t_{ClO_4}	$t_{\text{Pr}_4\text{N}}$	t_{Pi}
	$S_1 = \text{PC}$	$S_2 = \text{DMSO}$			$t'_{\text{Pr}_4\text{N}} = 0.4519$	
1.	0.31	1×10^{-2}	0.0228	0.0368	0.4249	0.5154
2.	0.31	1×10^{-3}	0.0024	0.0039	0.4490	0.5447
	$S_1 = \text{PC}$	$S_2 = \text{MeCN}$			$t'_{\text{Pr}_4\text{N}} = 0.4519$	
1.	0.31	1×10^{-2}	0.0606	0.0767	0.3898	0.4729
2.	0.31	1×10^{-3}	0.0075	0.0094	0.4442	0.5388

TABLE 33

Transport Numbers of Ag^+ , ClO_4^- , and Bu_4N^+ , and Pi^- Calculated for Various Solvent Pairs.

ID #	$\sim^c\text{Bu}_4\text{N}^+\text{Pi}^-$	$\sim^c\text{AgClO}_4$	t_{Ag}	t_{ClO_4}	$t_{\text{Bu}_4\text{N}}$	t_{Pi}
	$S_1 = \text{MeCN}$	$S_2 = \text{DMSO}$			$t'_{\text{Bu}_4\text{N}} = 0.4430$	
1.	0.19	1×10^{-2}	0.0212	0.0268	0.4217	0.5303
2.	0.24	1×10^{-2}	0.0171	0.0216	0.4258	0.5354
3.	0.19	1×10^{-3}	0.0023	0.0028	0.4407	0.5542
4.	0.24	1×10^{-3}	0.0018	0.0023	0.4412	0.5548
5.	0.24	1×10^{-4}	0.0002	0.0002	0.4428	0.5568
	$S_1 = \text{DMF}$	$S_2 = \text{DMSO}$			$t'_{\text{Bu}_4\text{N}} = 0.4038$	
1.	0.15	1×10^{-2}	0.0287	0.0434	0.3747	0.5532
2.	0.15	1×10^{-3}	0.0031	0.0046	0.4007	0.5916
3.	0.15	1×10^{-4}	0.0003	0.0004	0.4035	0.5958
	$S_1 = \text{DMF}$	$S_2 = \text{MeCN}$			$t'_{\text{Bu}_4\text{N}} = 0.4038$	
1.	0.15	1×10^{-2}	0.0614	0.0795	0.3469	0.5122
2.	0.15	1×10^{-3}	0.0072	0.0092	0.3972	0.5864
3.	0.15	1×10^{-4}	0.0007	0.0010	0.4031	0.5952
	$S_1 = \text{PC}$	$S_2 = \text{DMF}$			$t'_{\text{Bu}_4\text{N}} = 0.4147$	
1.	0.46	1×10^{-2}	0.0234	0.0361	0.3900	0.5504
2.	0.46	1×10^{-3}	0.0025	0.0039	0.4121	0.5815

TABLE 33 (con't.)

ID #	$\sim^c\text{Bu}_4\text{N}^+\text{Pi}^-$	$\sim^c\text{AgClO}_4$	t_{Ag}	t_{ClO_4}	$t_{\text{Bu}_4\text{N}}$	t_{Pi}
	$S_1 = \text{PC}$	$S_2 = \text{DMSO}$			$t'_{\text{Bu}_4\text{N}} = 0.4147$	
1.	0.40	1×10^{-2}	0.0072	0.0121	0.4068	0.5740
2.	0.40	1×10^{-3}	0.0018	0.0028	0.4128	0.5826
	$S_1 = \text{PC}$	$S_2 = \text{MeCN}$			$t'_{\text{Bu}_4\text{N}} = 0.4147$	
1.	0.40	1×10^{-2}	0.0517	0.0651	0.3663	0.5168
2.	0.40	1×10^{-3}	0.0062	0.0078	0.4089	0.5771

Salt-effect activity coefficients.

The salt-effect activity coefficients for AgClO_4 solutions were calculated using the Davies equation

$$\log y_{\pm} = -A \frac{I^{1/2}}{1 + I^{1/2} - (1/3)I} \quad (101)$$

where $y_{\pm}$ is the mean ionic activity coefficient, I is the ionic strength of the solution, in this case equivalent to its concentration, and A is the Debye-Huckel constant which is a function of the solvent and the temperature. The values of the A -constants used here were 1.543, 0.661, 1.115 and 1.551 for MeCN, PC, DMSO and DMF, in that order.

Transfer Activity Coefficients of the Tetraalkylammonium Cations.

Results.

Tables 34-37 list the experimental data, the calculated E_j terms and the individual (concentration-dependent) values of $\log_m \gamma_R$ calculated using Equation 96 for Me_4N^+ , Et_4N^+ , Pr_4N^+ and Bu_4N^+ ions, in that order. The final, averaged values of $\log_m \gamma_R$ are summarized in Table 38.

Tables 34-37 (one for each R^+ cation) list the concentrations of all the solutions used in Cell XX and the e.m.f. value, E_{Cell} , measured each time a fresh junction was formed. The solutions of AgClO_4 in MeCN and DMSO were stable over a long period of time; DMF solutions had to be prepared fresh each morning. Therefore, it was possible to complete e.m.f. measurements for cells involving the MeCN, DMSO, and DMF solutions for the concentrations 10^{-2} , 10^{-3} , and 10^{-4}M . On the other hand, solutions in PC were very unstable. When a 10^{-2}M stock solution of AgClO_4 in freshly triply-distilled PC was prepared, measurements were taken using that solution and a dilution was made to obtain 10^{-3}M solution of AgClO_4 . By the time the e.m.f. measurements were completed using the 10^{-3}M solution, it was visibly decomposing, turning dark and leaving a deposit of metallic silver on the glassware. Because of that, measurements using 10^{-4}M solutions were not completed.

TABLE 34

Data and Results for the Calculation of the Transfer Activity Coefficients of Me_4N^+
 (From S_1 to S_2).

ID #	$c_{\text{Me}_4\text{NClO}_4}$	$c_{\text{AgClO}_4}(S_1)$	$c_{\text{AgClO}_4}(S_2)$	E_{Cell}	E_j	$E_{j,H}$	$\text{Log}_m \gamma_{\text{Me}_4\text{N}}$
		$S_1 = \text{MeCN}$	$S_2 = \text{DMSO}$		millivolts		
1.	~0.1	0.9597×10^{-2}	0.9458×10^{-2}	-140.8	-1.9	-0.14	-0.760
2.	~0.1	1.163×10^{-2}	1.252×10^{-2}	-134.6	-4.5	-0.3	-0.889
				-134.2	-4.1		-0.904
3.	~0.1	0.9597×10^{-3}	0.9458×10^{-3}	-153.7	-19.8	0.0	-0.418
				-152.2	-17.5		-0.499
4.	~0.1	1.163×10^{-3}	1.252×10^{-3}	-144.8	-13.2	-0.1	-0.648
				-143.0	-11.1		-0.723
5.	~0.1	0.9597×10^{-4}	0.9458×10^{-4}	-159.7	-25.3	0.0	-0.233
				-159.3	-24.9		-0.247
6.	~0.1	1.163×10^{-4}	1.252×10^{-4}	-149.2	-17.0	-0.1	-0.521
				-154.1	-21.9		-0.347

TABLE 34 (con't.)

ID #	$c_{\text{Me}_4\text{NC104}}$	$c_{\text{AgClO}_4}(S_1)$	$c_{\text{AgClO}_4}(S_2)$	E_{Cell}	E_j	$E_{j,H}$	$\text{Log}_m \gamma_{\text{Me}_4\text{N}}$
		$S_1 = \text{DMF}$	$S_2 = \text{DMSO}$		millivolts		
1.	0.1024	0.9284×10^{-2}	0.9458×10^{-2}	-214.0	-32.1	-0.5	1.141
2.	0.1024	1.019×10^{-2}	1.252×10^{-2}	-205.8	-28.3	-1.2	1.052
				-205.6	-28.1		1.044
				-207.2	-30.1		1.129
3.	0.1024	0.9284×10^{-3}	0.9458×10^{-3}	-206.0	-22.6	-0.2	0.535
4.	0.1024	1.019×10^{-3}	1.252×10^{-3}	-212.2	33.5	-0.9	1.000
				-210.6	-31.9		0.936
				-207.2	-28.5		0.800
5.	0.1024	0.9284×10^{-4}	0.9458×10^{-4}	-199.0	-15.1	-0.1	0.216
				-197.7	-13.1		0.164
6.	0.1024	1.019×10^{-4}	1.252×10^{-4}	-198.2	-19.1	-0.8	0.400
				-201.3	22.2		0.523
				-190.7	-11.6		0.104
				-202.6	-23.5		0.575

TABLE 34 (con't.)

ID #	$c_{\text{Me}_4\text{NC104}}$	$c_{\text{AgClO}_4}(S_1)$	$c_{\text{AgClO}_4}(S_2)$	E_{Cell}	E_j	$E_{j,H}$	$\text{Log}_m \gamma_{\text{Me}_4\text{N}}$
		$S_1 = \text{DMF}$	$S_2 = \text{MeCN}$		millivolts		
1.	0.1024	0.9284×10^{-2}	0.9597×10^{-2}	-54.9	-5.4	-0.2	1.497
2.	0.1024	1.019×10^{-2}	1.163×10^{-2}	-55.2	-7.8	-0.1	1.212
				-52.9	-5.5		1.570
				-52.7	-5.3		1.561
3.	0.1024	0.9284×10^{-3}	0.9597×10^{-3}	-54.2	-4.7	-0.1	1.212
4.	0.1024	1.019×10^{-3}	1.163×10^{-3}	-45.6	1.5	-0.5	0.983
				-46.0	1.1		0.999
				-46.5	0.6		1.019
5.	0.1024	0.9284×10^{-4}	0.9597×10^{-4}	-36.0	13.4	-0.5	0.467
				-41.0	8.4		0.665
6.	0.1024	1.019×10^{-4}	1.163×10^{-4}	-32.4	14.6		0.438
				-36.2	10.8		0.588
				-33.7	13.3		0.489
				-34.1	12.9		0.505

TABLE 34 (con't.)

ID #	c_{Me4NC104}	$c_{\text{AgClO4}}(S_1)$	$c_{\text{AgClO4}}(S_2)$	E_{Cell}	E_j	$E_{j,H}$	$\text{Log}_m \gamma_{\text{Me4N}}$
		$S_1 = \text{PC}$	$S_2 = \text{DMF}$		millivolts		
1.	0.1008	1.055×10^{-2}	1.040×10^{-2}	-353.2	-60.5	+1.1	4.127
				-350.0	-57.3		3.980
2.	0.1008	1.055×10^{-3}	1.040×10^{-3}	-348.2	-58.7	0.3	2.924
				-348.3	-58.8		2.928
3.	0.1008	1.055×10^{-4}	1.040×10^{-4}	-321.1	-32.7	0.1	1.798
		$S_1 = \text{PC}$	$S_2 = \text{DMSO}$				
1.	0.1008	1.043×10^{-2}	1.252×10^{-2}	-547.4	-77.3	-0.3	4.399
2.	0.1008	1.043×10^{-3}	1.252×10^{-3}	-543.0	74.6	-0.5	3.176
				-546.2	-77.8		3.302
3.	0.1008	1.043×10^{-4}	1.252×10^{-4}	-494.0	-26.3	-0.6	1.185
				-493.2	-25.5		1.154

TABLE 34 (con't.)

ID #	c_{Me4NC104}	$c_{\text{AgCl04}}(S_1)$	$c_{\text{AgCl04}}(S_2)$	E_{Cell}	E_j	$E_{j,H}$	$\text{Log}_m \gamma_{\text{Me4N}}$
		$S_1 = \text{PC}$	$S_2 = \text{MeCN}$		millivolts		
1.	0.1008	1.179×10^{-2}	1.163×10^{-2}	-412.3	-69.1	1.3	7.307
				-411.7	-68.5		7.276
2.	0.1008	1.014×10^{-2}	1.163×10^{-2}	-409.7	-70.1	0.4	7.304
3.	0.1008	1.179×10^{-3}	1.163×10^{-3}	-390.9	-51.0	0.3	3.752
				-389.1	-49.2		3.679
4.	0.1008	1.014×10^{-4}	1.163×10^{-4}	-394.0	-56.2	-0.3	4.045

TABLE 35

Data and Results for the Calculation of the Transfer Activity Coefficients of Et_4N^+
 (From S_1 to S_2).

ID #	$c_{\text{Et}_4\text{NClO}_4}$	$c_{\text{AgClO}_4}(S_1)$	$c_{\text{AgClO}_4}(S_2)$	E_{Cell}	E_j	$E_{j,H}$	$\log_m \gamma_{\text{Et}_4\text{N}}$
		$S_1 = \text{MeCN}$	$S_2 = \text{DMSO}$		millivolts		
1.	0.0986	0.9597×10^{-2}	0.9458×10^{-2}	-150.5	-18.1	-0.2	-0.472
2.	0.1634	1.163×10^{-2}	1.252×10^{-2}	-144.0	-13.9	-0.5	-0.651
				-143.0	-12.9		-0.690
3.	0.3099	1.163×10^{-2}	1.252×10^{-2}	-146.1	-15.9	-0.5	-0.602
				-144.9	-14.8		-0.648
4.	0.0986	0.9597×10^{-3}	0.9458×10^{-3}	-161.1	-27.2	0.0	-0.221
				-160.8	-26.9		-0.232
5.	0.1634	1.163×10^{-3}	1.252×10^{-3}	-144.9	-13.3		-0.740
				-155.7	-24.1		-0.334
6.	0.3099	1.163×10^{-3}	1.252×10^{-3}	-156.6	-24.9	-0.3	-0.308
				-155.7	-24.1		-0.342

TABLE 35 (con't.)

ID #	c_{Et4NC104}	$c_{\text{AgCl04}}(S_1)$	$c_{\text{AgCl04}}(S_2)$	E_{Cell}	E_j	$E_{j,H}$	$\text{Log}_m \gamma_{\text{Et4N}}$
					millivolts		
7.	0.0986	0.9597×10^{-4}	0.9458×10^{-4}	-163.3	-28.9	0.0	-0.170
				-156.1	-21.7		-0.440
8.	0.3099	1.163×10^{-4}	1.252×10^{-4}	-162.2	-30.0	-0.2	-0.119
				-163.2	-31.0		-0.082
$S_1 = \text{DMF} \quad S_2 = \text{DMSO}$							
1.	0.1224	1.146×10^{-2}	0.9458×10^{-2}	-220.5	-34.0	0.4	1.239
				-219.9	-33.4		1.212
				-220.8	-34.3		1.253
2.	0.4105	1.015×10^{-2}	1.252×10^{-2}	-209.0	-31.0	-1.3	1.004
				-208.0	-30.0		0.961
3.	0.1224	1.146×10^{-3}	0.9458×10^{-3}	-223.3	-34.8	0.7	1.025
				-219.6	-31.1		0.868
				-224.6	-36.1		1.079

TABLE 35 (con't.)

ID #	c_{Et4NC104}	$c_{\text{AgCl04}}(S_1)$	$c_{\text{AgCl04}}(S_2)$	E_{Cell}	E_j	$E_{j,H}$	$\text{Log}_m \gamma_{\text{Et4N}}$
					millivolts		
4.	0.4105	1.015×10^{-3}	1.252×10^{-3}	-218.1	-38.9	-1.0	1.252
				-209.2	-30.0		0.878
				-214.2	-34.9		1.084
				-214.6	-35.4		1.105
5.	0.1224	1.146×10^{-4}	0.9458×10^{-4}	-226.4	-37.2	-0.9	1.097
6.	0.4105	1.015×10^{-4}	1.252×10^{-4}	-205.0	-25.3	-1.0	0.674
				-211.7	-32.0		0.954
				-210.1	-30.4		0.887
		$S_1 = \text{DMF}$	$S_2 = \text{MeCN}$				
1.	0.1224	1.190×10^{-2}	0.9597×10^{-2}	-49.7	-4.8	1.1	1.528
2.	0.4105	1.042×10^{-2}	1.163×10^{-2}	-49.8	-1.9	-0.5	1.286
				-48.0	-0.1		1.208
3.	0.1224	1.190×10^{-3}	0.9597×10^{-3}	-60.2	-4.7	1.0	1.278

TABLE 35 (con't.)

ID #	c_{Et4NC104}	$c_{\text{AgCl04}}(S_1)$	$c_{\text{AgCl04}}(S_2)$	E_{Cell}	E_j millivolts	$E_{j,H}$	$\text{Log}_m \gamma_{\text{Et4N}}$
4.	0.4105	1.042×10^{-3}	1.163×10^{-3}	-41.2	6.4	-0.5	0.856
				-40.2	7.4		0.815
				-45.5	2.1		1.038
5.	0.1224	1.190×10^{-4}	0.9597×10^{-4}	-48.4	7.3	1.1	0.747
6.	0.4105	1.042×10^{-4}	1.163×10^{-4}	-36.4	11.1	-0.5	0.653
				-35.1	12.4		0.598
$S_1 = \text{PC} \quad S_2 = \text{DMF}$							
1.	0.1000	0.925×10^{-2}	1.015×10^{-2}	-350.2	-60.1	0.6	4.297
				-347.4	-57.3		4.164
2.	0.1000	0.925×10^{-3}	1.015×10^{-3}	-342.1	-55.3	-0.1	2.939
				-337.3	-50.5		2.742
$S_1 = \text{PC} \quad S_2 = \text{DMSO}$							
1.	0.1000	0.9289×10^{-2}	1.252×10^{-2}	-549.4	-81.4	-1.0	4.797

TABLE 35 (con't.)

ID #	c_{Et4NC104}	$c_{\text{AgCl04}}(S_1)$	$c_{\text{AgCl04}}(S_2)$	E_{Cell}	E_j	$E_{j,H}$	$\text{Log}_m \gamma_{\text{Et4N}}$
					millivolts		
2.	0.1000	0.9289×10^{-3}	1.252×10^{-3}	-545.2	-79.7	-1.1	3.548
				-543.6	-78.4		3.495
				-545.2	-79.7		3.548
		$S_1 = \text{PC}$	$S_2 = \text{MeCN}$				
1.	0.1000	1.367×10^{-2}	1.163×10^{-2}	-425.0	-78.2	-2.4	8.333
				-422.5	-75.7		8.196
2.	0.1000	1.367×10^{-3}	1.163×10^{-3}	-411.6	-68.0	-1.0	4.661
				-413.4	-69.8		4.737
3.	0.1000	1.367×10^{-4}	1.163×10^{-4}	-388.8	-46.3	0.8	3.420
				-393.3	-50.6		3.603

TABLE 36

Data and Results for the Calculation of the Transfer Activity Coefficients of Pr_4N^+
 (From S_1 to S_2).

ID #	$c_{\text{Pr}_4\text{NClO}_4}$	$c_{\text{AgClO}_4}(S_1)$	$c_{\text{AgClO}_4}(S_2)$	E_{Cell}	E_j	$E_{j,H}$	$\log_m \gamma_{\text{Pr}_4\text{N}}$
		$S_1 = \text{MeCN}$	$S_2 = \text{DMSO}$		millivolts		
1.	0.1990	0.9597×10^{-2}	0.9458×10^{-2}	-160.8	-28.4	-0.4	-0.243
2.	0.1968	0.9597×10^{-2}	0.9458×10^{-2}	-159.9	-27.5	-0.4	-0.281
3.	0.3971	1.163×10^{-2}	1.252×10^{-2}	-156.2	-26.1	-0.8	-0.353
				-154.0	-24.1		-0.438
4.	0.1990	0.9597×10^{-3}	0.9458×10^{-3}	-172.3	-38.4	-0.1	+0.099
				-169.7	-35.8		-0.010
5.	0.1968	0.9597×10^{-3}	0.9458×10^{-3}	-173.0	-39.1	-0.1	+0.128
6.	0.3971	1.163×10^{-3}	1.252×10^{-3}	-167.1	-35.5	-0.5	-0.010
				-170.2	-38.6		+0.120
7.	0.1990	0.9597×10^{-4}	0.9458×10^{-4}	-172.6	-38.2	0.0	+0.078
				-176.3	-41.9		+0.232

TABLE 36 (con't.)

ID #	c_{Pr4NC104}	$c_{\text{AgCl04}}(S_1)$	$c_{\text{AgCl04}}(S_2)$	E_{Cell}	E_j	$E_{j,H}$	$\text{Log}_m \gamma_{\text{Pr4N}}$
					millivolts		
8.	0.1968	0.9597×10^{-4}	0.9458×10^{-4}	-178.2	-43.8	0.0	+0.311
9.	0.3971	1.163×10^{-4}	1.252×10^{-4}	-177.3	-45.1	-0.4	+0.386
				-177.7	-45.5		+0.403
				-175.2	-43.0		+0.298

$S_1 = \text{DMF}$ $S_2 = \text{DMSO}$

1.	0.1803	1.107×10^{-2}	0.9458×10^{-2}	-222.9	-37.2	0.3	1.444
2.	0.4374	0.9863×10^{-2}	1.252×10^{-2}	-215.1	-38.3	-2.3	1.496
				-214.1	-37.3		1.448
				-216.3	-39.5		1.526
3.	0.1803	1.107×10^{-3}	0.9458×10^{-3}	-225.4	-37.8	0.9	1.250
				-226.3	-38.7		1.293

TABLE 36 (con't.)

ID #	c_{Pr4NC104}	$c_{\text{AgCl04}}(S_1)$	$c_{\text{AgCl04}}(S_2)$	E_{Cell}	E_j	$E_{j,H}$	$\text{Log}_m \gamma_{\text{Pr4N}}$
					millivolts		
4.	0.4374	0.9863×10^{-3}	1.252×10^{-3}	-221.1	-43.2	-1.9	1.628
				-222.2	-44.3		1.677
				-222.2	-44.3		1.677
				-219.1	-41.2		1.533
5.	0.1803	1.107×10^{-4}	0.9458×10^{-4}	-218.5	-30.2	-1.1	0.861
				-213.3	-25.0		0.614
6.	0.4374	0.9863×10^{-4}	1.252×10^{-4}	-217.4	-39.1	-1.8	1.419
				-220.0	-41.7		1.543
$S_1 = \text{DMF} \quad S_2 = \text{MeCN}$							
1.	0.1803	1.107×10^{-2}	0.9597×10^{-2}	-55.8	-2.5	0.9	1.627
2.	0.4374	0.9863×10^{-2}	1.163×10^{-2}	-47.1	-0.4	-1.1	1.506
				-47.7	-1.0		1.536
				-47.2	-0.5		1.511
				-47.1	-0.4		1.506

TABLE 36 (con't.)

ID #	c_{Pr4NC104}	$c_{\text{AgClO4}}(S_1)$	$c_{\text{AgClO4}}(S_2)$	E_{Cell}	E_j millivolts	$E_{j,H}$	$\text{Log}_m \gamma_{\text{Pr4N}}$
3.	0.1803	1.107×10^{-3}	0.9597×10^{-3}	-49.8	4.0	1.0	1.119
4.	0.4374	0.9863×10^{-3}	1.163×10^{-3}	-39.1	7.2	-1.2	1.060
				-42.3	4.0		1.212
5.	0.1803	1.107×10^{-4}	0.9597×10^{-4}	-43.8	10.1	1.0	0.811
6.	0.4374	0.9863×10^{-4}	1.163×10^{-4}	-29.6	16.5	-1.2	0.613
				-27.2	18.9		0.499
$S_1 = \text{PC} \quad S_2 = \text{DMF}$							
1.	0.4743	1.039×10^{-2}	0.9935×10^{-2}	-353.2	-59.8	1.7	3.784
				-354.2	-60.8		3.833
$S_1 = \text{PC} \quad S_2 = \text{DMSO}$							
1.	0.4700	1.388×10^{-2}	1.252×10^{-2}	-571.2	-93.9	1.5	4.921
				-568.8	-91.5		4.805

TABLE 36 (con't.)

ID #	c_{Pr4NC104}	$c_{\text{AgCl04}}(S_1)$	$c_{\text{AgCl04}}(S_2)$	E_{Cell}	E_j millivolts	$E_{j,H}$	$\text{Log}_m \gamma_{\text{Pr4N}}$
2.	0.4700	1.388×10^{-3}	1.252×10^{-3}	-569.6	-94.0	1.0	4.560
				-565.3	-89.7		4.359
				-567.2	-91.7		4.453
$S_1 = \text{PC} \quad S_2 = \text{MeCN}$							
1.	0.4700	1.024×10^{-2}	1.163×10^{-2}	-404.7	-64.9	0.6	5.958
				-404.5	-64.7		5.948
2.	0.4700	1.024×10^{-3}	1.163×10^{-3}	-392.8	-56.5	-0.4	5.272
				-388.7	-52.4		5.079
				-390.3	-54.0		5.154

TABLE 37

Data and Results for the Calculation of the Transfer Activity Coefficients of Bu_4N^+
 (From S_1 to S_2).

ID #	$c_{\text{Bu}_4\text{NClO}_4}$	$c_{\text{AgClO}_4}(S_1)$	$c_{\text{AgClO}_4}(S_2)$	E_{Cell}	E_j	$E_{j,H}$	$\text{Log}_m \gamma_{\text{Bu}_4\text{N}}$
		$S_1 = \text{MeCN}$	$S_2 = \text{DMSO}$		millivolts		
1.	0.1969	0.9597×10^{-2}	0.9458×10^{-2}	-165.5	-33.1	-0.5	-0.120
2.	0.4479	1.163×10^{-2}	1.252×10^{-2}	-157.9	-27.8	-1.1	-0.382
				-156.0	-25.9		-0.470
3.	0.1969	0.9597×10^{-3}	0.9458×10^{-3}	-175.0	-41.1	-0.1	+0.143
				-176.0	-42.6		+0.213
4.	0.4479	1.163×10^{-3}	1.252×10^{-3}	-167.2	-36.2	-0.7	-0.059
				-172.8	-41.2		+0.168
5.	0.1969	0.9597×10^{-4}	0.9458×10^{-4}	-180.0	-45.6	0.0	+0.332
				-179.4	-45.0		+0.305
6.	0.4479	1.163×10^{-4}	1.252×10^{-4}	-179.9	-47.7	-0.5	+0.456

TABLE 37 (con't.)

ID #	c_{Bu4NC104}	$c_{\text{AgCl04}}(S_1)$	$c_{\text{AgCl04}}(S_2)$	E_{Cell}	E_j	$E_{j,H}$	$\text{Log}_m \gamma_{\text{Bu4N}}$
		$S_1 = \text{DMF}$	$S_2 = \text{DMSO}$		millivolts		
1.	0.2222	1.107×10^{-2}	0.9458×10^{-2}	-226.3	-40.6	-0.4	1.694
2.	0.4364	0.9767×10^{-2}	1.252×10^{-2}	-219.2	-42.6	-2.8	1.866
				-213.1	-36.5		1.541
				-218.6	-42.0		1.835
3.	0.2222	1.107×10^{-3}	0.9458×10^{-3}	-224.2	-36.6	1.1	1.255
4.	0.4364	0.9767×10^{-3}	1.252×10^{-3}	-224.3	-46.6	-2.4	1.951
				-222.9	-45.2		1.878
5.	0.2222	1.107×10^{-4}	0.9458×10^{-4}	-222.3	-34.0	1.3	1.098
				-218.2	-29.9		0.885
		$S_1 = \text{DMF}$	$S_2 = \text{MeCN}$				
1.	0.2222	1.107×10^{-2}	0.9597×10^{-2}	-58.6	-5.3	+1.1	1.955

TABLE 37 (con't.)

ID #	c_{Bu4NC104}	$c_{\text{AgClO4}}(S_1)$	$c_{\text{AgClO4}}(S_2)$	E_{Cell}	E_j millivolts	$E_{j,H}$	$\text{Log}_m \gamma_{\text{Bu4N}}$
2.	0.4364	0.9767×10^{-2}	1.163×10^{-2}	-47.2	-0.7	-1.4	1.746
				-46.1	0.4		1.687
				-46.2	0.3		1.692
3.	0.2222	1.107×10^{-3}	0.9597×10^{-3}	-47.2	6.6	1.2	1.139
4.	0.4364	0.9767×10^{-3}	1.163×10^{-3}	-39.8	6.2	-1.5	1.292
				-39.9	6.1		1.297
				-40.3	5.7		1.318
5.	0.2222	1.107×10^{-4}	0.9597×10^{-4}	-41.2	12.7	1.2	0.806
6.	0.4364	0.9767×10^{-4}	1.163×10^{-4}	-31.6	14.3	-1.5	0.867
				-34.0	11.9		0.991
$S_1 = \text{PC} \quad S_2 = \text{DMF}$							
1.	0.6847	1.162×10^{-2}	1.091×10^{-2}	-354.6	-60.6	2.3	4.150
				-354.5	-60.5		4.144

TABLE 37 (con't.)

ID #	c_{Bu4NC104}	$c_{\text{AgCl04}}(S_1)$	$c_{\text{AgCl04}}(S_2)$	E_{Cell}	E_j millivolts	$E_{j,H}$	$\text{Log}_m \gamma_{\text{Bu4N}}$
2.	0.6847	1.162×10^{-3}	1.091×10^{-3}	-348.9	-58.1	1.1	3.785
				-351.9	-61.1		3.940
$S_1 = \text{PC} \quad S_2 = \text{DMSO}$							
1.	0.4362	0.9945×10^{-2}	1.252×10^{-2}	-564.4	-95.1	-1.0	5.639
				-560.0	-90.7		5.404
2.	0.4362	0.9945×10^{-3}	1.252×10^{-3}	-561.3	-94.1	-1.7	5.188
$S_1 = \text{PC} \quad S_2 = \text{MeCN}$							
1.	0.4362	0.9144×10^{-2}	1.1632×10^{-2}	-405.0	-67.9	-0.4	7.037
				-403.3	-66.2		6.941
2.	0.4362	0.9144×10^{-3}	1.1632×10^{-3}	-367.3	-33.8	-1.5	4.187
				-385.2	-51.7		5.119

TABLE 38

Transfer Activity Coefficients of R^+ Ions In Dipolar Aprotic Solvents (Molar Scale, 25°C).

$^{-}C_{AgClO_4}$	$\log_m \gamma_{Me_4N}$	$\log_m \gamma_{Et_4N}$	$\log_m \gamma_{Pr_4N}$	$\log_m \gamma_{Bu_4N}$
Reference solvent (S_1) = MeCN S_2 = DMSO				
10^{-2}	-0.85 ± 0.08	-0.61 ± 0.08	-0.33 ± 0.09	-0.32 ± 0.18
10^{-3}	-0.57 ± 0.14	-0.36 ± 0.20	$+0.07 \pm 0.07$	$+0.12 \pm 0.12$
10^{-4}	-0.34 ± 0.13	-0.28 ± 0.23	$+0.29 \pm 0.12$	$+0.36 \pm 0.08$
Reference solvent (S_1) = DMF S_2 = DMSO				
10^{-2}	1.09 ± 0.05	1.13 ± 0.14	1.48 ± 0.04	1.73 ± 0.15
10^{-3}	0.82 ± 0.20	1.04 ± 0.13	1.51 ± 0.19	1.70 ± 0.40
10^{-4}	0.33 ± 0.20	0.90 ± 0.18	1.11 ± 0.44	0.99 ± 0.15
Reference solvent (S_1) = DMF S_2 = MeCN				
10^{-2}	1.58 ± 0.07	1.34 ± 0.17	1.54 ± 0.05	1.77 ± 0.13
10^{-3}	1.05 ± 0.11	0.98 ± 0.21	1.13 ± 0.08	1.26 ± 0.08
10^{-4}	0.53 ± 0.08	0.67 ± 0.08	0.64 ± 0.16	0.89 ± 0.09
Reference solvent (S_1) = PC S_2 = DMF				
10^{-2}	4.05 ± 0.10	4.23 ± 0.09	3.81 ± 0.04	4.15 ± 0.01
10^{-3}	2.93 ± 0.00	2.84 ± 0.14		3.86 ± 0.11
10^{-4}	1.80			
Reference solvent (S_1) = PC S_2 = DMSO				
10^{-2}	4.40	4.80	4.86 ± 0.08	5.52 ± 0.17
10^{-3}	3.24 ± 0.01	3.53 ± 0.03	4.46 ± 0.10	5.19
10^{-4}	1.17 ± 0.02			

TABLE 38 (con't.)

$\sim^c\text{AgClO}_4$	$\log_m \gamma_{\text{Me}_4\text{N}}$	$\log_m \gamma_{\text{Et}_4\text{N}}$	$\log_m \gamma_{\text{Pr}_4\text{N}}$	$\log_m \gamma_{\text{Bu}_4\text{N}}$
Reference solvent (S_1) = PC		S_2 = MeCN		
10^{-2}	7.30 ± 0.02	8.26 ± 0.10	5.95 ± 0.01	7.00 ± 0.07
10^{-3}	3.83 ± 0.20	4.70 ± 0.05	5.17 ± 0.10	4.65 ± 0.66
10^{-4}	4.05	3.51 ± 0.13		

We may recall that while E' accounts for the difference between the standard Nernstian potentials of the two silver electrodes, E_j represents the liquid-junction potential caused primarily by the migration of ions across the interface of the two solvents. It can be seen in Tables 34-37, that the actual value of E_j shows a very definite dependence on the concentration of the electrolyte in each half-cell (here AgClO_4), the most pronounced difference being found for $\text{MeCN}|\text{DMSO}$ and $\text{DMF}|\text{MeCN}$ junction (~ 14 to 20mV for 100-fold change in c_{AgClO_4}). The E_j values calculated for junctions with PC show a slightly altered concentration dependence: very small changes for 10^{-2} and 10^{-3}M solutions, and then a sudden decrease in the magnitude of E_j by as much as 30mV , for junctions between 10^{-4}M AgClO_4 solutions. Only the $\text{PC}|\text{MeCN}$ interface resulted in E_j values steadily decreasing in magnitude with decreased c_{AgClO_4} . In fact, of all the junctions studied here, this junction showed the most pronounced dependence on c_{AgClO_4} .

In the assumed absence of solvent contribution to E_j (i.e., assuming $E_{j,s} = 0$), the value of E_j is represented by the sum of two terms, $E_{j,G}$ (the transfer-free energy term) (Equation 93) and $E_{j,H}$ (the Henderson term) (Equation 95). The sixth column in Tables 34-37 shows the values of $E_{j,H}$ calculated for the various interfaces. It is easily seen that the Henderson term is a very small component of the total liquid-junction potential.

Table 38 lists the transfer activity coefficients of R^+ ions calculated for each concentration of $AgClO_4$ and averaged over all the measurements taken at a given concentration. The standard deviation reported for each result reflects the lack of reproducibility of individual e.m.f. values, which is much greater than the uncertainty of a single measurement and of the data used to calculate the final value of $\log_m \gamma_R$. (See the discussion on error analysis in Section III-A-2-f.) The reproducibility of results obtained with a junction involving a salt bridge seem to be in general poorer than that of a simple junction between solutions of similar concentrations.

Discussion

The values of $\log_m \gamma_R$ in Table 38 show a definite concentration dependence. In an attempt to account for this, I investigated further the assumption of negligible $E_{j,s}$ in cells containing interfaces between dipolar aprotic solvents. It has been observed previously that the value of $E_{j,s}$ tends to increase in magnitude with decreasing concentration of the electrolyte in each half-cell. With that in mind, in calculating $\log_m \gamma_R$ from the data in $10^{-3}M$ solutions, I introduced an assumed value of " $E_{j,s}$ " of such magnitude as to bring about agreement with the results obtained for $10^{-2}M$ solutions. Another " $E_{j,s}$ correction" was used to bring the results from $10^{-4}M$ solutions in line with the $10^{-2}M$ values. In effect, the value of E_j calculated

from the e.m.f. of Cell XX was represented now by the sum $E_{j,G} + E_{j,H} + "E_{j,s}"$. Since the final calculations of $\log_m \gamma_R$ involve a simple rearrangement of the expression for $E_{j,G}$ (Equation 93), the value of $E_{j,G}$ was calculated by subtracting from E_j a calculated value for $E_{j,H}$ as well as a postulated value for " $E_{j,s}$ ". A summary of the " $E_{j,s}$ " correction factors found in this manner is presented in Table 39. All the numbers represent positive values of $E_{j,s}$, except for the MeCN|DMSO junction, which requires a negative value for this postulated $E_{j,s}$.

Cox, et al. (51) proposed to investigate the presence of $E_{j,s}$ by considering free energies of solution for the two solvents forming the junction. This proposal relates to the formulation for $E_{j,s}$ derived from Equations 8 and 9:

$$E_{j,s} = - \frac{1}{F} \sum t_s^r G_s$$

which in Cox's application is reduced to the summation of standard free energies of solution only, with the solvent transport numbers ignored. Subsequently, because of lack of data, Cox decided to look at the enthalpies of solution for each solvent pair, with the implicit assumption that entropy changes are negligible when two dipolar aprotic solvents mix.

TABLE 39

Suggested Correction Factors (in Millivolts) Used to Eliminate the Concentration Dependence of $\text{Log}_m \gamma_R$ Values in Dipolar Aprotic Solvents.

$\sim c$	Me_4N^+	Et_4N^+	Pr_4N^+	Bu_4N^+
MeCN DMSO (multiply by -1)				
10^{-2}	0	0	0	0
10^{-3}	5-10	5-10	5-10	5-10
10^{-4}	10-15	5-10	10-15	10-15
DMF DMSO				
10^{-2}	0	0	0	0
10^{-3}	5-10	5	5	5-10
10^{-4}	15-20	5-10	10-15	15
DMF MeCN				
10^{-2}	0	0	0	0
10^{-3}	10-15	5-10	5-10	10
10^{-4}	25	10-15	15-20	15-20
PC DMF				
10^{-2}	0	0	0	0
10^{-3}	40	30-40	10	
10^{-4}	60			

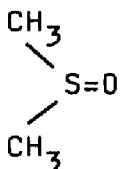
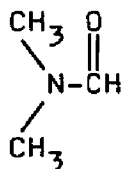
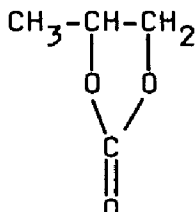
TABLE 39 (con't.)

$\sim c$	Me_4N^+	Et_4N^+	Pr_4N^+	Bu_4N^+
		PC DMSO		
10^{-2}	0	0	0	0
10^{-3}	30	30	10	10
10^{-4}	60			
		PC MeCN		
10^{-2}	0	0	0	0
10^{-3}	80	90	20	40
10^{-4}		120		

The enthalpies of mixing (51) calculated for the various pairs of dipolar aprotic solvents range from -0.05 kcal/mole (for PC|MeCN interface) to 0.74 kcal/mole (or PC|DMSO interface). By comparison, the same calculations for interfaces between nonaqueous solvents and water produce values at least an order of magnitude greater. From this, Cox, et al. (51) concluded that the $E_{j,s}$ contribution is very small for junctions between the dipolar aprotic solvents used here. While some of the correction factors used to account for the concentration dependence of $\log_m \gamma_R$ values are indeed fairly small, for junctions with PC they are as large as 100mV (Table 39). The calculations of $\log_m \gamma_R$ are sensitive not only to the exclusion of $E_{j,s}$, but also to the relationship between the various transport numbers used in each determination, so that the concentration dependence is rather complex. However, I believe that the assumption of negligible $E_{j,s}$ for all dipolar aprotic solvents pairs is not justified, specifically, when PC is present as one of the solvents. That conclusion seems logical when the extent to which PC differs from other solvents is considered. I already mentioned the low values of λ_1^0 in PC. Other properties, such as the dielectric constant, dipole moment, and viscosity (all listed in Table 40), set PC apart from other dipolar aprotic solvents.

TABLE 40

Properties of Dipolar Aprotic Solvents.*

	MeCN	DMSO	DMF	PC
Bp. °C	80.1	189	152.5	241.7
Mol. Wt. (M)	41	78	73.1	102.1
Density, d_4^{20} g/cm ³	0.7856	1.1014	0.9445	1.199 ^(a)
Dielectric constant ϵ (25°C)	39.3 ^(b) 35.87 ^(c)	46.7	41.9	64.92 ^(a) 65.1 ^(b)
Dipole moment, D	3.84	4.3	3.82	4.98
Viscosity (25°C) cP	0.336	2.000	0.793	2.53 ^(a) 2.48 ^(b)
Structure	CH ₃ -CN			

*Data from Ref. 75, except as noted.

(a) Reported by Salomon, et al. (87).

(b) Reported by Keller, et al. (60).

(c) Reported by Moreau (91).

There are very few literature data available which could be used to confirm (or disprove) the accuracy of the values of transfer activity coefficients for the four tetra-alkylammonium ions obtained here. Cox, et al. (85) report some transfer-free energies for Et_4N^+ and Bu_4N^+ ions (water is the reference) based on solubility studies and the $\text{Ph}_4\text{AsBPh}_4$ assumption. The results are shown in Table 41. It was possible to calculate the following values: for Et_4N^+ , $\log_m^{\text{MeCN}} \gamma^{\text{DMSO}} = -0.7$ (compared with our average value of -0.4), $\log_m^{\text{DMF}} \gamma^{\text{DMSO}} = -0.7$ (compared with our value of $+1.0$) and $\log_m^{\text{DMF}} \gamma^{\text{MeCN}} = -0.7$ (compared with our average value of 1.0); for Bu_4N^+ , only one transfer activity coefficient can be calculated, $\log_m^{\text{DMF}} \gamma^{\text{MeCN}} = -0.81$ (compared with our average value of $+1.3$).

As these comparisons show, the results obtained here do not in general agree with the few available literature data. Two points need to be made here. First, the values of the transfer activity coefficients reported by Cox and coworkers (85), based on solubility determinations, are of unknown precision and accuracy. Second, the values obtained in this study show an internal consistency for the solvent pairs chosen from DMF, DMSO, and MeCN. In an internal consistency test, the $\log_m^1 \gamma^2_R$ value is calculated using an expression similar to Equation 99:

$$\log_m^1 \gamma^2_R = \log_m^3 \gamma^2_R - \log_m^3 \gamma^1_R \quad (102)$$

TABLE 41

Comparison of $\log_m \gamma_R$ Obtained Here with Literature (85) Values.

Transfer	$\log_m \gamma_{Et4N}$		$\log_m \gamma_{Bu4N}$	
	this study	lit. value	this study	lit. value
MeCN→DMSO	-0.4	-0.7		
DMF→DMSO	+1.0	-0.7		
DMF→MeCN	+1.0	-0.07	1.3	-0.81
PC→DMF	+3.5	-0.6 ^(a)		
PC→DMSO	+4.2	-1.3 ^(a)		
PC→MeCN	+5.5	-0.8 ^(a)		

^(a) Calculated using $\log_m \gamma^{w, PC}$ reported by Goldberg and Popovych (49).

where the transfer activity coefficients of R on the right hand side are estimated from experimental data. The calculated value of $\log_m^1 \gamma_R^2$ is then compared with the value of $\log_m^1 \gamma_R^2$ obtained using experimental data determined for the solvent-pair $S_1|S_2$, and independent of the other two pairs of solvents present in Equation 102. If the calculated value of $\log_m^1 \gamma_R^2$ agrees with the experimentally estimated value of $\log_m^1 \gamma_R^2$, within limits imposed by the experimental errors, then we can say that the values of $\log_m^1 \gamma_R^2$, $\log_m^3 \gamma_R^2$ and $\log_m^3 \gamma_R^1$ show internal consistency. For example, for the Bu_4N^+ ion, using results obtained in 10^{-3}M solutions, $\log_m^{\text{DMF}} \gamma^{\text{DMSO}} - \log_m^{\text{MeCN}} \gamma^{\text{DMSO}} = 1.70 - 0.12 = 1.58 \pm 0.42$, compared with the experimental value for $\log_m^{\text{DMF}} \gamma^{\text{MeCN}}$ of 1.26 ± 0.08 , which is fair agreement within experimental error. On the other hand, when PC is used as the reference solvent, we get for $\log_m^{\text{PC}} \gamma^{\text{MeCN}} - \log_m^{\text{PC}} \gamma^{\text{DMF}} = 4.65 - 3.86 = 0.79 \pm 0.7$ for a calculated value of $\log_m^{\text{DMF}} \gamma^{\text{PC}}$. Although the relative error of the calculated value based on PC is high, at least it places the value of $\log_m^{\text{DMF}} \gamma^{\text{MeCN}}$ in the same range as the one obtained in the preceding calculation (based on DMSO). Similar results are obtained when other concentrations and other R^+ ions are used: there is a fair agreement among calculated and experimental values of transfer activity coefficients for the $\text{MeCN}|\text{DMSO}$, $\text{DMF}|\text{DMSO}$, and $\text{DMF}|\text{MeCN}$ pairs, and poorer agreement among values obtained with PC as one of the solvents.

Transfer activity coefficients of the picrate ion.

Preliminary calculations.

The same solutions of AgClO_4 in various dipolar aprotic solvents that were used to form junctions via a RClO_4 salt bridge were also used to study junctions formed with a RPi salt bridge. Equation 94 expresses the relationship between the $E_{j,G}$ component of E_j and the transport numbers as well as the transfer activity coefficients of all the relevant ions for a cell involving a RPi salt bridge:

$$E_{j,G} = -59.16 (t_{\text{Ag}} \log_m \gamma_{\text{Ag}} + t_{\text{R}} \log_m \gamma_{\text{R}} - t_{\text{Pi}} \log_m \gamma_{\text{Pi}} - t_{\text{ClO}_4} \log_m \gamma_{\text{ClO}_4}) \quad (94)$$

If we accept the values of the transfer activity coefficients for the tetralkylammonium ions estimated in the preceding section of this thesis, then using those values in Equation 94 would allow us to calculate the transfer activity coefficients of the picrate ion. This indirect approach is particularly useful because there are very few literature data available on the transfer activity coefficients of the picrate ion in dipolar aprotic solvents. Of course, this method of determining $\log_m \gamma$ of an ion is general and can be used for any ion that can exist as a constituent of a salt-bridge electrolyte.

The experimental values of the e.m.f. of Cell XX using RPi as a salt-bridge electrolyte were combined with the previously determined $\log_m \gamma_{\text{R}}$ values (different for each

concentration of AgClO_4) and other pertinent data, and transfer activity coefficients of the picrate ion were thus calculated for all the solvent pairs studied here. The results are shown in Tables 42-45, one table for each tetra-alkylammonium ion, starting with Me_4N^+ in Table 42. The results are tabulated in a manner similar to that used previously for the R^+ ions (Tables 34-37).

TABLE 42

Data and Results for the Calculation of the Transfer
Activity Coefficients of Pi^- Ion Using $\log_m \gamma_{\text{Me4N}^+}$.

ID #	$c_{\text{Me4N}^+ \text{Pi}^-}$	c_{AgClO_4} S_1	c_{AgClO_4} S_2	E_{Cell}	E_j	$\log_m \gamma_{\text{Pi}^-}$
		$S_1 = \text{MeCN}$	$S_2 = \text{DMSO}$		millivolts	
1.	0.1039	0.9597×10^{-2}	0.9458×10^{-2}	-141.3	-8.9	-1.446
				-140.9	-8.5	-1.430
2.	0.1039	0.9597×10^{-3}	0.9597×10^{-3}	-151.2	-17.3	-1.358
				-149.4	-15.5	-1.290
				-148.7	-14.3	-1.245
3.	0.1039	0.9597×10^{-4}	0.9597×10^{-4}	-153.3	-18.9	-1.124
				-151.4	-17.0	-1.053
				-145.9	-11.5	-0.846
				-150.1	-15.7	-1.004
				-151.6	-17.2	-1.060
		$S_1 = \text{DMF}$	$S_2 = \text{DMSO}$			
1.	0.1385	1.206×10^{-2}	1.252×10^{-2}	-202.0	-20.8	0.210
				-201.2	-19.4	0.239
2.	0.1385	1.206×10^{-3}	1.252×10^{-3}	-197.9	-15.1	0.312
				-200.3	-17.5	0.229
3.	0.1385	1.206×10^{-4}	1.252×10^{-4}	-201.0	-17.6	-0.266
				-195.8	-12.4	-0.086
				-192.4	-9.0	+0.032

TABLE 42 (con't.)

ID #	$C_{Me_4NPF_6}$	C_{AgClO_4} S_1	C_{AgClO_4} S_2	E_{Cell} millivolts	E_j millivolts	$\log_m \gamma_{PF_6}$
		$S_1 = DMF$	$S_2 = MeCN$			
1.	0.1385	1.206×10^{-2}	1.163×10^{-2}	-51.0	0.0	1.399
				-51.9	-0.9	1.363
2.	0.1385	1.206×10^{-3}	1.163×10^{-3}	-49.1	2.0	1.143
				-49.1	1.8	1.136
3.	0.1385	1.206×10^{-4}	1.163×10^{-4}	-44.0	7.2	0.793
				-39.7	11.5	0.941
				-41.0	10.2	0.897
		$S_1 = PC$	$S_2 = DMF$			
1.	0.1251	1.055×10^{-2}	1.040×10^{-2}	-366.0	-73.3	0.640
				-364.5	-71.8	0.703
2.	0.1251	1.055×10^{-3}	1.040×10^{-3}	-361.7	-72.2	0.550
				-362.3	-72.8	0.528
		$S_1 = PC$	$S_2 = DMSO$			
1.	0.1251	1.043×10^{-2}	1.252×10^{-2}	-548.4	-78.0	0.995
				-552.5	82.1	0.830
2.	0.1251	1.043×10^{-3}	1.252×10^{-3}	-547.2	-78.8	0.689
				-548.1	-79.7	0.656
3.	0.1251	1.043×10^{-4}	1.252×10^{-4}	-520.7	-53.0	0.500
				-520.8	-53.1	0.504

TABLE 42 (con't.)

ID #	C_{Me4NP1}	C_{AgClO4} S_1	C_{AgClO4} S_2	E_{Cell} millivolts	E_j	$\log_m \gamma_{P1}$
		$S_1 = PC$	$S_2 = MeCN$			
1.	0.1251	1.179×10^{-2}	1.163×10^{-2}	-417.0	-73.8	2.502
2.	0.1251	1.014×10^{-2}	1.163×10^{-2}	-414.3	-74.7	2.556
3.	0.1251	1.179×10^{-3}	1.163×10^{-3}	-396.1	-56.2	1.932
4.	0.1251	1.014×10^{-3}	1.163×10^{-3}	-405.3	-69.2	1.465

TABLE 43

Data and Results for the Calculation of the Transfer
Activity Coefficients of Pi^- Ion Using $\log_m \gamma_{\text{Et4N}^+}$

ID #	$c_{\text{Et4N}^+\text{Pi}^-}$	c_{AgClO_4} S_1	c_{AgClO_4} S_2	E_{Cell} millivolts	E_j millivolts	$\log_m \gamma_{\text{Pi}^-}$
		$S_1 = \text{MeCN}$	$S_2 = \text{DMSO}$			
1.	0.1316	0.9597×10^{-2}	0.9458×10^{-2}	-149.9	-17.5	-1.371
				-149.6	-17.2	-1.360
2.	0.1316	0.9597×10^{-3}	0.9597×10^{-3}	-161.3	-27.4	-1.383
				-160.3	-26.4	-1.347
				-158.0	-24.1	-1.265
3.	0.1316	0.9597×10^{-4}	0.9597×10^{-4}	-160.9	-26.5	-1.255
				-153.1	-18.7	-0.978
				-162.6	-28.2	-1.315
		$S_1 = \text{DMF}$	$S_2 = \text{DMSO}$			
1.	0.1558	1.125×10^{-2}	1.252×10^{-2}	-203.2	-23.5	0.107
				-201.7	-22.0	0.159
2.	0.1558	1.125×10^{-3}	1.252×10^{-3}	-206.7	-25.6	0.120
				-200.3	-19.2	0.331
3.	0.1558	1.125×10^{-4}	1.252×10^{-4}	-199.6	-18.0	0.256
				-189.8	-8.2	0.578

TABLE 43 (con't.)

ID #	C_{Et4NPi}	C_{AgClO4} S_1	C_{AgClO4} S_2	E_{Cell} millivolts	E_j millivolts	$\log_m \gamma_{Pi}$
		$S_1 = DMF$	$S_2 = MeCN$			
1.	0.1558	1.125×10^{-2}	1.163×10^{-2}	-44.1	5.4	1.255
				-46.4	3.1	1.169
2.	0.1558	1.125×10^{-3}	1.163×10^{-3}	-41.6	7.9	1.182
				-34.0	15.5	1.435
				-36.3	13.2	1.358
3.	0.1558	1.125×10^{-4}	1.163×10^{-4}	-35.1	14.3	1.096
				-31.6	17.8	1.211
		$S_1 = PC$	$S_2 = DMF$			
1.	0.1732	0.925×10^{-2}	1.015×10^{-2}	-365.9	-75.8	0.904
				-361.7	-71.6	1.067
2.	0.1732	0.925×10^{-3}	1.015×10^{-3}	-359.7	-72.9	0.350
				-356.7	-69.9	0.454
				-351.9	-65.1	0.622
		$S_1 = PC$	$S_2 = DMSO$			
1.	0.2108	0.9289×10^{-2}	1.252×10^{-2}	-547.0	-79.4	1.603
				-551.1	-83.5	1.452
2.	0.2108	0.9289×10^{-3}	1.252×10^{-3}	-544.5	-79.0	0.884
				-548.2	-82.7	0.755

TABLE 43 (con't.)

ID #	C_{Et4NPi}	C_{AgClO4} S_1	C_{AgClO4} S_2	E_{Cell} millivolts	E_j millivolts	$\log_m \gamma_{\text{Pi}}$
		$S_1 = \text{PC}$	$S_2 = \text{MeCN}$			
1.	0.2108	1.367×10^{-2}	1.163×10^{-2}	-429.0	-82.2	3.727
				-425.0	-78.2	3.894
2.	0.2108	1.367×10^{-3}	1.163×10^{-3}	-418.1	-74.5	2.098
				-420.0	-76.4	2.081
3.	0.2108	1.367×10^{-4}	1.163×10^{-4}	-406.7	-64.2	1.413
				-401.0	-58.5	1.610

TABLE 44

Data and Results for the Calculation of the Transfer
Activity Coefficients of Pi^- Ion Using $\log_m \gamma_{\text{Pr4N}^+}$

ID #	$c_{\text{Pr4N}^+ \text{Pi}^-}$	c_{AgClO_4} S_1	c_{AgClO_4} S_2	E_{Cell}	E_j millivolts	$\log_m \gamma_{\text{Pi}^-}$
		$S_1 = \text{MeCN}$	$S_2 = \text{DMSO}$			
1.	0.1622	0.9597×10^{-2}	0.9458×10^{-2}	-160.6	-28.2	-1.288
				-155.7	-23.3	-1.123
				-158.3	-25.9	-1.210
2.	0.1622	1.163×10^{-2}	1.252×10^{-2}	-152.2	-22.2	-1.104
				-151.7	-21.6	-1.083
				-151.1	-21.0	-1.063
				-153.3	-23.2	-1.138
3.	0.1523	1.163×10^{-2}	1.252×10^{-2}	-148.3	-18.2	-0.972
4.	0.1622	0.9597×10^{-3}	0.9458×10^{-3}	-169.2	-35.3	-1.089
				-164.3	-30.4	-0.931
5.	0.1622	1.163×10^{-3}	1.252×10^{-3}	-154.3	-22.7	-0.685
6.	0.1523	1.163×10^{-3}	1.252×10^{-3}	-154.0	-22.4	-0.675
				-160.3	-28.7	-0.880
				-160.3	-28.7	-0.880
7.	0.1523	1.163×10^{-4}	1.252×10^{-4}	-166.8	-34.6	-0.863
				-174.1	-41.9	-1.098
				-172.4	-40.2	-1.043

TABLE 44 (con't.)

ID #	C _{Pr4NPi}	C _{AgClO4} S ₁	C _{AgClO4} S ₂	E _{Cell} millivolts	E _j	log _m γ _{Pi}
		S ₁ = DMF	S ₂ = DMSO			
1.	0.1295	1.122x10 ⁻²	1.252x10 ⁻²	-209.3	-29.7	-0.006
				-210.0	-30.4	-0.029
2.	0.1295	1.122x10 ⁻³	1.252x10 ⁻³	-210.7	-29.6	0.244
				-205.2	-24.1	0.410
				-213.1	-32.0	0.171
3.	0.1295	1.122x10 ⁻⁴	1.252x10 ⁻⁴	-196.6	-15.0	0.394
				-198.7	-17.1	0.331
				-207.2	-25.6	0.076
		S ₁ = DMF	S ₂ = MeCN			
1.	0.1295	1.122x10 ⁻²	1.163x10 ⁻²	-41.9	7.6	1.201
				-40.1	9.4	1.265
2.	0.1295	1.122x10 ⁻³	1.163x10 ⁻³	-38.2	11.2	1.186
				-35.8	13.6	1.259
3.	0.1295	1.122x10 ⁻⁴	1.163x10 ⁻⁴	-29.9	19.5	1.075
				-31.1	18.3	1.039
				-30.0	19.4	1.072
		S ₁ = PC	S ₂ = DMF			
1.	0.3008	1.039x10 ⁻²	0.9935x10 ⁻²	-369.7	-76.3	0.285
				-366.8	-73.4	0.381
2.	0.3008	1.039x10 ⁻³	0.9935x10 ⁻³	-364.2	-74.0	
				-364.1	-73.9	

TABLE 44 (con't.)

ID #	$C_{\text{Pr4N}^+\text{Pi}^-}$	C_{AgClO_4} S_1	C_{AgClO_4} S_2	E_{Cell} millivolts	E_j millivolts	$\log_{10} \gamma_{\text{Pi}}$
		$S_1 = \text{PC}$	$S_2 = \text{DMSO}$			
1.	0.3105	1.388×10^{-2}	1.252×10^{-2}	-576.9	-99.6	0.398
				-571.7	-94.4	0.568
2.	0.3105	1.388×10^{-3}	1.252×10^{-3}	-576.6	-101.0	0.514
				-572.9	-97.3	0.623
		$S_1 = \text{PC}$	$S_2 = \text{MeCN}$			
1.	0.3105	1.024×10^{-2}	1.163×10^{-2}	-408.3	-68.5	1.555
				-408.9	-69.1	1.534
2.	0.3105	1.024×10^{-3}	1.163×10^{-3}	-398.1	-61.8	2.219

TABLE 45

Data and Results for the Calculation of the Transfer
Activity Coefficients of Pi^- Ion Using $\log_m \gamma_{\text{Bu4N}^+}$

ID #	$c_{\text{Bu4N}^+\text{Pi}}$	c_{AgClO_4} S_1	c_{AgClO_4} S_2	E_{Cell}	E_j millivolts	$\log_m \gamma_{\text{Pi}}$
		$S_1 = \text{MeCN}$	$S_2 = \text{DMSO}$			
1.	0.1900	1.163×10^{-2}	1.252×10^{-2}	-154.0	-23.9	-1.071
				-155.3	-25.2	-1.113
				-156.3	-26.2	-1.144
				-155.9	-25.8	-1.132
2.	0.2386	1.163×10^{-2}	1.252×10^{-2}	-154.7	-24.6	-1.078
				-156.2	-26.1	-1.126
3.	0.1900	1.163×10^{-3}	1.252×10^{-3}	-159.0	-27.4	-0.746
				-166.5	-34.9	-0.984
4.	0.2386	1.163×10^{-3}	1.252×10^{-3}	-163.3	-31.7	-0.885
				-167.2	-35.6	1.003
				-167.0	-35.4	-0.997
5.	0.2386	1.163×10^{-4}	1.252×10^{-4}	-176.0	-43.8	-1.049
				-173.5	-41.3	-0.973
				-174.6	-42.4	-1.007
		$S_1 = \text{DMF}$	$S_2 = \text{DMSO}$			
1.	0.1514	1.122×10^{-2}	1.252×10^{-2}	-209.9	-30.3	0.082
				-211.0	-31.4	0.048
				-205.8	-26.2	0.207

TABLE 45 (con't.)

ID #	C_{Bu4NPi}	C_{AgClO4} S_1	C_{AgClO4} S_2	E_{Cell} millivolts	E_j millivolts	$\log_m \gamma_{Pi}$
2.	0.1514	1.122×10^{-3}	1.252×10^{-3}	-215.7	-34.6	0.125
				-214.2	-33.1	0.168
3.	0.1514	1.122×10^{-4}	1.252×10^{-4}	-205.9	-24.3	-0.036
				-215.7	-31.1	-0.314
				-211.0	-26.4	-0.181
				-211.0	-26.4	-0.181
		$S_1 = DMF$	$S_2 = MeCN$			
1.	0.1514	1.122×10^{-2}	1.163×10^{-2}	-43.0	6.5	1.192
				-43.0	6.5	1.192
				-41.3	8.2	1.248
				-45.8	3.7	1.099
2.	0.1514	1.122×10^{-3}	1.163×10^{-3}	-34.0	15.4	1.271
				-34.3	15.1	1.263
3.	0.1514	1.122×10^{-4}	1.163×10^{-4}	-25.3	24.1	1.278
				-26.9	22.5	1.233
				-27.6	21.8	1.213
				-30.5	18.9	1.131
				-32.2	17.2	1.082
		$S_1 = PC$	$S_2 = DMF$			
1.	0.4650	1.162×10^{-2}	1.091×10^{-2}	-370.3	-76.3	0.395
				-369.9	-75.9	0.407

TABLE 45 (con't.)

ID #	$C_{Bu4N^+Pi^-}$	C_{AgClO_4} S_1	C_{AgClO_4} S_2	E_{Cell} millivolts	E_j	$\log_m \gamma_{Pi}$
2.	0.4650	1.162×10^{-3}	1.091×10^{-3}	-369.7	-78.9	0.436
				-367.9	-77.1	0.489
		$S_1 = PC$	$S_2 = DMSO$			
1.	0.3974	0.9945×10^{-2}	1.252×10^{-2}	-566.0	-96.7	0.950
				-565.0	-96.0	0.970
2.	0.3974	0.9945×10^{-3}	1.252×10^{-3}	-566.2	-99.0	0.754
		$S_1 = PC$	$S_2 = MeCN$			
1.	0.3974	0.9144×10^{-2}	1.163×10^{-2}	-405.2	-68.1	1.993
				-406.4	-69.3	1.973
2.	0.3974	0.9144×10^{-3}	1.163×10^{-3}	-385.8	-52.3	1.667
				-395.0	-61.5	1.398
				-400.8	-67.3	1.228

It was found that combining the experimental e.m.f. values for Cell XX with a RClO_4 salt bridge interposed between AgClO_4 solutions of concentration $\underline{c}$ with the e.m.f. values for the same cell, but with a RPI salt bridge interposed between the AgClO_4 solutions of the same concentration $\underline{c}$ resulted in calculated $\log_m \gamma_{\text{PI}}$ values which showed a greatly reduced dependence on the concentration of AgClO_4 . A conclusion may be drawn from this to the effect that the same factors that contribute to the concentration dependence of $\log_m \gamma_{\text{R}}$ values obtained via the RClO_4 salt bridge operate on the systems employing the RPI salt bridge. Since these factors are presumably different in magnitude for each concentration of AgClO_4 , the use of $\log_m \gamma_{\text{R}}$ values calculated separately for each c_{AgClO_4} (instead of some average value) in the calculations of $\log_m \gamma_{\text{PI}}$ seems to diminish the effect these factors have on the calculated values of $\log_m \gamma_{\text{PI}}$. One factor which would indeed behave in the way described in the preceding paragraph is the presence of $E_{j,s}$, the contribution of solvent molecules to E_j . The calculations of $\log_m \gamma_{\text{R}}$ and of $\log_m \gamma_{\text{PI}}$ are based on the premise that the $E_{j,s} = 0$. We have shown before (Table 39) that an inclusion of some value for $E_{j,s}$ in the calculations of $\log_m \gamma_{\text{R}}$ results in a disappearance of the concentration dependence of $\log_m \gamma_{\text{R}}$. Instead, we now have values of $E_{j,s}$, which depend on c_{AgClO_4} in a manner consistent with the behavior of $E_{j,s}$ observed by Goldberg (48) and by this author for junctions between water and methanol-water solvents (the magnitude of $E_{j,s}$ increases

with a decreasing concentration of the electrolyte). If we assume the existence of $E_{j,s}$ of some unknown magnitude δ (in mV), then using Equation 96 results in a value of $\log_m \gamma_R$ which differs from the "true" value by $\delta/59.16 t_R$. (The "true", or corrected value of $\log_m \gamma_R$ refers to the value obtained if the $E_{j,s}$ was included in the formulation for E_j of Cell XX.) For a hypothetical case of $E_{j,s} = 10\text{mV}$, and $t_R = 0.5$, that difference between the calculated and the "true" value of $\log_m \gamma_R$ is equal to 0.34 logarithmic units. However, when that calculated value of $\log_m \gamma_R$ is subsequently used in Equation 98 to calculate $\log_m \gamma_{Pi}$, that uncorrected value of $\log_m \gamma_{Pi}$ differs from the "true" value of $\log_m \gamma_{Pi}$ (obtained using Equation 98 with the "true" value of $\log_m \gamma_R$ as well as with inclusion of $E_{j,s}$ in the formulation of E_j) by the amount equal to $\delta \times (t'_R - t_R) / 59.16 t_{Pi} \times t_R$, where t'_R is the transport number of R^+ ion in R_{Pi} . In the extreme case of $t'_R = t_R$, that difference of "true" and uncorrected values of $\log_m \gamma_{Pi}$ is reduced to 0. In other cases it is nevertheless very small when compared to the difference between the "true" and corrected value of $\log_m \gamma_R$ calculated by the procedure outlined here. To summarize the preceding discussion, the use of $\log_m \gamma_R$ values calculated for each concentration of AgClO_4 in the calculations of $\log_m \gamma_{Pi}$ for the same C_{AgClO_4} tends to diminish the error in the value of $\log_m \gamma_{Pi}$ resulting from the assumption of negligible $E_{j,s}$. Since the value of $E_{j,s}$ has been shown to depend on the concentration of the electrolyte crossing the boundary be-

tween the two solvents, it is logical to expect that the values of $\log_m \gamma_R$ calculated with the presumably unjustified assumption of $E_{j,s} = 0$ will be also concentration-dependent, (as indeed is the case). The concentration dependence is still evident in the values of $\log_m \gamma_{Pi}$ (although greatly diminished), and it may be related to the very simple approach of calculating the transport numbers, described previously. In addition, the preceding analysis is based on the premise that the value of $E_{j,s}$ for the interface between solutions of $RClO_4$ and $AgClO_4$ is the same as for the interface between solutions of RPI and $AgClO_4$. While the only difference between the two interfaces is the presence of the PI^- ion instead of the ClO_4^- ion, that fact may contribute to different values of $E_{j,s}$ for each interface, although the difference may be slight if both ions are solvated weakly by the solvents present in the interphase region. The slightly different values of $E_{j,s}$ may be accompanied by somewhat different concentration dependence of $E_{j,s}$ present at the interface between $RClO_4$ and $AgClO_4$ solutions as compared to $E_{j,s}$ present at the interface between RPI and $AgClO_4$ solutions.

In conclusion, the concentration dependence of $\log_m \gamma_R$ values estimated from the e.m.f. measurements of Cell XX can be accounted for by assuming a definite value for $E_{j,s}$, the contribution of solvent molecules to E_j present at the interface of the two solvents in Cell XX. This hypothetical " $E_{j,s}$ " changes in magnitude with the c_{AgClO_4} in a manner

observed previously for methanol-water systems. Furthermore, the greatly reduced concentration dependence of the $\log_m \gamma_{Pi}$ values calculated using Equation 98 is consistent with the assumption of $E_{j,s} \neq 0$. While this analysis does not constitute a proof that $E_{j,s}$ is indeed present, it does indicate a presence of a factor which has the same effect as $E_{j,s}$, when the results of calculations using Equation 96 and 98 are considered.

A test of the "negligible E_j " assumption proposed by Alexander (25).

It is of particular interest to consider the values of E_j obtained in the present study for $\text{Et}_4\text{N}^+\text{Pi}^-$ (Table 43). Alexander (25) recommended the use of the extrathermodynamic assumption of a "negligible" (less than 20mV) liquid-junction potential in e.m.f. cells composed of two silver electrodes in 0.01M AgClO_4 solutions in a pair of solvents connected by a bridge of 0.1M $\text{Et}_4\text{N}^+\text{Pi}^-$ in that solvent of the pair which was the weaker solvator of silver ions. On the basis of our data in Table 43, we are now in a position to check Alexander's assumption for the solvent pairs used in this study. Thus, for the $\text{MeCN}|\text{DMSO}$ interface, the total E_j ranges from -17mV (for 10^{-2}M solutions) to -28mV (for 10^{-4}M solutions); the E_j values for the $\text{DMF}|\text{DMSO}$ interface range from -24mV to -8mV, while the $\text{DMF}|\text{MeCN}$ interface produces E_j values of less than 17mV. It would seem that Alexander's assumption of E_j being less than 20mV in magnitude may hold

up in general for the three solvent-pairs mentioned here; even though some of the E_j values are greater than 20mV, the differences are not large and may be due partly to the experimental error. However, a bigger problem is encountered when PC is present at the interface - the calculated E_j values reach ~80mV in magnitude, which is scarcely negligible, even by Alexander's standards. Of course the accuracy of our E_j calculations depends directly on the accuracy of the transfer activity coefficients for the Ag^+ ion. There has been a considerable amount of work done in order to estimate $\log_m \gamma_{\text{Ag}}$, based on various extrathermodynamic assumptions, but the results do not agree. The calculations performed in this study used $\log_m \gamma_{\text{Ag}}$ values estimated from solubility products of AgBPh_4 (84) and the transfer activity coefficients of BPh_4^- ion, which is part of the "reference electrolyte". As an example of $\log_m \gamma_{\text{Ag}}$ values produced by another method, we can look at the results of polarographic studies reported by Matsuura (47) and described here earlier (Table 3). For example, if the $\log_m \gamma_{\text{Ag}}$ reported by Matsuura were to be used (wherever possible), the calculated values of E_j for the DMF|DMSO interface (with $\log_m \gamma_{\text{Ag}} = -2.87$ compared to our value of -3.12) would be 14.2 mV lower than the values listed in Table 43, thus placing them outside the limits of "negligible E_j " of ± 20 mV proposed by Alexander. On the other hand, the E_j values calculated for the PC|DMSO interface (with $\log_m \gamma_{\text{Ag}} = -8.84$ compared to our value of 7.98) would be 51mV higher and for the PC/DMF interface

(with $\log_m \gamma_{Ag} = -5.97$ compared to our value of -4.86) 66mV higher than the corresponding E_j values listed in Table 43, making the E_j values for the last two solvent-pairs calculated with Matsuura's $\log_m \gamma_{Ag}$ values close to 20mV and thus negligible according to Alexander (25). This author feels that $\log_m \gamma_{Ag}$ values obtained from the solubility products of $AgBPh_4$ are in principle more accurate than those estimated by other methods. However, the available values of K_{sp} of $AgBPh_4$ in most of the solvents used in this study are described as tentative only (84). We have seen that a change of one logarithmic unit in the value of $\log_m \gamma_{Ag}$ results in a change of ~60mV in the calculated value of E_j . While we hope that the definitive values of $\log_m \gamma_{Ag}$ will not differ much from the values used by us, the conclusions drawn here regarding the magnitude of E_j at the interface between a solution of $Et_4N^+P^-$ and a solution of $AgClO_4$ in two different dipolar aprotic solvents, respectively, have to be regarded as tentative only, subject to revision when those definitive values of $\log_m \gamma_{Ag}$ are reported.

Final values of $\log_m \gamma_{P^-}$.

Table 46 lists the $\log_m \gamma_{P^-}$ values averaged for each concentration of $AgClO_4$. As before, the standard deviation reported here represents the scattering of individual e.m.f. measurements when fresh junctions were formed with the same solutions. Finally, values of $\log_m \gamma_{P^-}$ evaluated at a given concentration of $AgClO_4$ were averaged over the four R^+

cations used and are given in the last column of Table 46. While some concentration dependence is still observable, it is very weak and in some cases, nonexistent.

While the single step version of the new method of determining transfer activity coefficients of single ions using a cell with a salt bridge (such as one used for the R^+ ions) needs to be studied further, the secondary method, here illustrated for the medium effects of the PI^- ion in dipolar aprotic solvents, produces values which are in excellent agreement with each other, both as a function of concentration of $AgClO_4$ and as a function of the nature of R^+ ion used as the intermediate.

TABLE 46

Transfer Activity Coefficients of Pi^- Ion in Dipolar Aprotic Solvents.

Direction of Transfer	$\sim^c\text{AgClO}_4$	-----C a l c u l a t e d-----				$\log_m \gamma_{\text{Pi}}$ (overall average)
		using $\log_m \gamma_{\text{Me}_4\text{N}}$	using $\log_m \gamma_{\text{Et}_4\text{N}}$	using $\log_m \gamma_{\text{Pr}_4\text{N}}$	using $\log_m \gamma_{\text{Bu}_4\text{N}}$	
MeCN→DMSO	10^{-2}	-1.44 ± 0.01	-1.37 ± 0.01	-1.12 ± 0.09	-1.11 ± 0.03	-1.26
	10^{-3}	-1.30 ± 0.06	-1.33 ± 0.06	-0.86 ± 0.16	-0.92 ± 0.11	-1.10
	10^{-4}	-1.02 ± 0.10	-1.18 ± 0.18	-1.00 ± 0.12	-1.01 ± 0.04	-1.05
DMF→DMSO	10^{-2}	0.23 ± 0.02	0.13 ± 0.04	-0.02 ± 0.02	0.11 ± 0.08	0.11
	10^{-3}	0.27 ± 0.06	0.23 ± 0.15	0.28 ± 0.12	0.15 ± 0.03	0.23
	10^{-4}	-0.11 ± 0.15	0.42 ± 0.23	0.27 ± 0.17	-0.18 ± 0.11	-0.04
DMF→MeCN	10^{-2}	1.38 ± 0.03	1.21 ± 0.06	1.23 ± 0.05	1.18 ± 0.06	1.25
	10^{-3}	1.14 ± 0.01	1.33 ± 0.13	1.22 ± 0.05	1.27 ± 0.01	1.24
	10^{-4}	0.88 ± 0.08	1.15 ± 0.08	1.06 ± 0.02	1.19 ± 0.08	1.07
PC→DMF	10^{-2}	0.67 ± 0.04	0.99 ± 0.11	0.33 ± 0.07	0.40 ± 0.01	0.60
	10^{-3}	0.54 ± 0.02	0.47 ± 0.14	0.82 ± 0.01	0.46 ± 0.04	0.57

TABLE 46 (con't.)

Direction of Transfer	$\sim^c\text{AgClO}_4$	-----C a l c u l a t e d-----				$\log_m \gamma_{\text{Pi}}$ (overall average)
		using $\log_m \gamma_{\text{Me}_4\text{N}}$	using $\log_m \gamma_{\text{Et}_4\text{N}}$	using $\log_m \gamma_{\text{Pr}_4\text{N}}$	using $\log_m \gamma_{\text{Bu}_4\text{N}}$	
PC→DMSO	10^{-2}	0.91 ± 0.12	1.53 ± 0.11	0.48 ± 0.12	0.96 ± 0.01	0.97
	10^{-3}	0.67 ± 0.02	0.82 ± 0.09	0.57 ± 0.08	0.75	0.70
PC→MeCN	10^{-2}	2.53 ± 0.04	3.81 ± 0.08	1.55 ± 0.01	1.99 ± 0.02	2.47
	10^{-3}	1.70 ± 0.33	2.07 ± 0.03	2.22	1.43 ± 0.18	1.86
	10^{-4}		1.51 ± 0.10			1.51

Error analysis.

There are several factors contributing to the uncertainty of a single determination of $\log_m \gamma_R$ using Equation 96 and of $\log_m \gamma_{Pi}$ using Equation 98. These factors are:

1, the assumption of negligible $E_{j,s}$, 2, the uncertainty in the value of $\log_m \gamma_{Ag}$, 3, the uncertainty in the value of $\log_m \gamma_{ClO_4}$, and 4, the uncertainties in the values of transport numbers used in the calculations. We have already shown how the possible presence of $E_{j,s}$ may contribute to the concentration-dependence of the calculated $\log_m \gamma_R$ values. We have also shown that using these $\log_m \gamma_R$ in the subsequent $\log_m \gamma_{Pi}$ calculations greatly diminishes their concentration-dependence and reduces the error in the calculated value of $\log_m \gamma_{Pi}$ due to the exclusion of $E_{j,s}$ from the calculations.

A similar argument exists for the impact of the uncertainty in the $\log_m \gamma_{Ag}$ value on the value of $\log_m \gamma_R$ calculated in the first step and on the value of $\log_m \gamma_{Pi}$ calculated in the second step. This two-step procedure uses the same value of $\log_m \gamma_{Ag}$ in each step. It can be shown using simplified version of Equations 93 and 94, which ignore the presence of $AgClO_4$ in the diffusion layer, that an uncertainty of δ in the $\log_m \gamma_{Ag}$ value is reflected in the calculated $\log_m \gamma_{Pi}$ value by the quantity equal to $\delta \times (t_R' - t_R) / t_{Pi} \times t_R$, where t_R' is the transport number of R^+ in R_{Pi} , whereas for a single-step procedure the calculated value of $\log_m \gamma_R$ has a much larger uncertainty of δ / t_R .

Sample calculations show that an uncertainty of 0.1 in $\log_m \gamma_{Ag}$ ($\delta = 0.1$) introduces an uncertainty in the value of $\log_m \gamma_{BU4N}^{PC s_2}$ of 0.3, but an uncertainty in the value of $\log_m \gamma_{Pi}^{PC s_2}$ of only 0.05. Similar results are obtained for other R^+ ions. The conclusion here is that an uncertainty in the value of $\log_m \gamma_{Ag}$ has a considerable impact on the uncertainty of the calculated $\log_m \gamma_R$ value, but a much lower effect on the uncertainty of the $\log_m \gamma_{Pi}$ estimated in the second step of this two-step procedure.

Of course, this discussion applies only to the uncertainty in the value used in these calculations for the medium effect of the electroactive species to which both electrodes in a cell similar to Cell XX are reversible. The uncertainty in the value of the medium effect of ClO_4^- ion (or another ion which is a part of the salt-bridge electrolyte in the first step) has a more direct bearing on the calculated value of $\log_m \gamma_R$. In the first step, the simplified analysis of Equations 93 and 94 show that an uncertainty of δ in $\log_m \gamma_{ClO_4}$ results in an uncertainty of $\delta \times t_{ClO_4}/t_R$ in the calculated value of $\log_m \gamma_R$, and subsequently in an uncertainty of $\delta \times t_R' \times t_{ClO_4}/t_{Pi} \times t_R$ in the calculated value of $\log_m \gamma_{Pi}$. The last uncertainty can be shown to be very nearly equal to one. Thus, any uncertainty in the value of the transfer activity coefficient of an ion which is part of the salt-bridge electrolyte used in the first step of this new method, translates directly into

an almost equal uncertainty in the value of the transfer activity coefficient of an ion of the same sign, calculated in the second step of this new method for estimating medium effects of single ions.

It is very difficult to estimate the uncertainty in the calculated value of $\log_m \gamma_R$ and of $\log_m \gamma_{Pi}$ due to the uncertainties in the values of the transport numbers of all the ions used in the calculations. The transport numbers calculated according to Equation 100 have an uncertainty of no more than ± 0.001 and it would be a simple matter to evaluate the uncertainty in $\log_m \gamma_R$ due to the uncertainty in t_i values using the propagation of errors method. What is difficult is the estimation of validity of Equation 100, which is based on a very simple approach of treating the whole transition layer at the interface of two solutions as a single homogenous mixture. This model gains validity as the concentration of the electroactive species decreases so much compared to the concentration of the salt-bridge electrolyte that its contribution to the current-carrying process becomes negligible. We have seen that the ratios of c_{RC104}/c_{AgClO4} at which that happens depend on the nature of R as well as on the nature of both solvents participating in the formation of the junction. However, when the c_{RC104}/c_{AgClO4} ratio is less than 100, the contribution of $AgClO_4$ to the current-carrying process becomes significant. The situation is, of course, complicated by the fact that not only two different solutes, but also two different sol-

vents diffuse into each other at the boundary. In section III-A-3 a new formulation was developed which could be applied to interfaces between two different solvents when only one electrolyte was present in both solutions, and which accounted for the variations of the transport numbers of the cation and the anion with the composition of the solvent across the interphase. So far, there is no such formulation for a case when more than one cation and one anion cross the interface. This is certainly an area which merits further investigation. In the meantime, the best course of action is to maintain the ratio of the concentration of the salt-bridge electrolyte to the concentration of the electroactive species high enough so that the latter contributes essentially nothing to the current-carrying process across the interface between two different solvents. A small question remains regarding the use of λ^0 's in Equation 100.

It has been shown before (66) (Section III-A-2-c), that mobilities of ions (here approximated by λ^0 's) change with the concentration of the solution. Since no data are available on ionic conductances of concentrated solutions for the ions and solvents used in this study, the conductances at infinite dilution, λ^0 , had to be used in calculations. While the concentration dependence of λ 's in general is small, it should be accounted for eventually and thus bring on further improvement in the accuracy of the transfer

activity coefficients of single ions estimated by this new method.

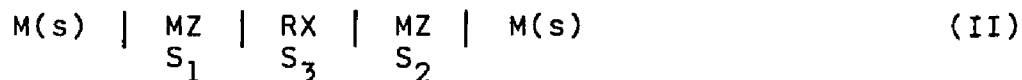
In conclusion, we have shown that a two-step procedure of this new method for estimating medium effects of single ions results in a value of $\log_m \gamma_i$ estimated in the second step, whose uncertainty, when compared with the results obtained in the one-step procedure, is significantly lowered. The impact of two of the three most important factors contributing to the uncertainty of the calculated values, that is the exclusion of $E_{j,s}$ from the calculations and the uncertainty in the transfer activity coefficient of the electroactive species is diminished by this two-step procedure. The problem mentioned here regarding the method of calculating the transport numbers of all the relevant ions can be avoided, at least partially, by an appropriate experimental design, that is by maintaining a $c(\text{salt bridge electrolyte})/c(\text{electroactive species})$ ratio high enough to render negligible the contribution of electroactive species to the E_j formation.

Tetraphenylarsonium Tetraphenylborate -- A New Salt-Bridge Electrolyte.

Introductory Remarks.

We have mentioned before that many workers have been using methods for the estimation of transfer activity coefficients of single ions, based on the e.m.f. measurements of cells with liquid junction. Such methods are applicable only if the liquid-junction potential, E_j , at the interface of the two solvent media can be minimized or evaluated. Under those conditions, it is possible to calculate the transfer activity coefficient of an ion to which reversible electrodes exist in both solvents of interest.

Historically, the first approach used in estimating transfer activity coefficients of single ions was the assumption that E_j can be minimized by interposition of a salt bridge containing a concentrated solution of an electrolyte. This approach has merit if the following conditions are satisfied for a cell of the general type



1. The conventional activities of the electroactive species M^+ are equal in both solvents.

2. The concentration of the salt-bridge electrolyte, RX, is high enough, relative to the concentration of MZ, to render negligible the contributions from M^+ and Z^- ions to the diffusion potential.

3. The value of $E_{j,s}$ (the solvent contribution) at the interface between the two different solvents is very small for the solvent pairs present in the cell and can be neglected.

4. The transport numbers and the transfer activity coefficients of the two ions comprising the salt-bridge electrolyte RX are the same for both ions.

The first and second condition can be met via experimental design. The third condition is presumably met when the solvents used are very similar, such as dipolar aprotic solvents. The justifications for and the limitations of the last assumption have been discussed here before (Section III-B-1-b-2). For the purpose of this study, we assume, as did Cox, et al. (51) that the $E_{j,s}$ is negligible at the interfaces between dipolar aprotic solvents.

The fourth condition can be met if the right salt-bridge electrolyte is chosen. Early workers (38, 39) who estimated $\log_m H$ values between water and alcohol-water media, used salt bridges of concentrated aqueous KCl. More recently, Alexander, et al. (25) recommended the use of a bridge of 0.1M $\text{Et}_4\text{N}^+\text{Pi}^-$ in either acetonitrile or methanol between pairs of nonaqueous media to minimize the E_j . In terms of fulfilling the requirements of an ideal salt-bridge electrolyte, $\text{Et}_4\text{N}^+\text{Pi}^-$ has the advantage of appreciable solubility in organic solvents and of compatibility with electroactive ions of interest, notably Ag^+ . Nevertheless, it is not free from shortcomings. The transference numbers of the

Et_4N^+ and the Pi^- ions in some media may differ by as much as 10% (Table 31), and the few data available until now on their $\log_m$ values in different solvents do not always support the assumption of their approximate equality. For example, in acetonitrile, $\log_m \text{Et}_4\text{N}$ and $\log_m \text{Pi}$ were estimated (21) to be -1.7 and -0.3, respectively (aqueous reference). More recently, the results obtained by this author show that for most solvent pairs studied here the transfer activity coefficients of Et_4N^+ and Pi^- ions are not even approximately equal (Tables 96 and 98). Our estimated values of $\log_m \gamma_{\text{Et}_4\text{N}}$ show a dependence on the concentration of AgClO_4 solution present in Cell XX, whose e.m.f. measurements were used to provide estimates of those $\log_m \gamma_{\text{Et}_4\text{N}}$ values, and therefore cannot be used directly. However, the average values of $\log_m \gamma_{\text{Et}_4\text{N}}$ for the various solvent-pairs studied here provide us with an estimate of the range for each transfer activity coefficient of Et_4N^+ ion. Subsequently, a comparison can be made with the transfer activity coefficient of the Pi^- ion for a given solvent pair, the value of which had been determined in the two-step procedure outlined previously (Section III-B-1-d). $\circ$ Thus, semiquantitative statements of comparisons of $\log_m \gamma_{\text{Et}_4\text{N}}$ and $\log_m \gamma_{\text{Pi}}$ are possible based on the results presented in the previous section. We have found that only for the DMF $\rightarrow$ MeCN transfer there is a fair agreement between the average values of $\log_m \gamma_{\text{Et}_4\text{N}}$ and $\log_m \gamma_{\text{Pi}}$ (1.00 and 1.19, respectively), while for all the other solvent-pairs there is a difference of at

least one logarithmic unit, which under simplified conditions of equal transport numbers of Et_4N^+ and Pi^- ions translates into a value of at least 30mV contributed to E_j by such unequal values of transfer activity coefficients of the two ions comprising the salt-bridge electrolyte. It is clear that an a priori assumption of negligible E_j when an Et_4NPi solution is interposed between two dipolar aprotic solvents is not justified.

Goldberg and Popovych (49) suggested the use of triisobutylbutylammonium tetraphenylborate $[(\text{tab}^+)(\text{BPh}_4^-)]$ as a more promising salt-bridge electrolyte. The limiting equivalent conductances and consequently the transport numbers of its ions were shown to be equal in a number of media to within 1% or better. Table 47 lists the values of λ^0 available from literature for the (tab^+) , BPh_4^- , as well as for the Ph_4As^+ ion in several dipolar aprotic solvents. The values of λ^0 for the (tab^+) ion are essentially equal to the values of λ^0 for the BPh_4^- ion in the solvents for which data is available (that is in MeCN and DMSO).

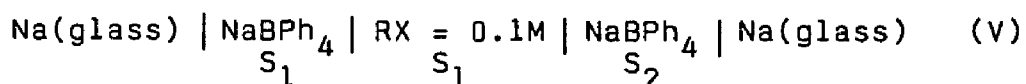
TABLE 47

Limiting Equivalent Conductances of BPh_4^- , (tba^+) , and Ph_4As^+
Ions in Dipolar Aprotic Solvents.

Solvent	λ^0 Values of		
	BPh_4^-	(tba^+)	Ph_4As^+
MeCN	57.96 (87)	57.8 (92)	55.8 (92)
	58.3 (92)	57.7 (96)	
	57.7 (30)		
DMSO	10.2 (89)	11.0 (95)	
	11.0 (94)		
DMF			31.0 (93)
PC	8.10 (87)		
	7.8 (29)		

Regarding the values of transfer activity coefficients of these two ions, for dipolar aprotic solvents, no estimates of $\Delta G_t^\circ(\text{tab}^+)$ were available for comparison with the corresponding literature values of $\Delta G_t^\circ(\text{BPh}_4^-)$. However, the transfer activity coefficients of the (tab^+) and the BPh_4^+ ions were demonstrated to be equal, within experimental error, in methanol and ethanol-water media (36). It was Goldberg's and Popovych's hope that the approximate equality of the transfer activity coefficients of the (tab^+) and the BPh_4^- ions would prevail also in dipolar aprotic media. The disadvantage of using a $(\text{tab}^+)(\text{BPh}_4^-)$ salt bridge lies in the fact that the BPh_4^- anion precipitates or decomposes upon reaction with most cations. Consequently, the choice of electrodes for the study of any salt-bridge electrolyte with BPh_4^- as the anion is limited to sodium-selective (glass) and hydrogen (glass) electrodes.

Goldberg and Popovych (49) have evaluated critically previous applications of Et_4NPI and have tested Et_4NPI , $(\text{tab}^+)(\text{BPh}_4^-)$ and Et_4NClO_4 as salt-bridge electrolytes (Et_4NClO_4 was used because sufficient literature data were available to calculate E_j) in a cell similar to Cell V:



The potential of Cell V is given by

$$E(\text{V}) = {}_2E_{\text{Na}}^\circ - {}_1E_{\text{Na}}^\circ - m_2 \log_2 a_{\text{Na}} + m_1 \log_1 a_{\text{Na}} + E_j \quad (103)$$

where $E(\text{V})$ is the experimental e.m.f. of Cell V, E° 's are

the standard electrode potentials and m_1 and m_2 are the Nernstian response factors of the two sodium glass electrodes in solvents S_1 and S_2 , and 1^a_{Na} and 2^a_{Na} are the conventional activities of Na^+ ions in the respective solvents. It is convenient to combine the E^0 's and the activity terms to define a new quantity $E(V)'$:

$$E(V)' = E(V) - m_2 \log 2^a_{Na} + m_1 \log 2^a_{Na} \quad (104)$$

which represents now a direct measure of $\log_m \gamma_{Na}$:

$$E(V)' = 59.16 \log_m \gamma_{Na} + E_j \quad (105)$$

If the E_j in Cell V is assumed to be negligible, then Equation 105 can be used to calculate the value of $\log_m \gamma_{Na}$ (uncorr.) directly. Furthermore, if all the relevant data are available, it is possible to calculate the value of E_j in Cell V via the following expression:

$$E_j = -(t_R - t_X) 59.16 \log \frac{2^a_{Na}}{1^a_{Na}} - 59.16 [t_R \log_m \gamma_R - t_X \log_m \gamma_X] \quad (106)$$

This E_j correction from Equation 106 can then be introduced into Equation 105 to calculate a corrected value of $\log_m \gamma_{Na}$. If one were ever to find an "ideal" salt-bridge electrolyte, one fulfilling the condition of equal transport numbers and transfer activity coefficients for both ions, then the uncorrected $\log_m \gamma_{Na}$ values obtained from the e.m.f. of cells using such an ideal salt bridge should agree with the ac-

cepted literature values or with the values corrected for E_j via Equation 106.

The $\log_m \gamma_{Na}$ values obtained by Goldberg and Popovych (49) using $(tab^+)(BPh_4^-)$ were not superior to those obtained with $Et_4N^+I^-$ and $Et_4N^+ClO_4^-$ salt bridges. If the $(tab^+)(BPh_4^-)$ bridge were superior, the uncorrected $\log_m \gamma_{Na}$ values derived from it would agree closely with the E_j -corrected $\log_m \gamma_{Na}$ values derived from the other two bridges. Since this was not observed, the authors concluded that their assumption of $\Delta G_t^\circ(tab^+) = \Delta G_t^\circ(BPh_4^-)$ must be generally incorrect for transfer between dipolar aprotic solvents and therefore $(tab^+)(BPh_4^-)$ does not satisfy all the requirements of an "ideal" salt bridge electrolyte. One objective of the research in this laboratory has been to find such an ideal salt-bridge electrolyte.

Experimental design.

An electrolyte whose cation and anion are known to be very nearly equal in size and chemical properties is tetraphenylarsonium tetraphenylborate, $\text{Ph}_4\text{AsBPh}_4$. This suggested to us that it might be a good candidate for an "ideal" salt-bridge electrolyte. Therefore, in this part of our investigation we chose to test $\text{Ph}_4\text{AsBPh}_4$ as the salt-bridge electrolyte and to compare its performance with that of the previously used salt-bridge electrolytes. While there are few data available regarding the actual values of the transport numbers (via the values of λ^0 listed in Table 47) of the Ph_4As^+ and the BPh_4^- ions in the solvents used here, it seems reasonable to assume that they would be very nearly the same for both ions. This assumption is based on the same considerations that were used in choosing $\text{Ph}_4\text{AsBPh}_4$ as the preferred reference electrolyte for the splitting of transfer activity coefficients into values for individual ions.

When the transport numbers and medium effects of R^+ and X^- are the same, E_j becomes zero according to Equation 106, and Equation 105 can then be used directly to calculate $\log_m \gamma_{\text{Na}}$.

Because of solubility limitations, only two solvents, DMF and DMSO, could be used to prepare a salt-bridge solution. The solubility of $\text{Ph}_4\text{AsBPh}_4$ in both solvents is $\sim 1.5 \times 10^{-2} \text{M}$. To satisfy the condition of a negligible contribution to E_j by the electroactive species, the concentra-

tions of NaBPh_4 in the end solutions ranged in general from $\sim 10^{-3}\text{M}$ to $4 \times 10^{-5}\text{M}$. The following solvent pairs were used in Cell V: DMF|DMSO, DMF|MeCN, DMF|PC, DMSO|PC, DMSO|MeCN, DMF|NMF, DMSO|NMF. In addition, the MeCN PC interface was used with a salt-bridge solution in DMF and later in DMSO.

Na(glass) electrodes were calibrated in each solvent in which they were used. NaPi was used to prepare the calibration solutions. The activities of the Na^+ ions in NaBPh_4 and NaPi solutions were calculated from the concentrations by using the Debye-Huckel equation with the ion-size parameter taken as $3\text{\AA}$ for the Na^+ ion. Table 48 lists the parameters used in the D-H calculations for the solvents employed in this study.

The calibration of sodium glass electrodes was performed using reference electrodes with a salt-bridge, so that the potential of each reference electrode was presumed to stay constant while the concentration of the NaPi solution, as well as the potential of the Na(glass) electrode varied. Table 49 lists all the Na(glass) electrodes used here and the Nernstian response factors determined in the calibration procedure. The Nernstian response factor corresponds to the average number of millivolts per tenfold change in sodium-ion activity.

TABLE 48

Calculated Parameters Used in the Debye-Huckel Equation as
Applied to Na⁺ Ion in Dipolar Aprotic Solvents (Molar Scale,
25°C).

Solvent	ϵ	A	B	Ba°
PC	65.1 (60)	0.676	0.361	1.083
DMSO	46.7 (75)	1.110	0.426	1.278
MeCN	35.87 (91)	1.650	0.486	1.458
DMF	36.7 (75)	1.594	0.481	1.443
NMF	182.4 (75)	0.144	0.216	0.645

TABLE 49

Nernstian Response Factors m_s of the Na(glass) Electrodes
Used in Dipolar Aprotic Solvents.

Na(glass) Electrode	Solvent	m_s	Corr. Coeff.
		mV/pa _{Na}	
#1	DMSO	64.35	0.997
#5	NMF	59.23	0.998
#7	DMF	71.39	0.9998
#7	MeCN	56.62	0.998
#8	MeCN	58.77	0.996
#9	PC	51.64	0.998
#10	PC	57.26	0.998

Results and discussion.

The uncorrected values of $\log_m \gamma_{Na}$, obtained from e.m.f. measurements using Ph_4BPh_4 salt bridge and calculated using Equation 105 with E_j set to 0, are listed in Table 50, along with the experimental parameters of the concentrations of $NaBPh_4$ in both solvents as well as the e.m.f. of Cell V for each concentration and solvent-pair combination. E'_{Cell} was calculated using Equation 104, where the Nernstian coefficients were determined in the calibration of Na(glass) electrodes and are listed in Table 49.

The calculated values of $\log_m \gamma_{Na}$ listed in Table 50, averaged for each concentration of $NaBPh_4$, show a concentration dependence similar to one observed by Goldberg and Popovych (49), although not always in the same direction. It is interesting to note that for the MeCN|PC transfer, the $\log_m \gamma_{Na}$ values derived from $(tab^+)(BPh_4^-)$ salt bridge decrease with decreasing c_{NaBPh_4} , while the same $\log_m \gamma_{Na}$ values derived from Et_4NClO_4 salt bridge and corrected for E_j increase with decreasing c_{NaBPh_4} ; for the DMF|DMSO, DMF|PC and DMSO|PC solvent-pairs, the $\log_m \gamma_{Na}$ based on $(tab^+)(BPh_4^-)$ behave in a fashion parallel to that of $\log_m \gamma_{Na}$ (corr.) based on Et_4NClO_4 ; and finally, for the DMSO|MeCN and the DMF|MeCN the concentration dependence of $\log_m \gamma_{Na}$ values derived from $(tab^+)(BPh_4^-)$ is clearly observable ($\log_m \gamma_{Na}$ values increase with decreasing c_{NaBPh_4}), but that dependence seems to disappear for $\log_m \gamma_{Na}$ (corr.) values based on Et_4NClO_4 salt bridge (49). In this study, while $\log_m \gamma_{Na}$

TABLE 50

Transfer Activity Coefficients of the Na^+ Ion Estimated from
the E.m.f. of Cell V, with $\text{Ph}_4\text{AsBPh}_4$ as the Salt-Bridge
Electrolyte ($c_{\text{Ph}_4\text{AsBPh}_4} = \sim 1.5 \times 10^{-2}\text{M}$).

I. Salt-bridge solvent: DMF

$1^{\text{C}}\text{NaBPh}_4$	$2^{\text{C}}\text{NaBPh}_4$	E_{Cell}	E'_{Cell}	$\log_m \gamma_{\text{Na}}$	
$S_1 = \text{DMF}$				$S_2 = \text{MeCN}$	
Na electrode #7				Na electrode #8	
9.728×10^{-4}	1.133×10^{-3}	+311.0	268.8	4.544	4.54
		+311.0	268.8	4.544	
4.864×10^{-4}	4.534×10^{-4}	306.0	265.6	4.490	4.49
		305.7	265.3	4.484	
9.728×10^{-5}	1.133×10^{-4}	315.1	260.5	4.403	4.41
		315.4	260.8	4.408	
3.891×10^{-5}	4.534×10^{-5}	319.4	259.8	4.391	4.34
		313.0	253.4	4.283	

$S_1 = \text{DMF}$				$S_2 = \text{DMSO}$	
Na electrode #7				Na electrode #1	
9.728×10^{-4}	1.066×10^{-3}	-69.6	-94.5	-1.597	-1.59
		-68.6	-93.5	-1.580	
4.864×10^{-4}	4.264×10^{-4}	-75.6	-96.2	-1.626	-1.63
		-76.3	-96.5	-1.631	
9.728×10^{-5}	1.066×10^{-4}	-67.9	-99.1	-1.675	-1.68
3.891×10^{-5}	4.264×10^{-5}	-72.9	-106.7	-1.804	-1.80

TABLE 50 (con't.)

$1^{\text{C}}\text{NaBPh}_4$	$2^{\text{C}}\text{NaBPh}_4$	E_{Cell}	E'_{Cell}	$\log_m \gamma_{\text{Na}}$	
$S_1 = \text{DMF}$				$S_2 = \text{PC}$	
Na electrode #7				Na electrode #9	
9.728×10^{-4}	9.99×10^{-4}	263.2	200.8	3.394	
		264.2	201.8	3.409	3.40
4.864×10^{-4}	3.996×10^{-4}	255.8	193.0	3.262	
		253.5	190.7	3.223	3.24
9.728×10^{-5}	9.99×10^{-5}	256.5	175.9	2.973	
		255.9	175.3	2.963	2.97
3.891×10^{-5}	3.996×10^{-5}	254.5	166.3	2.811	
		247.2	159.0	2.688	2.72
		246.2	158.0	2.671	
$S_1 = \text{DMF}$				$S_2 = \text{NMF}$	
Na electrode #7				Na electrode #5	
9.728×10^{-4}	1.001×10^{-3}	-24.7	-65.2	-1.10	
		-24.7	-65.2	-1.10	-1.10
4.864×10^{-4}	4.006×10^{-4}	-26.7	-64.3	-1.09	
		-26.7	-64.3	-1.09	-1.09
9.728×10^{-5}	1.001×10^{-4}	-2.7	-53.3	-0.90	
		+0.7	-49.9	-0.84	-0.87
3.891×10^{-5}	4.006×10^{-5}	+30.1	-24.9	-0.42	
		+27.1	-27.9	-0.47	-0.45

TABLE 50 (con't.)

$1^{\text{C}}\text{NaBPh}_4$	$2^{\text{C}}\text{NaBPh}_4$	E_{Cell}	E'_{Cell}	$\log_m \gamma_{\text{Na}}$	
$S_1 = \text{MeCN}$				$S_2 = \text{PC}$	
Na electrode #7				Na electrode #10	
9.20×10^{-4}	9.64×10^{-4}	+38.8	38.0	0.642	
		37.4	36.6	0.619	0.63
9.20×10^{-5}	9.64×10^{-5}	52.3	53.2	0.900	
		50	50.9	0.860	0.88

II. Salt-bridge solvent: DMSO

$S_1 = \text{DMSO}$				$S_2 = \text{MeCN}$	
Na electrode #1				Na electrode #8	
1.066×10^{-3}	1.133×10^{-3}	364.5	347.2	5.869	
		363.5	346.2	5.852	5.86
4.264×10^{-4}	4.534×10^{-4}	366.2	346.4	5.855	
		365.9	346.1	5.850	5.85
1.066×10^{-4}	1.133×10^{-4}	369.2	345.8	5.845	
		377.9	354.5	5.992	5.92
4.264×10^{-5}	4.534×10^{-5}	376.6	350.8	5.930	
		381.3	355.5	6.009	5.97

$S_1 = \text{DMSO}$				$S_2 = \text{PC}$	
Na electrode #1				Na electrode #10	
1.066×10^{-3}	9.99×10^{-4}	+313.3	269.8	4.561	
		311.7	268.2	4.533	4.55
4.264×10^{-4}	3.996×10^{-4}	313.0	264.1	4.464	
		315.3	266.4	4.503	4.48

TABLE 50 (con't.)

1^CNaBPh_4	2^CNaBPh_4	E_{Cell}	E'_{Cell}	$\log_m \gamma_{\text{Na}}$	
1.066×10^{-4}	9.99×10^{-5}	314.0	256.7	4.339	
		311.7	254.4	4.300	4.32
4.264×10^{-5}	3.996×10^{-5}	not stable			

$S_1 = \text{DMSO}$		$S_2 = \text{NMF}$			
Na electrode #1		Na electrode #5			
1.066×10^{-3}	1.001×10^{-3}	13.7	-1.9	-0.032	-0.03
4.264×10^{-4}	4.006×10^{-4}	15.7	-1.2	-0.020	
		11.0	-5.9	-0.099	-0.06
1.066×10^{-4}	1.001×10^{-4}	40.5	21.1	+0.357	
		37.5	18.1	0.306	0.33
4.264×10^{-5}	4.006×10^{-5}	66.6	45.4	0.767	
		56.2	35.0	0.592	0.68

$S_1 = \text{MeCN}$		$S_2 = \text{PC}$			
Na electrode #7		Na electrode #10			
9.20×10^{-4}	9.64×10^{-4}	33.6	32.8	0.555	
		33.6	32.8	0.555	0.56
9.20×10^{-5}	9.64×10^{-5}	43.8	44.7	0.756	
		47.5	48.4	0.818	0.79

values for all solvent-pairs changed with decreasing concentration of NaBPh_4 , for some they increased (for $\text{MeCN}|\text{PC}$, $\text{DMSO}|\text{MeCN}$, and $\text{DMSO}|\text{NMF}$ solvent pairs), and for all other solvent-pairs they decreased with decreasing c_{NaBPh_4} . We made a comparison between the degree of concentration dependence of $\log_m \gamma_R$ values of tetraalkylammonium cations estimated in Section III-B (Table 38) and that of $\log_m \gamma_{\text{Na}}$ values estimated here via the $\text{Ph}_4\text{AsBPh}_4$ salt bridge and by Goldberg and Popovych (49) via the $(\text{tab}^+)(\text{BPh}_4^-)$ salt bridge and found the one common characteristic: the degree of concentration dependence was mostly a function of the two solvents forming the junction. For example, for the $\text{DMF}|\text{PC}$ interface, the transfer activity coefficients of Na^+ ion estimated via $\text{Ph}_4\text{AsBPh}_4$ and via $(\text{tab}^+)\text{BPh}_4$, and the transfer activity coefficients of the R^+ ions estimated in the preceding section, all showed a strong dependence (relative to that for other solvent-pairs) on the concentration of the electroactive species, while for the $\text{DMSO}|\text{PC}$ solvent pair, that dependence was very weak. Similar behavior, although not always that clear-cut, was observed for other pairs of solvents studied here. While the degree of concentration dependence was mostly a function of the two solvents forming the junction, the nature of the electrolytes participating in the junction formation contributed to it too.

To summarize, the concentration dependence of $\log_m \gamma_X$ values derived from e.m.f. of cells with a salt bridge using a one-step procedure (Equation 96 or 105) is a function not

only of the nature of the two solvents, but also of the nature of the ions crossing the boundary between the solvents. This observation can be used to support the existence of $E_{j,s}$, the contribution of solvent molecules to the liquid-junction potential at the interface of two different solvents, which, for a given pair of solvents, has been observed to depend on the nature and the concentration of the electrolytes crossing the boundary.

While the concentration dependence of $\log_m \gamma_{Na}$ values is clearly observable, it is not nearly as strong as that of $\log_m \gamma_R$ values estimated in the preceding section. It is most pronounced for the DMF|PC solvent pair, with $\log_m \gamma_{Na}$ values based on Ph_4AsBPh_4 changing by 0.68 log units and those based on $(tab^+)(BPh_4)$ changing by 0.82 units for the same concentration decrease. For the other solvent pairs, the $\log_m \gamma_{Na}$ value changes are much smaller and meaningful comparisons can be made using the average values of $\log_m \gamma_{Na}$ derived from each salt-bridge electrolyte. Table 51 lists the average values of $\log_m \gamma_{Na}$ obtained with Ph_4AsBPh_4 as the salt-bridge electrolyte, along with the $\log_m \gamma_{Na}$ values obtained by Goldberg and Popovych (49) with the aid of other salt-bridge electrolytes, averaged over the same concentration range of $NaBPh_4$ as was employed in this study as well as with previous literature data. Because our own estimates of the transfer activity coefficients of the picrate ion became available through the work presented in the preceding part of this dissertation, we were able to correct the

$\log_m \gamma_{Na}$ values obtained by Goldberg and Popovych (49) with the $Et_4N^+Pi^-$ salt bridge by calculating the E_j using a simplified version of Equation 106, in which the first term (which is negligible) was ignored. The values of $\log_m \gamma_{Na}$ corrected by using $\log_m \gamma_{Et_4N}$ and $\log_m \gamma_{Pi}$ data determined in this study are included in Table 51 in the column labelled " $Et_4N^+Pi^-$ bridge, corr.". The other data in the same column come from Goldberg and Popovych (49), who used literature values of $\log_m \gamma$ for Et_4N^+ and Pi^- ions to make the same correction.

TABLE 51

A Comparison of the Average Values for $\log \gamma_{\text{Na}}$ Obtained with $\text{Ph}_4\text{AsBPh}_4$ (This Study) and with Other Salt-Bridge Electrolytes (49).

Direction of transfer	$\text{Ph}_4\text{AsBPh}_4$ bridge uncorrected	$(\text{tab}^+)(\text{BPh}_4^-)$ bridge	Et_4NPi bridge ^(a) uncorr.	Et_4NPi bridge corr.	Et_4NClO_4 bridge ^(a) corrected	Lit. value ^(c)
DMF→MeCN	4.44 ± 0.07	4.81	4.83	$4.06^{(a)}$ $4.68^{(b)}$	4.21	4.6
DMF→DMSO	-1.68 ± 0.08	-1.43	-1.24	$-0.8^{(b)}$	-1.48	-0.8
DMF→PC	3.08 ± 0.26	3.81	3.82	$4.09^{(a)}$ $2.74^{(b)}$	4.10	4.3
DMF→NMF	-0.88 ± 0.26					
MeCN→PC (via DMF)	0.75	-0.77	-0.66	$+0.38^{(a)}$	0.17	-0.3
DMSO→MeCN	5.90 ± 0.05	5.94	5.80	$5.48^{(b)}$	5.42	5.4
DMSO→PC	4.45 ± 0.01	5.31	5.18	$6.5^{(b)}$	5.77	5.1

TABLE 51 (con't.)

Direction of transfer	Ph ₄ AsPBPPh ₄ bridge uncorrected	(tab ⁺)(BPh ₄ ⁻) bridge uncorrected	Et ₄ NPi bridge ^(a) uncorr.	Et ₄ NPi bridge corr.	Et ₄ NClO ₄ bridge ^(a) corrected	Lit. value ^(c)
DMSO→NMF	0.23+0.30					
MeCN→PC (via DMSO)	0.68	-0.77	-0.66	+0.38 ^(a)	0.17	-0.3

(a) Obtained from Goldberg and Popovych (49).

(b) Calculated using $\log_m \gamma_{Pi}$ and $\log_m \gamma_{Et4N}$ obtained in this work.

(c) From the compilation in ref. (21).

As we can see from Table 51, the variations in the $\log_m \gamma_{Na}$ values with different salt-bridge electrolytes do not make a convincing case for Ph_4AsBPh_4 as an ideal salt-bridge electrolyte for use between all combinations of the dipolar aprotic solvents studied. Nevertheless, for the DMF|MeCN junction, the value obtained via the Ph_4AsBPh_4 is close to the corrected values obtained from cells with $Et_4N^+Pi^-$ and $Et_4N^+ClO_4^-$ salt bridges as well as to the previously reported value. In the case of the DMF|PC junction, there is fair agreement between the datum from the Ph_4AsBPh_4 bridge and that from the $Et_4N^+Pi^-$ bridge corrected in the present study. For the DMF|DMSO interface, the Ph_4AsBPh_4 bridge gives a result close to that of a "corrected" $Et_4N^+ClO_4^-$ bridge, but the $(tab^+)(BPh_4^-)$ bridge (uncorrected) seems to be superior here. On the other hand, the results using corrected $\log_m \gamma$ values of Et_4N^+ and Pi^- ions agrees with the only available other literature datum. For the other interfaces, the values of $\log_m \gamma_{Na}$ determined via Ph_4AsBPh_4 do not approach the corrected values in a manner which would indicate that the use of a Ph_4AsBPh_4 salt bridge renders the value of E_j negligible. In fact, there is one common source of error contributing to all of these results, and that is the assumption of negligible $E_{j,s}$, the component of E_j to which solvent molecules contribute. Again we have to point out that if "negligible" means $\pm 10mV$, it corresponds to ± 0.17 units on the logarithmic scale of transfer activity coefficients, $\log_m \gamma$. Unfortunately, no literature

data are available of direct estimates of $E_{j,s}$ values between pairs of dipolar aprotic solvents and therefore it is difficult to determine the extent of the error caused by exclusion of such $E_{j,s}$ in the calculations of $\log_m \gamma_{Na}$.

We have shown earlier (Section I-B-3-c) that under simplified conditions of constant transport numbers of all the ions crossing a given boundary, the nature of the salt-bridge solvent is irrelevant. We had an opportunity to test this theoretical premise for the MeCN|PC interface. Because of extremely low solubility of Ph_4AsBPh_4 in either MeCN or PC, we used a solution of Ph_4AsBPh_4 in DMF and later in DMSO as the salt-bridge between MeCN and PC. The results in Table 51 indicate that there is a good agreement between the values of $\log_m \gamma_{Na}$ for the transfer from MeCN to PC obtained via a DMF salt-bridge solution (0.75) and a DMSO salt-bridge solution (0.68).

Summary of Studies in Dipolar Aprotic Solvents.

The new method for estimating transfer activity coefficients of single ions was tested for several solvent pairs. This method consists of interpreting the e.m.f. measurements of cells with a salt-bridge electrolyte RX containing an ion for which a value of the transfer activity coefficients was sought (R^+ or X^-). The method proved to be very sensitive to the accuracy of the parameters used in calculating the value of $\log_m \gamma_R$ or $\log_m \gamma_X$, as well as to the assumption of a negligible $E_{j,s}$. Consequently, a two-step procedure was developed for estimating transfer activity coefficients of the single ions, R^+ or X^- , in which the $\log_m \gamma$ values obtained from experimental e.m.f. measurements for one of them were used in the interpretation of the experimental e.m.f. measurements of a cell with a salt bridge containing the other ion. This approach seems to minimize the sources of error inherent in the original one-step procedure such as the assumption of negligible $E_{j,s}$ and the uncertainty in the value of $\log_m \gamma$ of the electroactive species.

The use of $\text{Ph}_4\text{AsBPh}_4$ as a salt bridge between pairs of dipolar aprotic solvents was studied. Apart from the limitations imposed by the general low solubility of $\text{Ph}_4\text{AsBPh}_4$ in most dipolar aprotic solvents, the use of this electrolyte cannot be evaluated fully because of the presence of $E_{j,s}$ at the interface of two solvent media. Nevertheless, $\text{Ph}_4\text{AsBPh}_4$ is a promising salt-bridge electrolyte for cells with liquid junction between dipolar aprotic media.

Recommendations for Future Studies.

The new method for estimating transfer activity coefficients needs to be studied further in order to provide reliable $\log_m \gamma$ values for those ions for which no other method exists. For example, using NaPi as the salt-bridge electrolyte in the first step of this two-step procedure, known $\log_m \gamma_{Na}$ values can be used and concentration-dependent $\log_m \gamma_{Pi}$ values can be determined, which can then be used in the second step, where RPi electrolytes are used in the salt-bridge solutions; the $\log_m \gamma_{R4N}$ values arrived at ought to be much less concentration-dependent and thus more accurate.

We have seen that the presence of $E_{j,s}$, the solvent contribution to liquid-junction potential at the interface of two solvent media, is an important factor in the interpretation of e.m.f. of cells, where such junctions are formed. There is a great need for further investigations in this area. For dipolar aprotic solvents, the actual values of $E_{j,s}$ for various solvent pairs need to be known. Perhaps methods similar to those used here for water/methanol-water interfaces can be developed. Furthermore, $E_{j,s}$ values can be obtained from the e.m.f. of cells containing saturated solutions of the electroactive electrolyte in two solvents.

The work in methanol-water media should be extended to ethanol-water solvents, since the parameters needed to estimate the value of $E_{j,s}$ between water and methanol-water solvents are well known. A study of that kind would provide

more data needed for proper evaluation of the formulations used, including those developed in this dissertation.

Further investigation is required regarding the variation of λ_{Cl}° with the concentration of methanol in methanol-water solvents above 90% MeOH. Very accurate data for λ_{Cl}° are needed in order to interpret e.m.f. measurements of cells comprised of HCl solutions in water and MeOH-H₂O solvents at concentrations above 90% MeOH.

For the whole range of methanol-water solvents, studies of e.m.f. cells with solutions of electrolytes other than HCl and NaCl would provide more data for investigating the relationship between $E_{j,s}$ and the nature of the electrolyte crossing the boundary. One such electrolyte is KCl, which can be used in solutions, with potassium glass electrodes and calomel electrodes, reversible to both ions in the electrolyte.

Another study of specific nature needed to improve the values of $\log_m \gamma$ of single ions estimated via the new method is the determination of the transport numbers of the cation and anion for a concentrated (or even saturated) solution of the salt-bridge electrolyte used in the determination of $\log_m \gamma$ of one of its ions.

The recommendations mentioned so far deal with problems of practical nature (essentially they represent a need for collecting more data) and can be implemented in a laboratory.

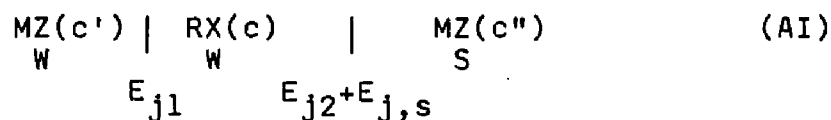
Two areas of investigation of more speculative nature suggested themselves in the course of conducting research for this dissertation. The first area would deal with the way transport numbers of various ions change across the diffusion layer at the interface of two different solvents, both as a function of the relative concentration as well as the composition of the two solutions both with respect to ions and solvents.

The second area of investigation, which could prove very fruitful in elucidating the cause of the concentration dependence of $E_{j,s}$, is the study of the relationship between the activity of a solute and the activity of the solvent. While a general relationship between these two properties of a system is known (the Gibbs-Duhem Equation), the formulations and methods developed for estimating those activities deal only with the solute. In addition to investigating the activity of the solvent in a single solution, more data are needed in the area of the free energies of mutual solution for two solvents. The results of studies of conventional activities of solvents in solutions combined with the knowledge of standard free energies of solution between two different solvents may be helpful in estimating the value of $E_{j,s}$ arising at the interface of two different solvent media.

APPENDIX 1

Henderson Equation Applied to the Interface Between Two Different Solvents.

Consider the following two junctions involving solvents W (water) and another solvent S



Applying the Henderson equation to each junction we get:

$$\begin{aligned} E_{j1} &= \frac{RT}{F} \frac{u_R^{c_{RX}} - u_M^{c'_{MZ}} - u_X^{c_{RX}} + u_Z^{c'_{MZ}}}{u_R^{c_{RX}} + u_X^{c_{RX}} - u_M^{c'_{MZ}} - u_Z^{c'_{MZ}}} \\ &\quad \times \ln \frac{u_M^{c'_{MZ}} + u_Z^{c'_{MZ}}}{u_R^{c_{RX}} + u_X^{c_{RX}}} \end{aligned} \quad (\text{A1.1})$$

$$\begin{aligned} E_{j2} &= \frac{RT}{F} \frac{u_M^{c''_{MZ}} - u_Z^{c''_{MZ}} - u_R^{c_{RX}} + u_X^{c_{RX}}}{u_M^{c''_{MZ}} + u_Z^{c''_{MZ}} - u_R^{c_{RX}} - u_X^{c_{RX}}} \\ &\quad \times \ln \frac{u_R^{c_{RX}} + u_X^{c_{RX}}}{u_M^{c''_{MZ}} + u_Z^{c''_{MZ}}} \end{aligned} \quad (\text{A1.2})$$

If $c_{RX} \gg c_{MZ}$, then $u_R^{c_{RX}}, u_X^{c_{RX}}, \gg u_M^{c_{MZ}}, u_Z^{c_{MZ}}$ and we can write

$$E_{j1} = \frac{RT}{F} \frac{u_R^{c_{RX}} - u_X^{c_{RX}}}{u_R^{c_{RX}} + u_X^{c_{RX}}} \times \ln \frac{u_M^{c'_{MZ}} + u_Z^{c'_{MZ}}}{u_R^{c_{RX}} + u_X^{c_{RX}}} \quad (\text{A1.3})$$

$$E_{j2} = \frac{RT}{F} \frac{u_R^{c_{RX}} - u_X^{c_{RX}}}{u_R^{c_{RX}} + u_X^{c_{RX}}} \times \ln \frac{u_R^{c_{RX}} + u_X^{c_{RX}}}{u_M^{c''_{MZ}} + u_Z^{c''_{MZ}}} \quad (\text{A1.4})$$

since

$$E_{j,H} = E_{j1} + E_{j2} \quad (A1.5)$$

we can combine Equations A1.3 and A1.4 and, after some rearrangement, get

$$E_{j,H} = \frac{RT}{F} \frac{u_R - u_X}{u_R + u_X} \ln \frac{c_{MZ}'}{c_{MZ}''} \quad (A1.6)$$

or

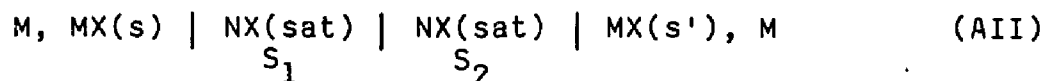
$$E_{j,H} = - \frac{RT}{F} (t_R - t_X) \ln \frac{c_{MZ}''}{c_{MZ}'} \quad (A1.7)$$

The same equation will, of course, apply if the solvent on the left side of the junction (the reference solvent) is not water, but some other nonaqueous medium, different from S.

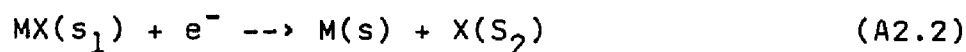
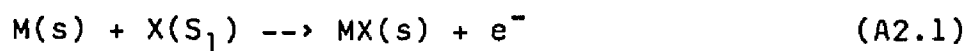
APPENDIX 2

Proof of Equation 47, Found in Reference (52).

For a cell



the half-cell reactions are



where $MX(s')$ is a solvate of MX with S_2 , and therefore $MX(s) \neq MX(s')$.

The e.m.f. of the above cell can be written as follows:

$$E = -\frac{1}{F} \int_L^R dG_M - \frac{1}{F} \int_L^R dG_X + \frac{1}{F} \int_L^R dG_{MX} + E_j \quad (A2.3)$$

We know the following:

$$\int_L^R dG_M = 0 \quad (A2.4)$$

and

$$\int_L^R dG_{MX} = \Delta G_{MX}^{\circ} \quad (A2.5)$$

(if MX forms a solid solvate).

We can also say that

$$E_j = - \frac{1}{F} \left[\int_L^R t_N dG_N - \int_L^R t_X dG_X \right] + E_{j,s} \quad (A2.6)$$

If NX is high enough (saturated solution), then $t_M \cong 0$ and $t_N + t_X = 1$. Rewriting E_j in terms of t_N only (using $t_X = 1 - t_N$) and then substituting this expression in the expression for e.m.f. (Equation A2.3) we finally get

$$E = - \frac{1}{F} \left[t_N \int_L^R dG_{NX} - \Delta G_{MX}^{\circ} \right] + E_{j,s} \quad (A2.7)$$

and if MX does not form a solid solvate with either solvent, then $\Delta G_{MX}^{\circ} = 0$ and we have

$$E = - \frac{t_N}{F} \int dG_{NX} + E_{j,s} \quad (A2.8)$$

APPENDIX 3

Densities of Methanol-Water Solvents at 25°C (59).

Wt % Methanol	Density
0.0	0.9971
10.0	0.9799
20.0	0.9644
40.0	0.9316
50.0	0.9119
60.0	0.8907
80.0	0.8425
90.0	0.8150
100.0	0.7866

APPENDIX 4

Dielectric Constants for Methanol-Water Solvents (59).

Wt % Methanol	ϵ
100	32.64
90	37.92
80	42.58
70	47.10
60	51.61
50	56.30
40	60.93
30	65.30
20	69.95
10	74.16
0	78.30

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