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DETERMINATION OF TRANSFER ACTIVITY COEFFICIENTS USING EMF CELLS WITH LIQUID JUNCTION

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DETERMINATION OF TRANSFER ACTIVITY COEFFICIENTS USING EMF CELLS WITH LIQUID JUNCTION

by

SIDNEY S. GOLDBERG

A dissertation submitted to the Graduate Faculty
in Chemistry in partial fulfillment of the
requirements for the degree of Doctor of
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1980

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.

June 30, 1980
date

Chairman of Examining Committee

30 June 1980
date

David C. Locke
Executive Officer

David C. Locke
Supervising Committee

The City University of New York

To my parents.

Abstract

DETERMINATION OF TRANSFER ACTIVITY COEFFICIENTS USING EMF CELLS WITH LIQUID JUNCTION

by

Sidney S. Goldberg

Adviser: Professor Orest Popovych

Transfer activity coefficients, log ${}_{m}\gamma_{i}$, of sodium (Na^+), hydrogen (H^+), triisoamyl-n-butylammonium (TAB^+), and picrate (Pi^-) ions were evaluated using e.m.f. cells with liquid junction between pairs of the following dipolar aprotic solvents: acetonitrile, N,N-dimethylformamide, dimethylsulfoxide, and propylene carbonate. Solutions of tetraethylammonium perchlorate (Et_4NClO_4), tetraethylammonium picrate (Et_4NPi), and triisoamyl-n-butylammonium tetraphenylborate ($TABBPh_4$) were used as salt bridges in these cells. Values of log ${}_{m}\gamma_{i}$ were calculated from the measured e.m.f. of the cells and calculated values of the liquid-junction potential.

The liquid-junction potential, E_j, in cells with junctions between two solvents was attributed to the transport of solvated ions across the solvent-solvent interface. Equations for the calculation of the E_j in cells with and without salt bridges were developed. The E_j was formally divided into

E_j', which accounts for terms due to the transport of ions across the interface and $E_{j\ solvent}$, which accounts for contributions to the E_j due to the transport of solvent molecules across the interface.

$E_{j\ solvent}$ was calculated independently for two different cells with a junction between the same solutions but with different pairs of indicator electrodes. $E_{j\ solvent}$ values between aqueous and methanol-water solvents were found to increase with increasing methanol content and showed an inverse dependence on the concentration of the current-carrying species in solution. Values of $E_{j\ solvent}$ were lowered by the addition of saturated aqueous KCl salt bridges between the solutions studied. In addition, literature data of measurements of pH-cells with liquid junction in methanol-water and ethanol-water media were interpreted.

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I would like to express my sincere appreciaton to Professor Orest Popovych for his interest and guidance throughout the years of our association. While other graduate students just have advisors, I consider Professor Popovych to be a close friend and am looking forward to a long continuing relationship with him in the future. I would, also, like to thank Dr. David Berne and Professor Joseph Glickstein for inspiring me to pursue my career as a chemist.

It is only with the support of my parents, family, and fiancée, Shari, that this thesis has become a reality. Their confidence in me is duly appreciated.

In addition, I would like to thank the faculty and staff of the Chemistry Department of Brooklyn College, with special thanks to Ottmar Safferling, Sylvia Smolensky and Bill Knoop, for their help and support throughout my years at the college.

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Table of Contents

List of Tables

List of Figures

INTRODUCTION

Presentation of the Problem.

Introduction.

With the increased availability of nonaqueous solvents in large quantities, chemists have shifted some of their interest from the physico-chemical properties of aqueous solutions to those of nonaqueous solutions. Analytical chemists have been using nonaqueous solvents as a means of shifting chemical equilibria to effect separations and identifications which would be impossible in aqueous solutions. Physical-organic chemists have discovered that transfer from alcohols to dipolar aprotic solvents increase some reaction rates by many orders of magnitude.

At the same time, it should not seem strange that chemists have retained many of the conventions used in aqueous systems. Electrode potential and ion-activity scales are conventionally referred to ideal solutions of unit activity in the solvent of interest as the standard state. Thus, there are as many conventional electrode-potential and ion-activity scales as there are solvent systems studied.

With the growing interest in nonaqueous solvent chemistry, it has become increasingly important to develop a system of correlating data in these solvents to a universal solvent scale (single standard state). Prediction of the changes in the chemical properties of solutes when transferred from one solvent to another is one of the major objectives. Quantitatively, this can be attained with knowledge of the free energies of transfer of the solutes between different media.

While a correlation of chemical properties of solutes in different solvents is of great interest, the key to establishing single scales of electrode potentials and ion-activities lies with knowledge of the free energies of transfer of single ions, or the corresponding transfer activity coefficients, also known as the medium effects. Although measurements of the free energy of transfer of single ions are not thermodynamically feasible, various extrathermodynamic assumptions have been employed to obtain values of the transfer activity coefficient of single ions, which is a measure of the free energy of transfer.

In this thesis, we will be studying e.m.f. cells with liquid junction as a means of obtaining values of the transfer activity coefficients for single ions. Measurements will be made in a series of dipolar aprotic solvents. New equations will be developed for these systems. In addition, detailed interpretation of existing literature data on cells with liquid junction in methanol-water and ethanol-water media will be carried out, particularly with pH cells. Measurements of e.m.f. cells with liquid junction in methanol-water solvents will be made and analyzed.

Transfer Activity Coefficient.

The chemical potential of a solute i in a solvent s referred to the standard state in the given solvent is defined as

$$\bar{G}_i = {}_sG_i^\circ + RT \ln a_i^* \qquad (1)$$

where $\bar{G}_i$ is the chemical potential or partial molal free energy of the solute, i, ${}_sG_i^\circ$ is the standard free energy of solute i in the solvent of interest, and a_i is the activity of solute i in that solvent expressed as

$$a_i^* = m_i \, {}_s\gamma_i \qquad (2)$$

where m_i is the molality and ${}_s\gamma_i$ is the salt-effect activity coefficient which becomes unity at infinite dilution in given solvent. Similarly, the chemical potential of a solute i in water is defined as

$$\bar{G}_i = {}_wG_i^\circ + RT \ln a_i \qquad (3)$$

where subscript w refers to the aqueous standard state, ${}_wG_i^\circ$ is the standard free energy of solute i in water and a_i is the conventional aqueous activity given as

$$a_i = m_i \, {}_w\gamma_i \qquad (4)$$

where m_i is the molality of solute i and the aqueous activity coefficient ${}_w\gamma_i$ approaches unity only at infinite dilution in water. The chemical potential of any nonaqueous solution can be formulated referring to either aqueous or nonaqueous standard states. For a given nonaqueous solution, the difference between the nonaqueous and aqueous standard free energies is expressed by

$$ {}_{s}G_i^{\circ} - {}_{w}G_i^{\circ} = RT \ln \frac{a_i}{a_i^{*}} \qquad (5) $$

The ratio term, a_i/a_i^{*}, represents the activity of a solution referred to its aqueous standard state divided by the activity of the same solution referred to its nonaqueous standard state. This term is defined as the transfer activity coefficient, or medium effect:

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

Thus, the transfer activity coefficient is a measure of the difference in the standard free energy of a solute i in water and in the nonaqueous solvent:

$$ {}_{s}G_i^{\circ} - {}_{w}G_i^{\circ} = RT \ln {}_{m}\gamma_i $$

The transfer activity coefficient os a solute i is a function only of the two standard states, temperature and pressure but is independent of the concentration of solute i or other solutes.

The salt-effect nonaqueous activity coefficient, ${}_{s}\gamma_i$, is related to its equivalent value on the aqueous scale, ${}_{w}\gamma_i$, by the transfer activity coefficient:

$$ {}_{w}\gamma_i = {}_{s}\gamma_i \; {}_{m}\gamma_i \qquad (8) $$

For an aqueous system, the value of the transfer activity coefficient will be unity.

Similarly, the transfer activity coefficient can be considered a conversion factor from a nonaqueous to the aqueous activity scale:

$$a_i = a_i^* \, {}_m\gamma_i \tag{9}$$

For example, with knowledge of the transfer activity coefficient, log ${}_m\gamma_H$, the pa_H^* of a nonaqueous solution can be expressed on the aqueous pa_H scale

$$pa_H = pa_H^* - \log {}_m\gamma_H \tag{10}$$

where $pa_H^* = -\log m_H \, {}_s\gamma_H$ and m_H and ${}_s\gamma_H$ are the molality and the nonaqueous salt-effect activity coefficient, respectively.

For the reaction

$$A + B = C + D \tag{11}$$

the equilibrium constant in water, ${}_wK$, and in a nonaqueous solvent, ${}_sK$, are related by the transfer activity coefficients:

$${}_wK = {}_sK \, \frac{{}_m\gamma_C \; {}_m\gamma_D}{{}_m\gamma_A \; {}_m\gamma_B} \tag{12}$$

Up to now, we have defined the transfer activity coefficient as the difference between the standard free energies between a nonaqueous solvent and water. Water has generally been chosen because of the vast amount of relevant physio-chemical information available in that solvent. However, 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 ${}^{\mathrm{MeCN}}_{\mathrm{m}}\gamma^{\mathrm{DMSO}}_{\mathrm{i}}$ refers to the transfer of solute i from acetonitrile (reference) to dimethylsulfoxide.

There is much confusion in the literature as to the nomenclature used to describe the difference in the standard free energies of a solute in two different solvents. An excellent discussion of this topic is written by Popovych in the "Treatise on Analytical Chemistry" (1). At present, the term, "transfer activity coefficient," is the most frequently used term in recent literature (1-3). However, the older term, "medium effect," is still used. In this thesis, the term, "transfer activity coefficient," will be used exclusively for ${}_{\mathrm{m}}\gamma_{\mathrm{i}}$.

Establishment of a Universal Activity Scale.

Chemists measure the pH of solutions to obtain values of hydrogen ion activities in solution. The activity of any species, e.g., hydrogen ion, electolyte, is referred to infinite dilution of that species in the solvent of interest. Measuremencs in a nonaqueous solvent are, generally, referred to infinite diultion in the nonaqueous solvent. In other words, activity scales are dependent on the reference solvent chosen.

Is the activity of an aqueous solution of $pa_H = 3$ equivalent to a solution of $pa_H^* = 3$ in glacial acetic acid medium? The solution in acetic acid is intuitively more acidic than the aqueous solution of the same activity. Similarly, a solution of $pa_H^* = 3$ in liquid ammonia should, intuitively, be more basic than an aqueous solution at the same pa_H as was mentioned earlier. Thus, there are as many solvent activity scales as solvents with no means of intercomparing these scales without knowledge of the transfer activity coefficient.

By definition (Equation 6), the transfer activity coefficient is a ratio of the activities of a solute *i*

$$_m\gamma_i = \frac{a_i}{a_i^*} \tag{6}$$

in two different solvents, provided the solutions are at the same chemical potential (or we are talking about the same solution). The value of $_m\gamma_i$ can only equal unity if the solute activities in both solutions are equal. The nonaqueous activity, a_i^*, can be converted to an aqueous activity by means of Equation 13

$$pa_i = pa_i^* - \log {}_m\gamma_i \tag{13}$$

with pa_i and pa_i^* being the negative logarithm of the aqueous and nonaqueous activities, respectively. For example, the activity of a solution of silver ion in acetonitrile, pa_{Ag}^*, can be equated to a pa_{Ag} on the aqueous scale by:

$$pa_{Ag} = pa_{Ag}^* - \log {}_m\gamma_{Ag} \tag{13a}$$

Establishment of a Solvent-Independent Scale of Electrode Potentials.

By convention, the standard electrode potential of the hydrogen electrode, E°_{H}, is considered equal to zero in every solvent. All measurements of potential differences in a solvent are therefore referred to the standard hydrogen electrode (SHE) in that solvent. Thus, direct intercomparison of potential scales in different solvents will lead to erroneous results. For instance, when comparing the conventional standard potential value of Cu^{+2}/Cu in acetonitrile of 0.74 volts with the conventional standard potential of Ag^{+}/Ag in water of 0.80 volts, it would be assumed that silver salts would oxidize copper metal in acetonitrile. However, the opposite is true; cupric salts oxidize silver metal in acetonitrile.

The idea that the standard potential of the hydrogen electrode is independent of solvent seems difficult to accept. Is the hydrogen ion solvated to the same extent in every solvent? Our chemical knowledge suggests otherwise. The hydrogen ion tends to be less tightly solvated in acidic solvents, such as glacial acetic acid and formic acid, than in basic solvents, like hydrazine and pyridine. The convention of $E^{\circ}_{H} = 0$ is only applicable for comparisons within a single solvent system.

The conventional standard potential of an electroactive ion, i, is defined by

$$ {}_{s}E^{\circ}(i,s) = E^{\circ}(i,s) - E^{\circ}(H,s) \qquad (14) $$

where ${}_{s}E^{\circ}(i,s)$ is the potential of i in solvent s and $E^{\circ}(H,s)$ is the standard potential of the hydrogen electrode in solvent s. Similarly, the standard potential of the electroactive ion i on the water scale, ${}_{w}E^{\circ}(i,s)$, is defined by

$$ {}_{w}E^{\circ}(i,s) \equiv E^{\circ}(i,s) - E^{\circ}(H,H_2O) \qquad (15)$$

where $E^{\circ}(i,s)$ is the absolute standard potential of i in solvent s and $E^{\circ}(H,H_2O)$ is the absolute potential of the hydrogen electrode in water. $E^{\circ}(H,H_2O)$ is assumed to be zero volts. An expression converting the conventional standard potential on the nonaqueous scale to a corresponding aqueous value is obtained by combining Equations 14 and 15, yielding

$$ {}_{w}E^{\circ}(i,s) = {}_{s}E^{\circ}(i,s) + E^{\circ}(H,s) - E^{\circ}(H,\ H_2O) \qquad (16)$$

The term $E^{\circ}(H,s) - E^{\circ}(H,H_2O)$ represents the difference in the standard potentials of the hydrogen electrode on the nonaqueous and aqueous scales. This expression is directly related to the transfer activity coefficient of the proton:

$$E^{\circ}(H,s) - E^{\circ}(H,H_2O) = \frac{RT}{nF} \ln {}_{m}\gamma_{H} \qquad (17)$$

Substituting Equation 17 into Equation 16, we find:

$$ {}_{w}E^{\circ}(i,s) = {}_{s}E^{\circ}(i,s) + \frac{RT}{nF} \ln {}_{m}\gamma_{H} \qquad (18)$$

The standard potential of any electrode on any solvent scale can be converted to its value on the aqueous scale using the transfer activity coefficient on the hydrogen ion, ${}_m\gamma_H$. Hence, a universal scale of electrode potentials can be developed if values of ${}_m\gamma_H$ for the solvents of interest are known.

Evaluation of Liquid-Junction Potentials Across the Interface of Two Solvents.

The potential of an electrochemical cell which contains an interface between two different solutions will include a liquid-junction potential, E_j, across that interface. In aqueous solutions, the E_j is primarily due to the differences in the concentration of the ions and in their mobilities in the two solutions across the interface. Chemists have minimized the value of this potential experimentally by including in the e.m.f. cells, salt bridges between the two half cells. Salt bridges must contain electrolytes of high concentration, relative to the other ions present. However, the liquid-junction potential between two dissimilar solvents cannot be simply suppressed by addition of a salt bridge. The reason why this is so will be developed in detail in what follows.

Consider Cell I, which is composed of two half cells that are standard hydrogen electrodes in water and in solvent s:

$$\begin{array}{l|l|l|l} \mathrm{Pt},\ H_2 & H^+\ (a_H=1) & H^+\ (a_H{}^*=1) & H_2,\ \mathrm{Pt} \\ & H_2O & s & \\ & \qquad\quad E_j & & \end{array} \qquad \text{(Cell I)}$$

The potential $\underline{E}$ for the above cell can be expressed:

$$\underline{E} = E^\circ(H,s) - E^\circ(H,H_2O) + E_j \qquad (19)$$

with E_j being the liquid-junction potential across the interface between the aqueous and the nonaqueous solutions.

As previously discussed, the first two terms on the right hand side of Equation 19 are directly related to the transfer activity coefficient:

$$E^{\circ}(H,s) - E^{\circ}(H,H_2O) = \frac{RT}{nF} \ln {}_m\gamma_H \qquad (17)$$

Thus, Equation 19 reduces to:

$$\underline{E} = \frac{RT}{nF} \ln {}_m\gamma_H + E_j \qquad (20)$$

Thus, the value of the liquid-junction potential across the interface between two solvents can be directly obtained from an e.m.f. measurement if the value of the relevant transfer activity coefficient is known.

In summary, three major problems can be solved with knowledge of transfer activity coefficients for single ions: 1) establishment of a universal activity scale, 2) establishment of a solvent-independent electrode potential scale and 3) evaluation of liquid-junction potentials across the interface of two solvents.

Methods of Determination of Thermodynamic Transfer Activity Coefficients.

While the transfer activity coefficients of single ions can only be determined via extrathermodynamic means, 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 activity coefficients are discussed below.

Solubility Method.

The solubility method is generally most widely used in determining thermodynamic transfer activity coefficients. When water and a nonaqueous solvent is saturated with solute i, the chemical potentials of the solutions are expressed by:

$$_{w}G_{i} = {_{w}G_{i}^{\circ}} + RT \ln a_{i} \text{ (satd.)} \tag{21a}$$

and

$$_{s}G_{i} = {_{s}G_{i}^{\circ}} + RT \ln a_{i}^{*} \text{ (satd.)} \tag{21b}$$

where a_i (satd.) and a_i^* (satd.) are the activities of saturated aqueous and nonaqueous solutions. The free energies of a solute in the solid state and in a saturated solution are equal. Thus, in the absence of any crystal solvates, the free energies of any two saturated solutions of solute i must be equal. Equating Equations 21a and 21b yields:

$$\frac{{_{s}G_{i}^{\circ}} - {_{w}G_{i}^{\circ}}}{RT} = \ln \frac{a_{i}\text{(satd.)}}{a_{i}^{*}\text{(satd.)}} = \ln {_{m}\gamma_{i}} \tag{22}$$

The transfer activity coefficient of an uncharged solute is the ratio of the activities of saturated solutions in the aqueous and nonaqueous solvents. For an electrolyte, the activity of a saturated solution is equivalent to the solubility product, K_{sp}. Expressed in logarithmic form, Equation 22 becomes:

$$\log {}_{m}\gamma_{i} = p({}_{s}K_{sp}) - p({}_{w}K_{sp}) \qquad (23)$$

At this point, it is important to reiterate that the choice of water as a reference solvent is only as a convenience; any solvent can be used as reference.

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

$$\log {}_{m}\gamma_{(\mathrm{electrolyte})} = \log {}_{m}\gamma_{\pm}^{2} = (\log {}_{m}\gamma_{+} + \log {}_{m}\gamma_{-}) \qquad (24)$$

where ${}_{m}\gamma_{\pm}^{2}$, ${}_{m}\gamma_{+}$, ${}_{m}\gamma_{-}$ are the transfer activity coefficients for the electrolyte, cation and anion, respectively. Calculations of transfer activity coefficients for the electroneutral differences between ions can be made. For example,

$$\log {}_{m}\gamma_{Cl} - \log {}_{m}\gamma_{Br} = \log {}_{m}\gamma_{AgCl} - \log {}_{m}\gamma_{AgBr} \qquad (25)$$

Similarly, transfer activity coefficients for electrolytes for which ion-activity products in a solvent cannot be accurately determined experimentally, can sometimes be calculated. For example, values for log ${}_{m}\gamma$ for tetraphenylarsonium tetraphenylborate (Ph_4AsBPh_4), which is extremely insoluble in water, are obtained from log ${}_{m}\gamma$ values of other electrolytes:

$$\log {}_{m}\gamma_{Ph_4AsBPh_4} = \log {}_{m}\gamma_{Ph_4AsPi} + \log {}_{m}\gamma_{KBPh_4} - \log {}_{m}\gamma_{KPi} \qquad (26)$$

While the solubility method is generally the most applicable, there are several complications involved in its use. First, the free energies of saturated solutions of a solute are only equal if no crystal solvates are formed with either solvent. In such cases where they are formed, another method for the determination of $_m\gamma_i$ must be used. Second, in solvents of low dielectric constants, the possible association of ions must be taken into account. In cases of appreciable ion-pairing, the solubility product must be expressed as

$$K_{sp} = m^2 \alpha^2 \gamma^2 \qquad (27)$$

where m is the molality, α is the degree of dissociation of the ion-pairs, and γ is the salt-effect activity coefficient. The degree of dissociation is generally determined experimentally from electrolytic conductance measurements.

A third problem encountered involves obtaining values of the 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-Hückel equation or a Davies equation, are commonly used for solutions of electrolytes of concentrations up to approximately 10^{-2} molar. However, experimental determinations of activity coefficients are more desirable, of course. In nonaqueous solvents, in particular, it is advisable to investigate how the literature values of solubility products were obtained. Many of these measurements are of poor precision and accuracy.

E.m.f. Method.

Transfer activity coefficients of electroneutral combinations of ions can often be determined using e.m.f. measurements. The standard free energy of an electroactive ion is directly related to its electrode potential by:

$$G_i^\circ = -nFE_i^\circ \tag{23}$$

Hence, the difference in the standard potential, E_i°, of galvanic cells in two different media can be used to calculate the transfer activity coefficient:

$$\Delta E_i^\circ = -\frac{RT}{nF} \ln {}_m\gamma_i \tag{29}$$

In actuality, the standard potential of any electrode is equal to the potential difference of the given standard electrode and a standard reference hydrogen electrode in the solvent of interest. Thus, the difference in standard potential of an electrode in two media is a measure of the sum or the difference of log ${}_m\gamma_i$ and log ${}_m\gamma_H$. For example, Cell II represents a hydrogen-silver-silver chloride cell:

$$\text{Pt, } H_2(g) \;\Big|\; \text{HCl } (a = 1) \;\Big|\; \text{AgCl(s), Ag} \qquad \text{(Cell II)}$$

The value of E_{AgCl}° is simply equal to the standard potential of Cell II. Thus, the difference between the standard potential of the silver-silver chloride electrode in water and nonaqueous solvent is related to log ${}_m\gamma_{HCl}$:

$$\log {}_m\gamma_{HCl} = (\log {}_m\gamma_H + \log {}_m\gamma_{Cl}) = \frac{{}_wE^\circ_{AgCl} - {}_sE^\circ_{AgCl}}{0.05916}, \text{ at } 25°C. \quad (30)$$

Similarly, the difference between the standard potentials of any metal-metal ion electrode in any two solvents is a measure of the difference of the transfer activity coefficient of the metal ion and the hydrogen ion:

$$\log {}_m\gamma_M - \log {}_m\gamma_H = \frac{{}_sE^\circ_M - {}_wE^\circ_M}{0.05916} \text{ at } 25°C. \quad (31)$$

Thus, only transfer activity coefficients for electroneutral combinations of ions are thermodynamically determinable.

Distribution Method.

The use of the distribution method for determination of transfer activity coefficients is quite limited. In cases where two solvents are totally immiscible, the value of ${}_m\gamma_i$ 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 is that dilute solutions may be used; thus, uncertain corrections for salt-effect activity coefficients and the degree of dissociation required in the solubility method can be neglected. However, in practice, most solvents of interest are miscible. In addition, so-called immiscible solvents are nevertheless saturated with each other at equilibrium. Thus, there is no distribution of the solute between the two pure solvents.

Transfer Activity Coefficients of Single Ions.

Although thermodynamic transfer activity coefficients of electrolytes are experimentally attainable, their usefulness in terms of solution chemistry is rather limited. For example, they do not provide a correlation of e.m.f. and pH scales in different solvents. The key to the correlation of e.m.f. scales, universal ion-activity scales and the evaluation of liquid junctions lies with knowledge of transfer activity coefficients of single ions. Since these quantities are not thermodynamically attainable, various extrathermodynamic methods have been developed to determine them. Popovych (1,4) has written excellent critical reviews of these methods. However, in this thesis, we shall discuss only a few of them.

Reference-Electrolyte Method.

In the reference-electrolyte method, the transfer activity coefficients of the cation and anion of the reference electrolyte are assumed to be equal. Thus,

$$\log {}_m\gamma_{\text{cation}} = \log {}_m\gamma_{\text{anion}} = 1/2 \log {}_m\gamma_{\substack{\text{reference}\\\text{electrolyte}}} \qquad (32)$$

The transfer activity coefficient for a single ion is obtained by equally dividing the thermodynamic transfer activity coefficient of the reference electrolyte.

What makes a good choice of reference electrolyte? It must be a 1:1 electrolyte with equivalent anion and cation. Our main consideration is that the difference in solvation energy between two solvents be identical for both ions. Therefore, the reference ions should be large ($r > 4$Å), have small surface charge densities, low polarizabilities, should not interact specifically with solvent molecules, and be as equal in size and similar as possible. The transfer free energies of these ions would be determined mainly by the nonelectrostatic energies of solvation and could be considered equal.

There are three electrolytes that fit the above criteria. The first is tetraphenylphosphonium tetraphenylborate (Ph_4PBPh_4). Grunwald, Baughman and Kohnstam (5) used Ph_4PBPh_4 to estimate free energy changes for the transfer of single ions between dioxane-water mixtures. Triisoamyl-n-butylammonium tetraphenylborate ($TABBPh_4$) was used by Popovych (6) to determine transfer activity coefficients in methanol and the ASTM mixture, consisting of 50.0% toluene, 49.5% isopropanol and 0.5% water and by Popovych and Dill (7) in ethanol-water mixtures. Currently, the electrolyte of choice is tetraphenylarsonium tetraphenylborate (Ph_4AsBPh_4) (1,7-12). When the Ph_4AsBPh_4 assumption is applied, the transfer activity coefficient of the reference electrolyte is divided equally between its ions:

$$\log {}_m\gamma_{Ph_4As} = \log {}_m\gamma_{BPh_4} = \tfrac{1}{2} \log {}_m\gamma_{Ph_4AsBPh_4} \qquad (32a)$$

Once the transfer activity coefficient is available for one ion, values of $\log {}_m\gamma$ for all other single ions can be calculated from available data, for example:

$$\log {}_m\gamma_K = \log {}_m\gamma_{KBPh_4} - \log {}_m\gamma_{BPh_4} \tag{32b}$$

$$\log {}_m\gamma_{Cl} = \log {}_m\gamma_{KCl} - \log {}_m\gamma_K \tag{32c}$$

$$\log {}_m\gamma_H = \log {}_m\gamma_{HCl} - \log {}_m\gamma_{Cl} \tag{32d}$$

Potentiometric Methods.

Introduction.

As we have seen earlier, it is possible to calculate transfer free energies and transfer activity coefficients of electroneutral combinations of ions from standard potentials of electrodes reversible to these ions. However, when attempts are made to extend the interpretation of e.m.f. measurements to individual ionic species, a problem as to the choice of reference electrode arises. In cells without liquid junction, where the reference electrode is transferred from solvent to solvent along with the indicator electrode, the measured e.m.f. reflects the solvation-energy changes not only for the ion of interest (to which the indicator electrode acts reversibly), but also for the ion to which the reference electrode responds. For example, in our previous discussion, a comparison of the standard silver-silver chloride electrode potentials (Cell II) in water and a nonaqueous solvent yielded the <u>sum</u> of the transfer activity coefficients of chloride and hydrogen ions:

$$\log {}_m\gamma_H + \log {}_m\gamma_{Cl} = \frac{{}_wE^\circ_{AgCl} - {}_sE^\circ_{AgCl}}{0.05916} \text{ at } 25^\circ\text{C} \qquad (30)$$

and would not be a suitable method for determining the transfer activity coefficient for chloride ion alone.

One approach to the above problem has been to search for a reference electrode whose potential would remain nearly constant in all solvents (13). Another approach is to obtain the value of the transfer activity coefficient, $_m\gamma$, for one of the ions by some extrathermodynamic assumption not involving electrodes and then calculate the ${}_{m}\gamma$ for the ion of interest.

An alternative is to study the effect of solvent on electrode potentials using e.m.f. cells with liquid junction. Here the reference electrode is always kept immersed in the same medium (e.g. aqueous) while the solvent is varied only in the indicator-electrode compartment. The widely used calomel electrode with a salt bridge of saturated aqueous KCl is the most familiar reference electrode of this type. Unfortunately, in that experimental arrangement, the measured e.m.f. includes not only the electrode potentials, but also an uncertain and varying liquid-junction potential, E_j, at the interface of the two solutions. Therein lies the dilemma: in cells without liquid junction, extrathermodynamic estimates must be made as to the effect of the solvent on the potential of the reference electrode; on the other hand, if the reference electrode is always kept in the same medium, we must deal with the liquid-junction potential at the boundary of electrolyte solutions in different solvent media.

Assumption of Negligible Liquid-Junction Potentials.

As an example of the application of this assumption to the estimation of transfer activity coefficients of single ions, the potential of Cell I:

$$\begin{array}{llllll} \mathrm{Pt,H_2(g)} & \Big| \begin{array}{c}\mathrm{HCl\ (a=1)} \\ \mathrm{H_2O}\end{array} & \vdots & \begin{array}{c}\mathrm{HCl\ (a^{*}=1)} \\ \mathrm{S}\end{array} & \Big| \ \mathrm{H_2(g),Pt} & \mathrm{(Cell\ I)} \\ & & E_j & & & \end{array}$$

expressed in Equation 20, is a measure of the combination of the transfer activity coefficient of the hydrogen ion and liquid-junction potential, E_j:

$$E\ \mathrm{cell} = \frac{RT}{nF} \ln {}_m\gamma_H + E_j \qquad (20)$$

When the value of the liquid-junction potential can be considered negligible or calculated by some means, the transfer activity coefficient can be determined from Equation (20).

This is what Bjerrum and Larsson (14) assumed when they estimated values of transfer activity coefficients of the hydrogen ion in ethanol-water media. E.m.f. measurements of Cell III, composed of a hydrogen electrode in the nonaqueous solvent and a 3.5N aqueous calomel electrode as a reference.

$$\mathrm{Pt,H_2(g)} \ \Big| \begin{array}{c}\mathrm{HCl} \\ \mathrm{ETOH\text{-}H_2O}\end{array} \ \vdots \ \mathrm{3.5N\ KCl(aq.)} \ \Big| \ \mathrm{Hg_2Cl_2\ ,Hg} \qquad \mathrm{Cell\ III}$$

By assuming that the potential at the calomel electrode remained constant, they calculated values of ${}_m\gamma_H$ for the proton using the equation at 25°C:

$$\log {}_m\gamma_H = \frac{E^{\circ}(\mathrm{cell,\ H_2O}) - E^{\circ}(\mathrm{cell,\ EtOH\text{-}H_2O})}{0.05916} \qquad (33)$$

where $E^\circ(\text{cell},H_2O)$ and $E^\circ(\text{cell, EtOH-}H_2O)$ are the standard potentials of Cell III measured with an aqueous and nonaqueous hydrogen electrode, respectively. In effect, these measurements could be represented by the e.m.f. of Cell I, which is:

$$E_{cell} = \frac{RT}{nF} \ln {}_m\gamma_H + E_j \qquad (30)$$

Of course, by assuming that $E_j = 0$, they were able to derive values of log ${}_m\gamma_H$ in ethanol-water media.

Oiwa (15), using Cell IV:

$$\text{Pt},H_2(g) \left|\begin{matrix}\text{HCl}\\ \text{MeOH-}H_2O\end{matrix}\right| \text{KCl(sat.aq.)} \,\Big|\, Hg_2Cl_2,Hg \qquad \text{(Cell IV)}$$

derived values for ${}_m\gamma_H$ in methanol-water mixtures by estimating the liquid-junction potential using the Planck equation.

Parker and his associates (9,16-19) have proposed that the liquid-junction potential of Cell V be considered negligible:

$$\text{Ag} \left|\begin{matrix}AgClO_4\ (0.01M)\\ \text{Reference Solvent}\end{matrix}\right| \begin{matrix}Et_4NPi\ (0.1M)\\ \text{Reference Solvent}\\ \text{or S}\end{matrix} \left|\begin{matrix}AgClO_4\ (0.01M)\\ \text{Solvent S}\end{matrix}\right| \text{Ag}$$

Cell V

Here the reference solvent is either acetonitrile or methanol and the bridge solution of 0.1M tetraethylammonium picrate (Et_4NPi) is contained either in the reference solvent or in solvents, whichever is the poorer solvator of silver ions. By assuming that E_j in Cell V is negligible, the transfer activity coefficient of silver ion was calculated from:

$$\log {}_m^{o}\gamma^{s}_{Ag} = \frac{E_{cell}}{0.05916} \qquad (34)$$

Parker chose tetraethylammonium picrate as the salt bridge electrolyte because its ions have similar mobilities in several different solvents. In addition, he claimed that neither of thse ions have strong specific interactions with the solvents studied and so the solvation numbers of the two ions may be constant and approximately equal.

In their attempts to correlate standard electrode potentials in different solvent media, Rondinini, et.al. (20,21) evaluated the liquid-junction potential of Cell VI:

$$\begin{array}{l|l|l|l|l} \mathrm{Hg,Hg_2Cl_2} & \text{sat LiCl} & \mathrm{LiCl + CH_3COOH} & \text{(Sat)KCl} & \mathrm{Hg_2Cl_2,Hg} \\ & \text{in } \mathrm{CH_3COOH} & \quad \text{in S} & \quad \text{S} & \\ & \multicolumn{1}{r}{E_j{}'} & \multicolumn{1}{r}{E_j{}''} & & \end{array}$$

(Cell VI)

The e.m.f. of this cell was measured in different solvents S at various concentrations of acetic acid, C_{CH_3COOH} in the middle compartment of the cell, the molar ratio $C_{LiCl}:C_{CH_3COOH}$ being fixed at 1:6.87 and equal to that of saturated LiCl in 100% CH_3COOH. They contend that the liquid-junction potential $E_j{}''$ can be assumed to be negligible over the whole (LiCl + CH_3COOH) concentration range in each solvent " because the increasing of CH_3COOH drastically lowers the actual dielectric constant of the solvent concerned resulting in a minimization of the ionized part of LiCl with respect to the KCl bridge." (21). The $E_j{}'$ was eliminated by plotting the Ecell vs. the log ($C_{CH\ COOH}$) and extrapolating to the point of "C_{CH_3COOH}, solventless". Rondinini, et.al. claim that the $E_j{}'$ term cancels out "because at that limiting C_{CH_3COOH} the junction is between two identical solutions" (21).

The validities of all of the above assumptions (Bjerrum and Larsson, Oiwa, Parker and Rondinini will be critically evaluated in the theoretical discussion of liquid-junction potentials.

Theoretical Discussion of Liquid-Junction Potentials.

Cells without Salt Bridge.

Alfenaar, Deligny and Remijnse (22) derived an equation for the liquid-junction potential across the interface of two media. Their cell, Cell VII, is composed of silver-silver halide electrodes in solutions of alkali halides in water and methanol-water solvents, S:

$$\begin{array}{l|l|l|l} \mathrm{Ag,AgZ(s)} & \mathrm{MZ} & \mathrm{MZ} & \mathrm{AgZ(s),Ag} \\ & (\mathrm{H_2O}) & (\mathrm{S}) & \end{array} \qquad \text{Cell VII}$$

The liquid-junction potential between the two solvents is due to the transport of ions and solvent molecules across the interface:

$$E_j = -\sum_{\text{ions}} t_i\, \Delta G_{\text{ions}} + \sum_i \Delta G_{i\ \substack{\text{solvent}\\ \text{molecules}}} \qquad (35)$$

This can also be expressed by:

$$E_j = -(t_M - t_Z)\,\frac{RT}{F}\,\ln\frac{s^{m}MZ}{w^{m}MZ} - (t_M - t_Z)\,\frac{RT}{F}\,\ln\frac{s^{\gamma}MZ}{w^{\gamma}MZ}$$

$$- {}^1/F\ (t_M\ \Delta G_t^{\circ}(M) - t_Z\ \Delta G_t^{\circ}(Z)) + E_{j\ \text{solvent}} \qquad (36)$$

where m and γ are the molalities and salt-effect activity coefficients of electrolyte MZ and subscripts w and s refer to aqueous and nonaqueous solutions, respectively. The transport numbers t_M and t_Z were considered solvent independent and ΔG_t° (M) and ΔG_t° (Z) are the standard free energies of transfer for ions M^+ and Z^-, respectively, from water to nonaqueous solvent. $E_{j\ \text{solvent}}$ represents the component of the liquid-junction potential due to the transport of solvent molecules across the interface. The $E_{j\ \text{solvent}}$ term can be exactly evaluated from the e.m.f. of Cell VII:

$$E_{j\ \text{solvent}} = E_{\text{cell VII}} - \frac{t_M}{F}\,\Delta G^\circ_t(\text{MZ}) \qquad (37)$$

and $\Delta G^\circ_t(\text{MZ})$, the transfer free energy of the complete electrolyte.

Although the movement of ions and solvent molecules is mutually interdependent, Alfenaar, et. al. (22) divided the E_j formally into E_j', which contains all the contributions due to ions and to $E_{j\ \text{solvent}}$, the contribution due to transport of solvent molecules. Thus, Equation 36 can be formally written as

$$E_j = E_j' + E_{j\ \text{solvent}} \qquad (38)$$

The reason why the transport of solvent molecules is believed to contribute to E_j is based on the fact that some solvated ions are carried across the interface along with the solvent molecules. This phenomenon will be discussed in greater detail later in the text.

Cells with Salt Bridges.

In the work of Alfenaar, DeLigny and Remijnse (22), equations were formulated to express the liquid-junction potential between two media without a salt bridge solution present. In this thesis, equations are derived for the liquid junction potential of e.m.f. cells containing a salt bridge between two different solvent media. Consider Cell VIII

$$\mathrm{M}\left|\begin{array}{c}\mathrm{MZ}\\ S_1\end{array}\right|\begin{array}{c}\mathrm{RX}\\ S_1\end{array}\left|\begin{array}{c}\mathrm{MZ}\\ S_2\end{array}\right|\mathrm{M} \qquad \text{(Cell VIII)}$$

the liquid-junction potential in this cell is expressed by

$$E_j = -(t_M - t_Z)\,\frac{RT}{F}\log\frac{m_2}{m_1} - (t_M - t_Z)\,\frac{RT}{F}\log\frac{\gamma_2}{\gamma_1}$$
$$-\frac{1}{F}[t_M \Delta G^\circ_t\ (M) - t_Z \Delta G^\circ_t\ (Z) + t_R \Delta G^\circ_t\ (R) - t_X \Delta G^\circ_t\ (X)]$$
$$+ E_j \text{ solvent} \qquad (39)$$

where m is the molality of electrolyte MZ, γ is the conventional activity coefficient, RX is the salt bridge electrolyte, and 1 and 2 refer to different solvents.

An equation can be derived evaluating E_j solvent from the measured cell potential and other thermodynamic data. The sum of the transport number of all the ions in solutions is equal to unity:

$$t_M + t_Z + t_R + t_Z = 1 \qquad (40)$$

thus,

$$t_M = 1 - t_Z - t_R - t_X \qquad (41)$$

Substituting Equation 41 into Equation 39 yields:

$$E_j = E_{jA} - \frac{1}{F}[(1 - t_Z - t_R - t_X)\Delta G_t^\circ(M) - t_Z\Delta G_t^\circ(Z) + t_R\Delta G_t^\circ(R) - t_X\Delta G_t^\circ(X)] + E_{jsolvent} \tag{42}$$

where E_{jA} is equal to the first two terms in Equation 39. Expanding this equation and combining terms yields

$$E_j = E_{jA} - \frac{1}{F}[\Delta G_t^\circ(M) - t_Z(\Delta G_t^\circ(M) - \Delta G_t^\circ(Z) + t_R(\Delta G_t^\circ(R) - \Delta G_t^\circ(M)) - t_X(\Delta G_t^\circ(X) + \Delta G_t^\circ(M))] + E_{jsolvent} \tag{43}$$

Since:

$$\Delta G_t^\circ(R) - \Delta G_t^\circ(M) = \Delta G_t^\circ(RX) - \Delta G_t^\circ(MX) \tag{44a}$$

$$\Delta G_t^\circ(M) + \Delta G_t^\circ(X) = \Delta G_t^\circ(MX) \tag{44b}$$

and $\Delta G_t^\circ(R) + \Delta G_t^\circ(Z) = \Delta G_t^\circ(RZ)$ (44c)

Equation 43 can be written as:

$$E_j = E_{jA} - \frac{1}{F}[\Delta G_t^\circ(M) - t_Z\Delta G_t^\circ(MZ) + t_R(\Delta G_t^\circ(RX) - \Delta G_t^\circ(MX)) - t_X(\Delta G_t^\circ(MX)] + E_{jsolvent} \tag{45}$$

Combining Equation 45 and the e.m.f. of Cell VIII described by:

$$E_{cell} = \frac{1}{F}\Delta G_t^\circ(M) + E_j \tag{46}$$

and rearranging terms, we obtain:

$$E_{jsolvent} = E_{cell} - E_{jA} - \frac{1}{F}[t_Z\Delta G_t^\circ(MZ) - t_R(\Delta G_t^\circ(RX) - \Delta G_t^\circ(RX) - \Delta G_t^\circ(MX) + t_X\Delta G_t^\circ(MX)] \tag{47}$$

Equation 47 contains no single ion terms; only thermodynamic data and the cell potential.

Critique of Previous Approaches Using E.m.f. Cells With Liquid Junction.

In light of Equation 39, the assumption of negligible E_j in Bjerrum and Larsson's work (14) is obviously incorrect. They failed to take into account the contributions due to the transfer free energies, ΔG_t°, for any of the ions (the entire bracketed term in Equation 39), nor to $E_{j\text{solvent}}$. In addition, Bjerrum's use of a cube root formula $\log f = -k\sqrt[3]{c}$ to calculate activity coefficients is questionable. Therefore, it is not surprising that differences between their estimated values of $\log {}_m\gamma$ for single ions are not consistent with thermodynamic data.

Similarly, the Planck equation used by Oiwa (15) to calculate E_j only takes into account the first two terms in Equation 39. However, the major contribution to the liquid-junction potential is due to terms containing the transfer activity coefficients.

Parker (9, 16-19), in his derivation of equations for Cell V (17), fails to take into account the contribution of Ag^+ and ClO_4^- ions to the liquid-junction potential. While the mobilities of Et_4N^+ and Pi^- ions may be similar and, hence, their transport numbers equal, transport of Ag^+ and ClO_4^- ions across the interface must be considered. This contribution of E_j can be reduced to a negligible value by adjusting the concentration ratio of $Et_4NPi/AgClO_4$ to at least a hundred-fold value. In Parker's cells, however, that ratio is only ten.

Moreover, the transfer free energies, ΔG_t, of the salt bridge ions, Et_4N^+ and Pi^-, are not generally equal. Transfer activity coefficients of these ions differ by as much as two log ${}_m\gamma$ units (1). The assumption of negligible liquid-junction potential in Cell V, therefore, falls short of its mark.

Since an analysis and derivation of equations of Rondinini's work (20,21) is quite complicated and of little practical value because their approach was based on unsound principles and assumptions, a few general comments seem more appropriate. Rondinini, et. al. fail to consider any contributions to the liquid-junction potential due to differences in the transfer free energies of any of the ions in Cell VI. Moreover, their assumption of negligible liquid-junction in Cell VI seems odd. Every time the concentration of acetic acid in the middle compartment is changed, a totally new solvent mixture is created. The solvation properties of 10% acetic acid are not the same as those of 20% acetic acid. Thus, they are making extrapolations using a different cell each time.

Objectives of the Present Work

The first objective of this work is to estimate the value of transfer activity coefficients for single ions in several dipolar aprotic media using e.m.f. cells with liquid junction. Experimental data from the present study and from the literature are analyzed toward that end. Although the assumptions of the previous authors (9, 14-19) as to the value of the liquid-junction potential across the interface between two solvent media were incorrect (usually assumed to be negligible), transfer activity coefficients could be calculated from their data if the E_j values were really known.

In our present work, we calculate the E_j of e.m.f. cells containing salt bridges between two different solvent media (Cell VIII). The E_j of such a cell is expressed by Equation 39:

$$E_j = -(t_M - t_Z)\frac{RT}{F}\log\frac{m_2}{m_1} - (t_M - t_Z)\frac{RT}{F}\log\frac{\gamma_2}{\gamma_1}$$

$$- \frac{1}{F}[t_M\Delta G^\circ_t(M) - t_Z\Delta G^\circ_t(Z) + t_R\Delta G^\circ_t(R) - t_X\Delta G^\circ_t(X)]$$

$$+ E_{j\text{solvent}} \qquad (39)$$

Recalling Equation 7:

$$\Delta G_t(i) = RT \ln {}_m\gamma_i \qquad (7)$$

Equation 39 can be rewritten as:

$$E_j = -(t_M - t_Z)\cdot(0.05916)\ \log \frac{m_2}{m_1}\cdot\frac{\gamma_2}{\gamma_1} - 0.05916$$

$$[t_M \log {}_m\gamma_M - t_Z \log {}_m\gamma_Z + t_R \log {}_m\gamma_R - t_X \log {}_m\gamma_X]$$

$$+ E_{j\mathrm{solvent}} \qquad \text{(at 25°C)} \qquad (48)$$

If we substitute values of the transfer activity coefficients, log ${}_m\gamma_i$, transference numbers of these ions, an approximation for $E_{j\mathrm{solvent}}$, and correct for the differences in salt-effect activities (first two terms in Equations 39 and 48), we can calculate the liquid-junction potential of Cell VIII. Values of transfer activity coefficients of single ions required for this calculation are based on the tetraphenylarsonium tetraphenylborate (Ph_4AsBPh_4) assumption (Equation 32a) and were obtained from literature data (1,10) or from data determined experimentally by the author.

Once the value for E_j was obtained, it was substituted into Equation 49:

$$\log {}_m\gamma_M = \frac{E_{\mathrm{cell}} - E_j}{0.05916} \qquad \text{at 25°C} \qquad (49)$$

from which the transfer activity coefficient for the electrode active ion (M) was calculated.

Measurements of Cell VIII were carried out in dipolar aprotic solvents, using three different salt bridge electrolytes, RX, using sodium and hydrogen glass indicator electrodes. Parker's cell (Cell V) was, also, analyzed.

The second objective of this research is the interpretation of e.m.f. measurements of cells with liquid junction between water and alcohol-water media. Measurements using e.m.f. cells (similar to Cells VI and VIII) with and without concentrated salt bridge electrolytes are made, using calomel and sodium glass electrodes. Attempts are made to elucidate the $E_{j\,solvent}$ term. In addition, literature data of measurements of pH-cells in methanol-water and ethanol-water mixtures with saturated aqueous calomel and hydrogen electrodes are analyzed.

EXPERIMENTAL

Preparation of Solvents.

Acetonitrile (MeCN).

Acetonitrile was purified by the method of Coetzee, et. al. (23). ACS Reagent-Grade acetonitrile (Fisher or Mallinckrodt) was shaken successively with silica gel (6-16 mesh), activated alumina (80-200 mesh) and P_2O_5. Approximately five liters of decantate from these treatments were used to charge a distillation flask. The solvent was fractionally distilled with fresh P_2O_5 using a 30-cm vigreux column. The first and last liters were rejected and the middle fraction collected.

N,N - Dimethylformamide (DMF).

Certified ACS-Spectranalyzed N,N - dimethylformamide (Fisher) was fractionally distilled under reduced pressure through a 30-cm vigreux column. Out of a five-liter charge, the first and last liters were rejected and the middle three liters were used.

Dimethylsulfoxide (DMSO).

Certified ACS-Grade dimethylsulfoxide (Fisher) was fractionally distilled over CaH_2 under reduced pressure using a 30-cm vigreux column. The first and last fractions of about one liter each were discarded and the middle fraction was collected for use.

N - Methylformamide (NMF).

N - Methylformamide (Matheson, Coleman and Bell or Pfaltz and Bauer) was treated with P_2O_5. The solution was decanted into a one-liter distillation flask and then distilled under reduced pressure using a 30-cm vigreux column. The middle 400-ml fraction of the one liter of decantate was collected with the rest discarded.

Methanol (MeOH).

Spectranalyzed methanol (Fisher) was used without any further purification. Methanol-water mixtures were prepared volumetrically using approximate required amounts of spectranalyzed 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 (24). Appendix 1 contains a table of densities of methanol-water solvents.

Propylene Carbonate (PC).

Propylene carbonate (Eastman) was treated with portions of CaO and fractionally distilled under reduced pressure using a 30-cm vigreux column. The middle three-liter fraction of a five-liter charge was collected for use with the other fractions discarded.

Preparation and Purification of Solutes.

Triisoamyl-n-butylammonium Iodide (TABI).

Triisoamyl-n-butylammonium iodide was prepared by reluxing triisoamylamine (Eastman) and 1-iodobutane (Eastman) in 95% ethanol at 85°C for 48 hours. The reaction mixture was added to cold water and separated from the upper aqueous phase. Crude TABI was obtained in the form of a brown oil. At this point, the crude product was either used as is in the synthesis of $TABBPh_4$ or further purified. In the latter case, the oil was placed in a dry ice-isopropanol bath. After allowing time for all the salt to freeze out of solution, the solution was slowly brought up to room temperature and filtered. This filtered salt was redissolved in ethyl acetate and the above procedure repeated until a snow-white powder was formed. The salt was then dried in the vacuum oven for a few hours at 60°C.

Sodium Tetraphenylborate ($NaBPH_4$).

Sodium tetraphenylborate (Eastman Chemical - highest purity) was used without further purification.

Triisoamyl-n-butylammonium Tetraphenylborate ($TABBPh_4$).

Triisoamyl-n-butylammonium tetraphenylborate was prepared by the metathesis of triisamyl-n-butylammonium iodide and sodium tetraphenylborate in a 1:1 (by volume) methanol-water mixture. Crude $TABBPh_4$ was filtered and thoroughly washed with deionized water. The crude salt was dissolved in a 3:1 (by volume) acetone-water mixture and heated. Water was added until a slight cloudiness appeared, followed by a small amount of additional acetone to dissolve all of the $TABBPh_4$. Upon slow cooling, long white needles were formed. This procedure was repeated twice and the solute was dried in the vacuum oven at 60°C for six hours.

Tetraethylammonium Picrate (Et_4NPi).

Tetraethylammonium picrate was prepared by the metathesis of hot picric acid in a 1:1 (by volume) methanol-water mixture with tetraethylammonium bromide in methanol. Precipitation of crude Et_4NPi was completed upon addition of cold water. The crude product was filtered, washed and recrystallized twice from 95% ethanol. Long orange-yellow needles formed. The product was dried in the vacuum oven at 60°C for a few hours.

Tetraethylammonium Perchlorate (Et_4NClO_4).

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

Tetrabutylammonium Picrate (Bu_4NPi).

Tetrabutylammonium picrate was prepared exactly as Et_4NPi except that Bu_4NCl was used instead of Et_4NBr.

2,6-Dinitrophenol (DNP).

2,6-Dinitrophenol was purified by the method of Kolthoff, Chantooni and Bhowmik (25). Crude DNP (Eastern Chemical) was recrystallized from deionized water and dried overnight in the vacuum oven at room temperature.

Picric Acid (HPi).

Picric acid was purified using the method of Kolthoff and Chantooni (26). Reagent-Grade picric acid (Allied Chemical) was dissolved in hot reagent-grade benzene. After cooling, the solution was transferred to a one-liter separatory funnel and shaken with three 5-ml portions of 12M HCl to convert any ammonium picrate (a common contaminant) to picric acid. The benzene layer was shaken with portions of water, testing for any presence of chloride ion. The organic layer was separated and evaporated to dryness. The product was recrystallized from benzene and dried overnight in vacuo at room temperature.

Tetraethylammonium 2,6-Dinitrophenolate (Et_4NDNP).

Tetraethylammonium 2,6-dinitrophenolate was synthesized using the method of Kolthoff, Chantooni and Bhowmik (25). Tetraethylammonium hydroxide (Eastern Chemical, 25% in H_2O) was used to titrate 2,6-dinitrophenol until almost equivalence, monitored by a pH-meter. The solution was evaporated to dryness and the residue was washed with several portions of anhydrous ethyl ether to remove the excess phenol. The salt was recrystallized from a mixture of ethyl acetate-petroleum ether ("B" fraction) and dried in vacuo at 60°C for four hours.

Potassium Picrate (KPi), Sodium Picrate (NaPi).

Picric acid was dissolved by heating in a 1:1 (by volume) methanol-water mixture and combined with an equimolar solution of the desired alkali hydroxide in water. On cooling, large needles separated. More cold water was added to complete precipitation and the precipitate was washed by decantation. The KPi was recrystallized twice from deionized water; whereas, NaPi was recrystallized from a 1:1 (by volume) ethanol-water mixture. The crystals were dried in a vacuum oven for 6 hours at room temperature.

Tetraethylammonium Bromide (Et_4NBr), Benzoic Acid, Salicylic Acid.

Tetraethylammonium bromide, benzoic acid and salicyclic acid were all recrystallized from 95% ethanol and vacuum dried for a few hours at 60°C.

Sodium Salicylate.

Sodium salicylate was recrystallized from acetone and dried in vacuo at 60°C for a few hours.

Lithium Benzoate.

Lithium benzoate (ICN Pharmaceuticals) was used without any further purification.

Potassium Perchlorate.

Potassium perchlorate (Baker Analyzed) was used without any further purification.

E.m.f. Measurements.

The e.m.f. of galvanic cells with liquid junction of two different designs was measured with and without salt bridge electrolytes.

Sodium glass electrodes (Fisher Scientific 13-639-20) and hydrogen glass electrodes (Fisher Scientific 13-639-3) were used and the voltages measured with either an Electro Scientific Instruments portametric voltage bridge or a Hewlett-Packard digital voltmeter. Due to the high impedance of the glass electrode, a series of operational amplifiers had to be employed in the circuit. Figure 1 shows the circuit diagram of the amplifier system. The gain of the amplifier system was 3.00. All cell voltages reported have been corrected for this factor. Keithley Instruments Model 301 solid-state operational amplifiers were used as amplifiers A and B; while, an Analog Devices 40J amplifier was used as amplifier C.

Measurements were first made using a H-cell design. The H-cell (Figure 2) is divided into three compartments by one-centimeter diameter sintered glass frits of fine porosity. The outer compartments were filled with solutions of the electroactive ion in the solvent of interest with the middle compartment containing a solution of salt bridge electrolyte. The cell voltages using the H-cell were stable to within 1-2 millivolts.

After evaluation of the H-cell data, it was decided to use a cell of different design. The new design comprised

Figure 1

Circuit Diagram of Amplifier System

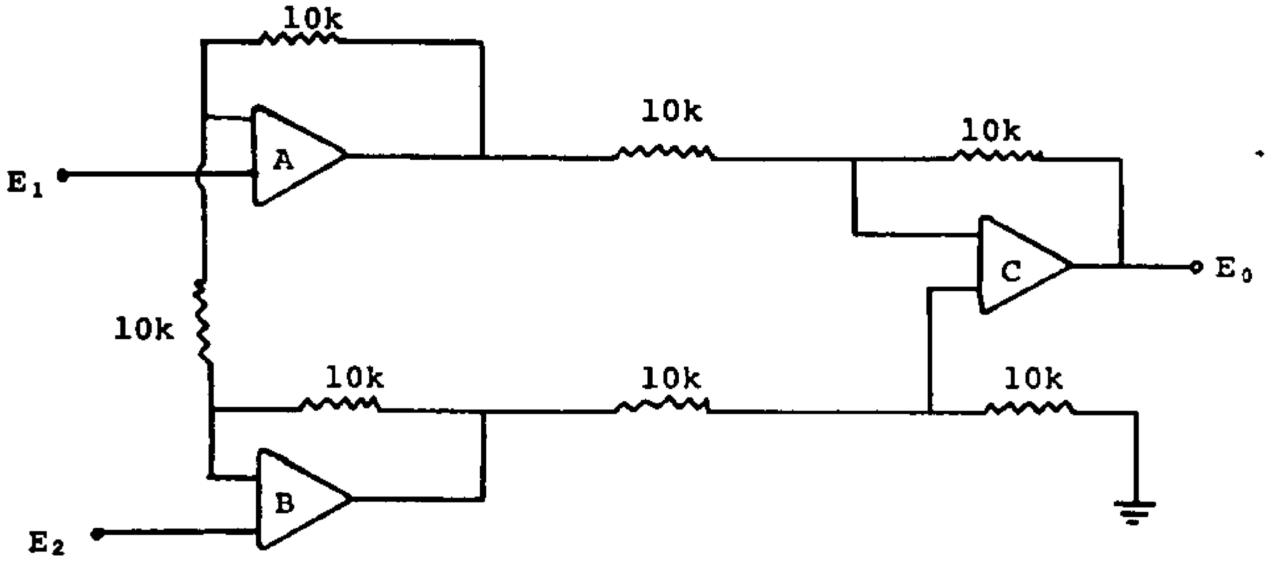
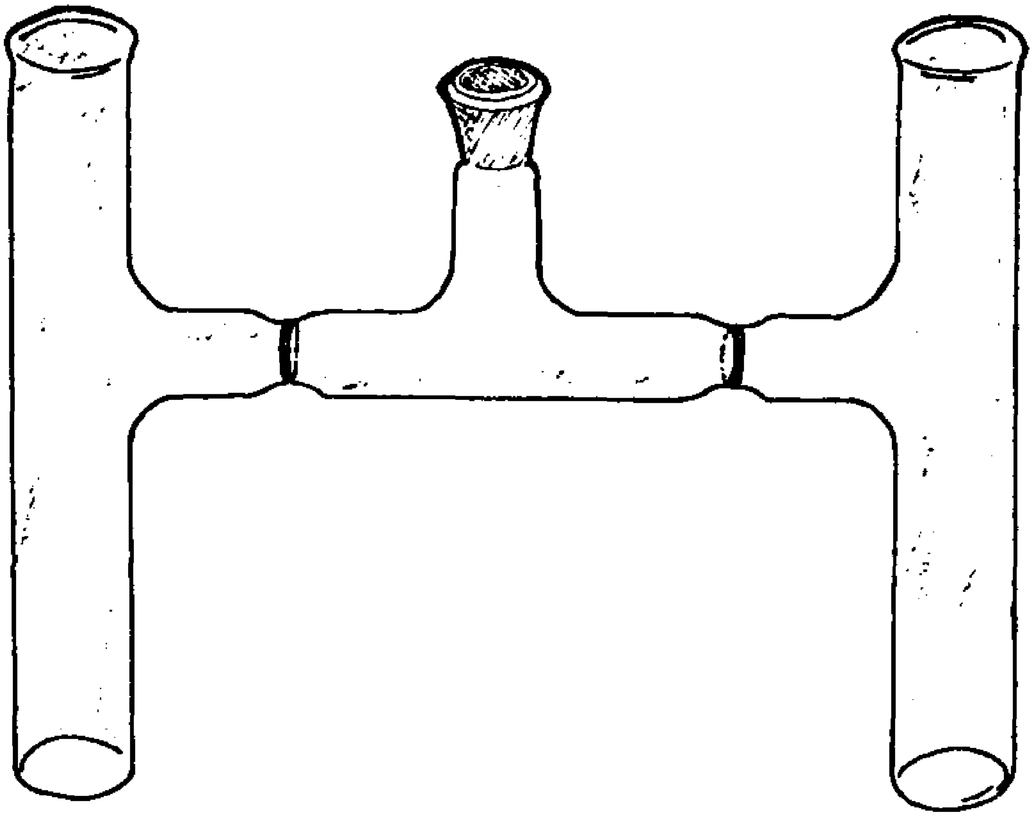


Figure 2

Illustration of the H-Type Cell



electrodes with sleeve-type junction. It was hoped that, by using sleeve-type junctions, diffusion would be minimized in comparison with the H-cell with its relatively large interface area across the frits, thus leading to increased stability in voltage readings.

The cell of new design with sleeve-type electrodes is shown in Figure 3. Each electrode consists of a glass tube of precision bore enclosing a stainless-steel tube. The bottom of the glass tube was 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 contains the teflon wires and screws into part B which snuggly fits in the ground ball (Figure 4).

The electrochemical cell was composed of two of these ground-glass sleeve electrodes immersed in a beaker containing the salt bridge solution. The glass tube moved freely up and down to allow for filling with the solution of interest. The glass tube was clamped in position atop the ball by a collar to obtain a tight fit. In this position, the sleeve is full of solution with the surface of the ground-glass ball wetted with solution. The outside of the sleeve was repeatedly rinsed and the second sleeve filled in a similar manner. Finally, the outside of both sleeves was wash repeatedly and placed in the salt brige solution. The glass electrodes were lowered through the steel tube

Figure 3

Illustration of the Sleeve-Type Cell

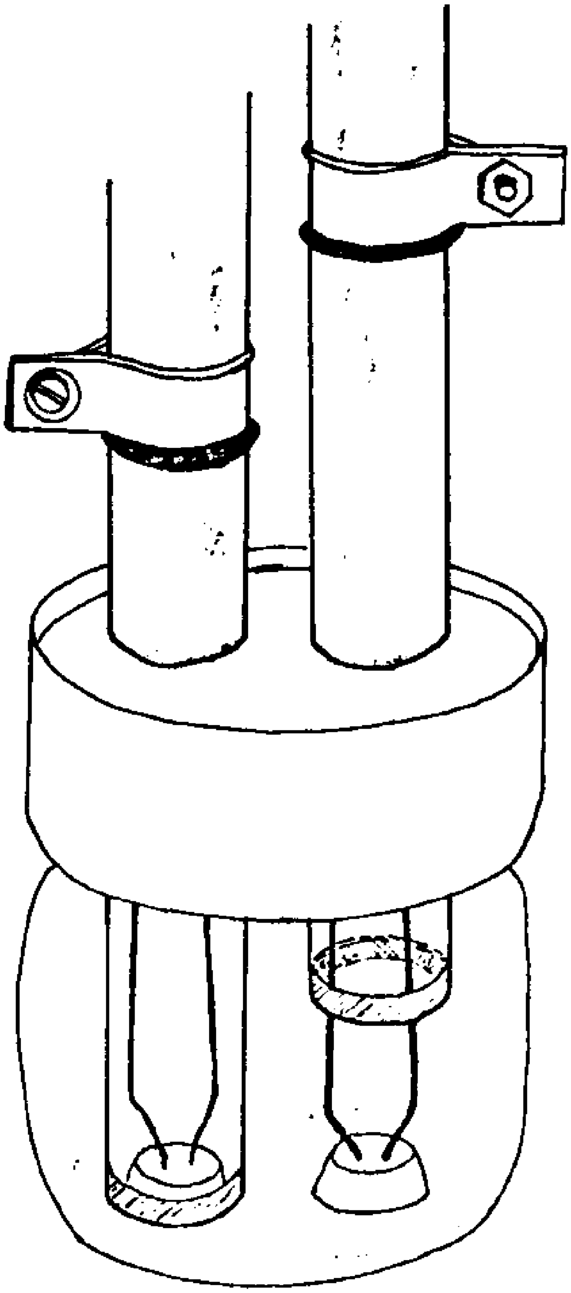
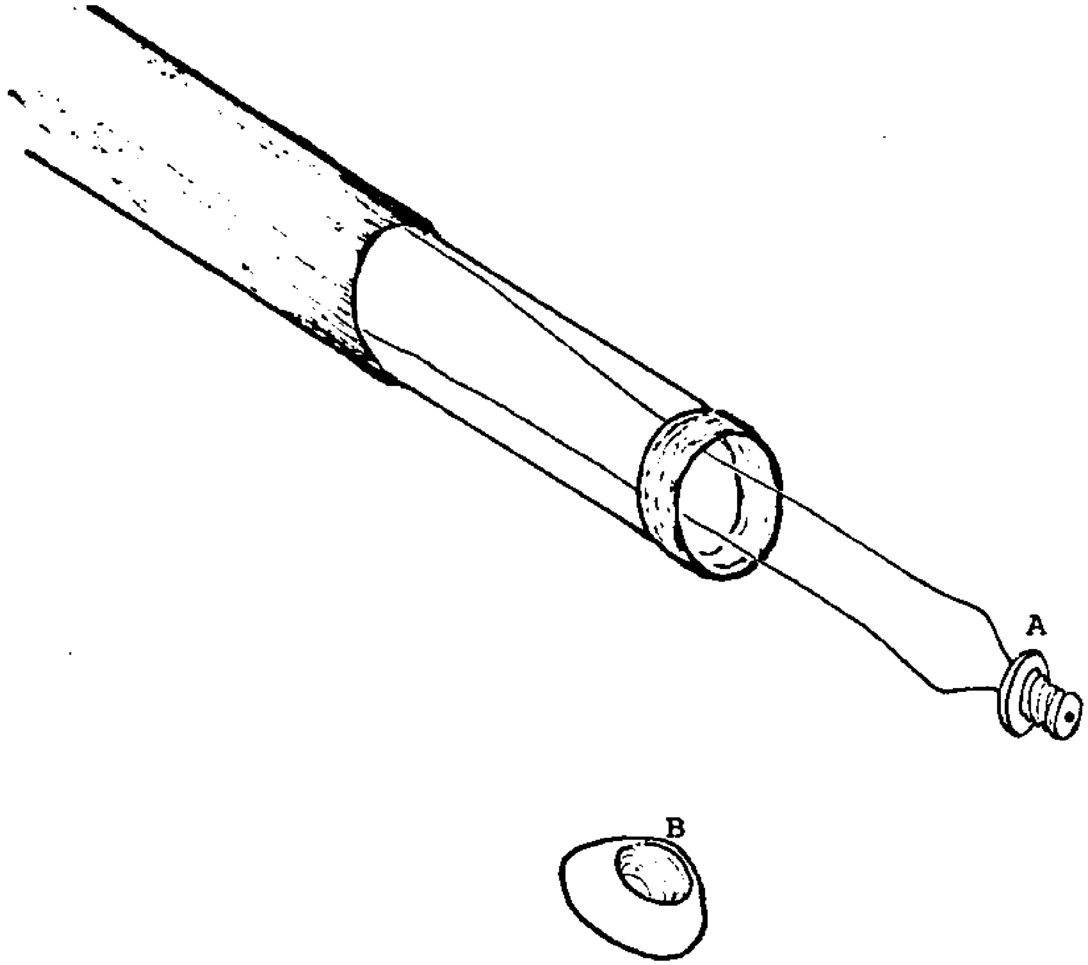


Figure 4

Detailed Illustration of Sleeve-Type Electrode



into the solutions and the voltage was measured. Using this cell design, the stability of measurements was improved to a tenths of a millivolt.

The immersion of a platinum electrode into the salt bridge solution and connecting it to the ground terminal of the amplifier circuit was found to aid in stabilizing the cell voltage. The platinum electrode eliminates stray ac currents, which compounded with the high impedance of the glass electrode, led to unstability. Thus, all measurements were made with a platinum electrode used as ground. All glass electrodes were modified for use with BNC input connectors for further stabilization.

Many other reference electrodes were prepared. Silver-silver chloride electrodes were prepared electrolytically. The surface of a silver electrode (Thomas 4859-H20) was cleaned by first soaking it in ammonia to remove any old silver chloride deposits followed by rubbing the metal with emery paper until the surface appeared clean and shiny. The silver electrode was placed in a 1M HCl solution as the anode with a platinum electrode as the cathode. Application of current density of approximately 5-10 milliamperes per square centimeter produced a greyish coating of silver chloride. The electrolysis was stopped after a few minutes and the electrodes were aged in deionized water for a few days before use.

Commercial silver electrodes (Thomas 4859-H20) were used in acetonitrile. Either a platinum leaf or wire electrodes were used in all the solvents.

Calomel electrodes were made with the aid of a Kontes Universal Electrode Kit. An internal platinum electrode was placed into a removable glass tube containing a mixture of calomel and mercury. The electrode was either placed in another tube with a cracked-glass junction containing saturated potassium chloride in dimethylformamide for use in that solvent or used directly, as in methanol-water solvents. In the latter case, the tube containing calomel was changed for every measurement. Contact with the outer solutions was made via a hole in the tube wall with care taken to be certain that no air bubbles were present. The calomel electrodes were tested vs. silver-silver chloride electrodes in water and found to be within excellent agreement (±1 mV) with the expected values.

Sodium amalgam electrodes containg approximately 0.02 wt % sodium were prepared by electrolysis of 1 N NaOH. The electrolysis was carried out in a vessel which functioned as a separatory funnel, so that the amalgam could be drawn off from the NaOH solution. Mercury served as the cathode and platinum wire served as the anode. Dry argon was bubbled through the mercury during the electrolysis in order to stir the amalgam. After the electrolysis proceeded for the required period of time, the amalgam was drawn off into an evacuated vessel for storage. All further transfers of the amalgam took place under an atmosphere of dry argon. The percentage of sodium in the amalgam was determined by decomposition in hot standard sulfuric acid and back-titration with a standard base. In use, the amalgam contained in the reservoir was dropped through a 1-cm length of polarographic capillary at a rate of one to two drops per second. This capillary was fastened to the electrode assembly by means of a Teflon tubing connector, so as to facilitate replacement if it became clogged during a run. The spent amalgam dropped through the solution into the trap at the bottom of the electrode compartment, where it was isolated from the bulk of the solution. Isolation of the spent amalgam was necessary to prevent reaction with the solvent. Electrical contact with the amalgam was made by a platinum wire sealed into the neck of the electrode assembly.

All measurements were made at 25.00°C ±0.01° by immersing the electrochemical cell in a water bath at that temperature. The temperature of the water bath was kept constant 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.

The cell voltages were monitored by using a Varian A-25 strip chart recorder. It was found that the voltage leveled off to a steady value after a maximum of thirty to forty minutes. After this time, all voltages were measured using the calibrated voltmeters previously described.

Solubility Determinations

Solubilities of solutes were determined by the analysis of saturated solutions in solvents of interest. Six to eight solutions of each of the salts were shaken in thermostated flasks until there was no change in concentration. The flasks were either of the water-jacketed type with water from a 25.00°C bath circulating through them, or were ordinary volumetric flasks placed in a Lab-Line platform shaker bath thermostated at 25.00°C.

Solutions of picrates in propylene carbonate were analyzed spectrophotometrically using a Cary Model 17 Spectrophotometer. One-milliliter aliquots of solutions were drawn up from each of eight flasks and diluted to 100 ml. These new solutions were further diluted by taking 10 ml of this picrate solution and diluting it to 100 ml. The final dilution ratio was equal to 1 ml of the saturated picrate solution to 1000 ml of solution. Spectra of these solutions were obtained and the absorption peaks at 375 nm used for analysis. The molar absorptivity of 375 nm was determined by preparing solutions of known concentration of picrate ion in propylene carbonate and analyzing its spectrum.

The solubilities of $KClO_4$ and Et_4NBr were determined gravimetrically. Aliquots of the saturated solutions were placed in a weighing bottle (40 x 80 mm) of known weight and dried in a vacuum oven at 180°C. After all the solvent was dried off, the samples were cooled to room temperature in a vacuum dessicator and reweighed. The oven temperature was kept well below the melting or decomposition temperatures of the solutes.

Solutions of NaCl in propylene carbonate were analyzed using a Perkin-Elmer Model 372 Atomic Absorption Spectrophotometer in the emission mode. Saturated solutions of NaCl were aspirated directly without dilutions and compared to standard solutions of $NaBPh_4$ in propylene carbonate.

Electrolytic Conductance.

Conductance measurements were performed using a Wayne-Kerr Model B-224 Universal Bridge and a dip-type conductance cell with a cell constant of 1.00 cm^{-1}.

Several solutions of known concentration in the range of 10^{-3} to 10^{-2} M were prepared. The conductance cell was repeatedly rinsed with the sample solution. Special care was taken to make sure no air bubbles were present between the two platinum electrodes. The beaker was immersed in a water bath of constant temperature of 25.00°C, controlled by a Yellow Springs Instruments Co. Model 72 proportional temperature controller.

RESULTS AND DISCUSSION

Dipolar Aprotic Solvents.

Solubilities and Transfer Activity Coefficients of Electrolytes.

Introduction.

As previously discussed, values of transfer activity coefficients of single ions, log ${}_m\gamma$, are required to calculate the liquid-junction potential, E_j, in Cell VIII. Although log ${}_m\gamma$ for most of the ions studied are available in the literature (1, 10), measurements of the transfer activity coefficients of some electrolytes, and the subsequent calculation of log ${}_m\gamma$ values for single ions from those measurements, were found necessary.

Transfer activity coefficients of electrolytes were obtained from solubility measurements, using Equation 23a:

$$\log {}_m\gamma_i = p({}_sK_{sp}) - p({}_rK_{sp}) \tag{23a}$$

where s and r refer to the solvent of interest and the reference solvent, respectively. Values of log ${}_m\gamma$ for the ions of interest were calculated from available data for the transfer activity coefficient of other ions, previously calculated using the tetraphenylarsonium tetraphenylborate (Ph_4AsBPh_4) assumption (Equation 32a). For example,

$$\log {}_m\gamma_{ClO_4} = \log {}_m\gamma_{KClO_4} - \log {}_m\gamma_K \tag{50a}$$

$$\log {}_m\gamma_{Pi} = \log {}_m\gamma_{KPi} - \log {}_m\gamma_K \tag{50b}$$

Solubility Measurements.

The solubility of $KClO_4$ and Et_4NBr in propylene carbonate was determined gravimetrically, while the solubility of KPi in that solvent was found spectrophotometrically. The experimentally determined value of the molar absorptivity of 1.82×10^4 was obtained using solutions of known concentration of KPi. The solubility of NaCl in propylene carbonate was determined by flame emission using standards in that solvent.

Salt-effect activity coefficients (molar scale) for these compounds were calculated by means of the Davies equation:

$$\log f = -A \frac{\sqrt{c}}{(1 + \sqrt{c})} - \frac{1}{3}C \qquad (51)$$

where f is the activity coefficient, A is the Debye-Hückel constant, and C is the solubility. Solubility products (K_{sp}) for $KClO_4$, KPi, Et_4NBr, and NaCl were calculated by:

$$K_{sp} = (cf)^2$$

The degree of dissociation was assumed to be unity because of the high dielectric constant of propylene carbonate (D = 64.4).

Values of the solubility, solubility products, and transfer activity coefficients referred to water for these compounds in propylene carbonate are listed in Table 1. Attempts were made to determine experimentally the solubility of KPi in dimethylsulfoxide and of TABI in a few solvents. However, this proved impractical due to their high solubility in those solvents.

Table 1

Solubility and Solubility Products of $KClO_4$, KPi, Et_4NBr and NaCl in Propylene Carbonate (molar scale).

Solute	$C_1(M) \times 10^2$	pK_{sp}	$\log {}^{H_2O}_{m}\gamma_i^{PC}$
KPi	4.34 ±.09	2.96	-0.45
$KClO_4$	4.97 ±.03	2.83	0.85
Et_4NBr	8.61 ±.44	2.54	4.37
NaCl	0.0197 ±.0006	7.43	8.93

E.m.f. Cells with Salt Bridges.

Studies Using Sodium Glass Electrodes.

H-Cell.

The e.m.f. of Cell IX using $TABBPh_4$ as

$$\text{Na-electrode} \left| \begin{array}{c} \text{Na}^{+}\text{ solution} \\ \text{(Solvent I)} \end{array} \right| \begin{array}{c} \text{RX} \\ \text{0.1M(Solvent I)} \end{array} \left| \begin{array}{c} \text{Na}^{+}\text{ solution} \\ \text{(Solvent II)} \end{array} \right| \text{Na-electrode}$$

(Cell IX)

salt bridge, RX, was measured using the H-type cell design. Experimental values of the e.m.f. of these cells and of the cell potential divided by $\frac{RT}{F}$ (59.16 mV at 25°C) are given in Tables 2-6. The precision of the values of $E_{cell}/59.16$ (an approximation of log ${}_{m}\gamma_{Na}$) is ±0.2 units or better.

Voltage measurements using the sleeve-type design were found to be much more stable than those using the H-cell. The cell voltages are stable to a few tenths of a millivolt for the sleeve-type design, but only to 1-2 millivolts for the H-cell.

The salt-effect activities of the sodium ion in solution were calculated by means of the Debye-Hückel equation:

$$\log f_1 = - \frac{A\sqrt{c}}{1 + B\,\mathring{a}\sqrt{c}} \tag{52}$$

where f_1 refers to the salt-effect activity coefficient, A and B are the Debye-Hückel coefficients, C refers to the analytical molar concentration of sodium ion and $\mathring{a}$ is the ion-size parameter, assumed to be 3 Å for sodium ions in dipolar aprotic solvents. Appendix 2 lists values of the Debye-Hückel coefficients in various solvents. All measurements of Cell IX were made with solutions in the 10^{-2} to 10^{-4} M concentration range.

Nernstian Response.

The Nernstian response of each sodium glass electrode was tested versus a reference electrode in each solvent of interest. Reference electrodes were selected from the literature (27). In dimethylsulfoxide, N-methylformamide, and propylene carbonate, a silver-silver chloride electrode in a 10^{-3} M solution of tetraphenylphosphonium chloride was used. A silver-silver nitrate electrode was used in acetonitrile. A calomel electrode containing saturated KCl in dimethylformamide was used in that solvent. The e.m.f. of all these cells with 0.1 M Et_4NPi as a salt bridge was measured using sodium solutions at various concentrations and plotted vs. pa_{Na}. The slopes were found to be linear, although not strictly Nernstian, down to 10^{-4} molar. Table 7 lists the Nernstian factors for each electrode used as well as the correlation coefficient, R, as a measure of the linearly of the electrode response (linear being equal to 1):

$$R = \frac{m\sigma_x}{\sigma_y} \tag{53}$$

where m is the slope, σ_x and σ_y are the standard deviations in the pa_{Na}-array and e.m.f.-array, respectively.

Table 2

E.m.f. Values of Cell IX in the DMSO-MeCN System.

(H-type) 25.00°C.

Solvent I = MeCN Solvent II = DMSO

RX = 0.1 M $TABBPh_4$ in MeCN

$NaBPh_4$ Solutions

Molarity (MeCN)	Molarity (DMSO)	E_{cell} (mV)	pa_{Na} (MeCN)	pa_{Na} (DMSO)	E'_{cell} (mV)	$\frac{E'_{cell}}{59.16}$
1.078×10^{-2}	1.044×10^{-2}	-355	2.115	2.081	-353	-6.0
1.078×10^{-3}	1.044×10^{-3}	-363	3.019	3.016	-363	-6.1
1.078×10^{-4}	1.044×10^{-4}	-353	3.984	3.992	-353	-6.0
1.078×10^{-5}	1.044×10^{-5}	-341	4.973	4.985	-353	-5.8
			NaPi Solutions			
1.270×10^{-2}	1.296×10^{-2}	-339	2.055	1.997	-336	-5.6
1.270×10^{-3}	1.296×10^{-3}	-353	2.952	2.926	-352	-6.0
6.350×10^{-4}	6.480×10^{-4}	-351	3.237	3.216	-351	-5.9
1.270×10^{-4}	1.296×10^{-4}	-339	3.914	3.900	-339	-5.7
6.350×10^{-5}	6.480×10^{-5}	-348	4.210	4.197	-348	-5.9
1.270×10^{-5}	1.296×10^{-5}	-336	4.902	4.891	-336	-5.7

$$\frac{E'_{cell}}{59.16}(\bar{x}) = -5.9 \pm 0.2$$

Table 3

E.m.f. Values of Cell IX in the DMF-MeCN System.

(H-type) 25.00°C.

Solvent I = MeCN Solvent II = DMF

RX = 0.1 M TABBPh₄ in MeCN

NaBPh₄ Solutions

Molarity (MeCN)	Molarity (DMF)	E_{cell} (mV)	pa_{Na} (MeCN)	pa_{Na} (DMF)	E'_{cell} (mV)	$\frac{E'_{cell}}{59.16}$
1.029×10^{-2}	1.001×10^{-2}	-295	2.133	2.139	-295	-5.0
1.029×10^{-3}	1.001×10^{-3}	-301	3.038	3.048	-301	-5.1
5.145×10^{-4}	5.050×10^{-4}	-302	3.335	3.331	-302	-5.1
1.027×10^{-4}	1.001×10^{-4}	-290	4.005	4.015	-290	-4.9
5.145×10^{-5}	5.050×10^{-5}	-284	4.311	4.307	-284	-4.8
1.027×10^{-5}	1.001×10^{-5}	-275	4.994	5.005	-275	-4.7

NaPi Solutions

Molarity (MeCN)	Molarity (DMF)	E_{cell} (mV)	pa_{Na} (MeCN)	pa_{Na} (DMF)	E'_{cell} (mV)	$\frac{E'_{cell}}{59.16}$
9.853×10^{-3}	1.110×10^{-3}	-290	3.056	3.005	-287	-4.8
4.927×10^{-4}	5.550×10^{-4}	-299	3.343	3.292	-296	-5.0
9.853×10^{-5}	1.110×10^{-4}	-281	4.022	3.971	-278	-4.7
4.927×10^{-5}	5.550×10^{-5}	-288	4.319	4.267	-285	-4.8
9.853×10^{-6}	1.110×10^{-5}	-260	5.012	4.960	-257	-4.3

$\frac{E'_{cell}}{59.16}(\bar{x}) = -4.8 \pm 0.2$

Table 4

E.m.f. Values of Cell IX in the NMF-MeCN System.

(H-type) 25.00°C.

Solvent I = MeCN   Solvent II = NMF

RX = 0.1 M $TABBPh_4$ in MeCN

$NaBPh_4$ Solutions

Molarity (MeCN)	Molarity (NMF)	E_{cell} (mV)	pa_{Na} (MeCN)	pa_{Na} (NMF)	E'_{cell} (mV)	$\frac{E'_{cell}}{59.16}$
1.040×10^{-2}	1.122×10^{-2}	-239	2.129	1.964	-229	-3.8
1.040×10^{-3}	1.122×10^{-3}	-242	3.033	2.955	-237	-4.0
5.200×10^{-4}	5.610×10^{-4}	-240	3.320	3.254	-236	-4.0
1.040×10^{-4}	1.122×10^{-4}	-250	3.999	3.952	-248	-4.2
5.200×10^{-5}	5.610×10^{-5}	-220	4.296	4.252	-218	-3.7
1.040×10^{-5}	1.122×10^{-5}	-209	4.988	4.950	-207	-3.5
			NaPi Solutions			
4.865×10^{-4}	5.960×10^{-4}	-243	3.348	3.228	-236	-4.0
9.728×10^{-5}	1.192×10^{-4}	-231	4.028	3.925	-225	-3.8
4.865×10^{-5}	5.960×10^{-5}	-223	4.324	4.226	-217	-3.7
9.729×10^{-6}	1.192×10^{-5}	-259	5.017	4.924	-254	-4.3

$\frac{E'_{cell}}{59.16}$ ($\bar{x}$) = 3.9 ±0.2

Table 5

E.m.f. Values of Cell IX in the PC-MeCN System.

(H-type) 25.00° C.

Solvent I = MeCN Solvent II = PC

RX = 0.1 M TABBPh$_4$ in MeCN

NaBPh$_4$ Solutions

Molarity (MeCN)	Molarity (PC)	E_{cell} (mV)	pa_{Na} (MeCN)	pa_{Na} (NMT)	E'_{cell} (mV)	$\frac{E'_{cell}}{59.16}$
1.095×10^{-2}	9.909×10^{-3}	-21	2.110	2.066	-19	-0.4
1.095×10^{-3}	9.909×10^{-4}	-26	3.012	3.025	-26	-0.4
5.475×10^{-4}	4.954×10^{-4}	-26	3.299	3.320	-25	-0.4
3.285×10^{-4}	2.973×10^{-4}	-30	3.512	3.538	-29	-0.5
1.095×10^{-4}	9.909×10^{-5}	-34	3.977	4.011	-33	-0.6

$$\frac{E_{cell}}{59.16}(\bar{x}) = -0.5 \pm 0.1$$

Table 6

E.m.f. Values of Cell IX in the DMF-DMSO System. (H-type) 25.00°C.

Solvent I = DMSO Solvent II = DMF

RX = 0.1 M $TABBPh_4$ in DMSO

$NaBPh_4$ Solutions

Molarity (DMSO)	Molarity (DMF)	E_{cell} (mV)	pa_{Na} (DMSO)	pa_{Na} (DMF)	E'_{cell} (mV)	$\frac{E'_{cell}}{59.16}$
1.013×10^{-2}	1.020×10^{-2}	72	2.093	2.132	70	1.1
1.013×10^{-3}	1.020×10^{-3}	73	3.028	3.040	73	1.2
5.065×10^{-4}	5.100×10^{-4}	73	3.320	3.327	71	1.1
1.013×10^{-4}	1.020×10^{-4}	65	4.005	4.007	65	1.1
			NaPi Solutions			
1.308×10^{-2}	1.105×10^{-2}	72	1.994	2.102	66	1.1
1.308×10^{-3}	1.105×10^{-3}	70	2.922	3.007	65	1.1
6.540×10^{-4}	5.525×10^{-4}	76	3.212	3.294	71	1.2
1.308×10^{-4}	1.105×10^{-4}	67	3.896	3.973	62	1.0
6.540×10^{-5}	5.525×10^{-5}	57	4.193	4.269	52	0.9
1.308×10^{-5}	1.105×10^{-5}	60	4.887	4.962	52	0.9

$$\frac{E'_{cell}}{59.16}(\bar{x}) = 1.1 \pm 0.1$$

Table 7

Nernstian Factors of Sodium Glass Electrodes in Dipolar Aprotic Solvents.

	Electrode C		Electrode D		Electrode B	
Solvent	$\frac{\Delta E}{\Delta pa_{Na}}$	R	$\frac{\Delta E}{\Delta pa_{Na}}$	R	$\frac{\Delta E}{\Delta pa_{Na}}$	R
MeCN	58.7	.997	57.5	.998		
DMSO	59.9	.999	60.5	1.00		
DMF	61.9	.999	61.9	.999		
PC	56.2	.995	57.4	.995	53.2	.995
NMF	57.5	.992	57.6	.994		

Concentration Range = $10^{-2} - 10^{-5}$ M Na^+ ion

Correlation of the Standard Potentials of Sodium Glass and Amalgam Electrodes.

Measurements of the e.m.f. of Cell IX require the use of sodium glass electrodes in different solvents. If these measurements are to be accurate, the standard potential, E°, of the glass electrode must be independent of the nature of the solvent studied.

While the behavior of cationic glass electrodes in aqueous solvents is well known (28), few studies have been carried out on their response in nonaqueous solvents. Norberg (29) studies the behavior of hydrogen electrodes in isopropanol and methyl ethyl ketone, while Karlberg (30) discussed their response times in isopropanol. McClure and Reddy (31) determined the slopes of concentration response curves of cationic glass electrodes in some dipolar aprotic solvents.

In the present study, sodium glass electrodes were compared to sodium amalgam electrodes in dipolar aprotic solvents. Equation 54 describes the response of a sodium amalgam electrode in a solvent s :

$$E_{Na(Hg)} = E^{\circ}_{Na(Hg)} - .06 \log a_{Na} - .06 \log a_{Na(Hg)} \qquad (54)$$

where a_{Na} is the activity of sodium ion in the solvent of interest, $a_{Na(Hg)}$ is the activity of sodium in the amalgam, $E^{\circ}_{Na(Hg)}$ is the standard potential of sodium amalgam electrode and $E_{Na(Hg)}$ is the potential of the sodium amalgam electrode. Similarly, Equation 55 represents the electrode response of of a sodium glass electrode in the same solution:

$$E_{Na(g)} = E^{\circ}_{Na(g)} - .06 \log a_{Na(s)} + E_A \tag{55}$$

where $E_{Na(g)}$ and $E^{\circ}_{Na(g)}$ are the potential and the standard potential of the sodium glass electrode, respectively, and E_A is the "asymmetry potential" term. The "asymmetry potential" includes any potentials that are not included in the $E^{\circ}_{Na(g)}$ term. Equation 56 represents the potential difference between the amalgam electrode and the glass electrode in the same solution of sodium ions:

$$E_{Na(Hg)} - E_{Na(g)} = E^{\circ}_{Na(Hg)} - E^{\circ}_{Na(g)} - .06 \log a_{Na(Hg)} - E_A \tag{56}$$

The only way the difference $E_{Na(Hg)} - E_{Na(g)}$ can remain constant in different solvent solutions is if the "asymmetry potential", E_A, is to remain unchanged or to be zero. Thus effective ΔE° of the glass electrode would be independent of the solvent.

The potential difference between sodium glass and sodium amalgam electrodes was measured in acetonitrile, dimethylformamide, propylene carbonate and dimethylsulfoxide and found to be constant to ±3 mV, which is within the experimental error of our measurements.

E.m.f. Measurements.

The measured e.m.f. of Cell IX can be expressed as a combination of four different terms:

$$E_{\text{cell IX}} = E^\circ_{(S_2)} - E^\circ_{(S_1)} + E_{\text{conc.}} + E_j \qquad (57)$$

where $E^\circ_{(S_1)}$ and $E^\circ_{(S_2)}$ are the standard potentials for the standard potentials of the electrodes in solvents 1 and 2, $E_{\text{conc.}}$ is the potential due to the difference in activities of the electroactive species in the two solvents and E_j is the liquid-junction potential. The experimentally determined slopes of $\frac{\Delta E}{\Delta pa_{Na}}$ were used as Nernstian factors (NF):

$$E_{\text{conc.}} = NF(S_2)Xpa_{Na(S_2)} - NF(S_1)Xpa_{Na(S_1)} \qquad (58)$$

The corrected values of the e.m.f. of Cell IX are listed in Tables 8-14 with:

$$E'_{\text{cell}} = E_{\text{cell}} - E_{\text{conc.}} \qquad (59)$$

Values of $\frac{E'_{\text{cell}}}{59.16}$ vs. concentration for each solvent pair studied are correlated in Table 15. As pointed out earlier, the precision of the values of $\frac{E_{\text{cell}}}{59.16}$, using the sleeve-type cell design is generally better than ±0.1 units, which is an improvement in comparison with the H-cell design with precision of ±0.2 units.

Table 8

E.m.f. Values for Cell IX in the DMSO-MeCN System.

(Sleeve-Type) 25.00°C.

Solvent I = MeCN   Solvent II = DMSO

RX = 0.1 M $TABBPh_4$ in MeCN

Molarity (MeCN)	Molarity (DMSO)	E_{cell} (mV)	pa_{Na} (MeCN)	pa_{Na} (DMSO)	E_{conc} (mV)	E'_{cell} (mV)
1.068×10^{-2}	1.040×10^{-2}	-346.6	2.119	2.077	2.6	-349.2
1.037×10^{-2}	1.034×10^{-2}	-352.7	2.130	2.079	0.8	-353.5
1.068×10^{-3}	1.040×10^{-3}	-357.2	3.023	3.015	6.8	-364.0
1.037×10^{-3}	1.034×10^{-3}	-356.3	3.035	3.018	4.4	-360.7
8.296×10^{-4}	8.272×10^{-4}	-359.6	3.126	3.111	4.7	-364.3
4.273×10^{-4}	4.159×10^{-4}	-355.3	3.402	3.402	8.2	-363.5
4.148×10^{-4}	4.136×10^{-4}	-362.7	3.415	3.404	5.4	-368.1
RX = 0.1 M Et_4NPi in MeCN						
1.068×10^{-2}	1.040×10^{-2}	-342.5	2.119	2.077	2.6	-345.1
1.037×10^{-2}	1.034×10^{-2}	-343.1	2.130	2.079	0.8	-343.9
1.068×10^{-3}	1.068×10^{-3}	-345.0	3.023	3.015	6.8	-351.8
1.037×10^{-3}	1.034×10^{-3}	-350.5	3.035	3.018	4.4	-354.9
8.296×10^{-4}	8.272×10^{-4}	-349.3	3.126	3.111	4.7	-354.0
4.148×10^{-4}	4.136×10^{-4}	-353.7	3.415	3.404	5.4	-359.1
RX = 0.1 M Et_4NClO_4 in MeCN						
1.068×10^{-2}	1.040×10^{-2}	-336.3	2.119	2.077	2.6	-338.9
1.037×10^{-2}	1.034×10^{-2}	-336.3	2.130	2.079	0.8	-337.1
1.068×10^{-3}	1.040×10^{-3}	-340.6	3.023	3.015	6.8	-347.4
1.037×10^{-3}	1.034×10^{-3}	-347.7	3.035	3.018	4.4	-351.1
8.296×10^{-4}	8.272×10^{-4}	-348.3	3.126	3.111	4.7	-353.0
4.148×10^{-4}	4.136×10^{-4}	-352.3	3.415	3.404	5.4	-357.7

Table 9

E.m.f. Values for Cell IX in the DMF-MeCN System.

(Sleeve-Type) 25.00°C.

Solvent I = MeCN Solvent II = DMF

RX = 0.1 M TABBPh$_4$ in MeCN

Molarity (MeCN)	Molarity (DMF)	E_{cell} (mV)	pa_{Na} (MeCN)	pa_{Na} (DMF)	E_{conc} (mV)	E'_{cell} (mV)
1.052×10^{-2}	1.067×10^{-2}	-285.5	2.124	2.115	6.2	-291.7
1.052×10^{-3}	1.067×10^{-3}	-298.0	3.029	3.021	9.2	-307.2
8.416×10^{-4}	8.536×10^{-4}	-300.3	3.121	3.113	9.5	-309.8
4.208×10^{-4}	4.268×10^{-4}	-299.9	3.409	3.402	10.5	-310.4
2.104×10^{-4}	2.134×10^{-4}	-297.1	3.700	3.694	11.5	-308.6
RX = 0.1 M Et$_4$NPi in MeCN						
1.052×10^{-2}	1.067×10^{-2}	-293.5	2.124	2.115	6.2	-299.7
1.052×10^{-3}	1.067×10^{-3}	-297.1	3.029	3.021	9.2	-306.3
8.416×10^{-4}	8.536×10^{-4}	-298.3	3.121	3.113	9.5	-307.8
2.104×10^{-4}	2.134×10^{-4}	-303.0	3.700	3.694	11.5	-314.5
RX = 0.1 M Et$_4$NClO$_4$ in MeCN						
1.052×10^{-2}	1.067×10^{-2}	-285.8	2.124	2.115	6.2	292.0
1.052×10^{-3}	1.067×10^{-3}	-289.6	3.029	3.021	9.2	298.8
8.416×10^{-4}	8.536×10^{-4}	-290.5	3.121	3.113	9.5	300.0
2.104×10^{-4}	2.134×10^{-4}	-291.5	3.700	3.694	11.5	303.0

Table 10

E.m.f. Values for Cell IX in the PC-MeCN System.

(Sleeve-Type) 25.00°C.

Solvent I = MeCN Solvent II = PC

Molarity (MeCN)	Molarity (PC)	E_{cell} (mV)	pa_{Na} (MeCN)	pa_{Na} (PC)	E_{conc} (mV)	E'_{cell} (mV)
RX = 0.1 M $TABBPh_4$ in MeCN						
1.057×10^{-3}	1.103×10^{-3}	-38.9	3.027	2.979	-6.7	-32.2
8.456×10^{-4}	8.824×10^{-4}	-38.2	3.119	3.074	-6.6	-31.6
4.228×10^{-4}	4.412×10^{-4}	-39.2	3.407	3.369	-6.6	-32.6
2.114×10^{-4}	2.206×10^{-4}	-36.6	3.698	3.666	-6.6	-30.0
RX = 0.1 M Et_4NPi in MeCN						
1.057×10^{-2}	1.103×10^{-2}	-28.9	2.123	2.022	-8.6	-21.3
1.057×10^{-3}	1.103×10^{-3}	-34.3	3.027	2.979	-6.7	-27.6
8.456×10^{-4}	8.824×10^{-4}	-30.6	3.119	3.074	-6.6	-24.0
4.228×10^{-4}	4.412×10^{-4}	-29.4	3.407	3.369	-6.6	-22.8
2.114×10^{-4}	2.206×10^{-4}	-34.7	3.698	3.666	-6.6	-28.1
RX = 0.1 M Et_4NClO_4 in MeCN						
1.057×10^{-2}	1.103×10^{-2}	-32.2	2.123	2.022	-8.6	-23.6
1.057×10^{-3}	1.103×10^{-3}	-39.5	3.027	2.979	-6.7	-32.8
8.456×10^{-4}	8.824×10^{-4}	-39.2	3.119	3.074	-6.6	-32.6
4.228×10^{-4}	4.412×10^{-4}	-41.6	3.407	3.369	-6.6	-35.0

Table 11

E.m.f. Values for Cell IX in the DMF-DMSO System.

(Sleeve-Type) 25.00°C.

Solvent I = DMSO Solvent II = DMF

RX = 0.1 M $TABBPh_4$ in DMSO

Molarity (DMSO)	Molarity (DMF)	E_{cell} (mV)	pa_{Na} (DMSO)	pa_{Na} (DMF)	E_{conc} (mV)	E'_{cell} (mV)
2.631×10^{-2}	2.634×10^{-2}	72.5	1.769	1.788	4.7	67.8
2.631×10^{-3}	2.634×10^{-3}	74.9	2.633	2.655	6.6	68.3
2.105×10^{-3}	2.107×10^{-3}	75.3	2.725	2.745	6.7	68.6
1.052×10^{-3}	1.054×10^{-3}	75.1	3.013	3.026	6.8	68.3
5.262×10^{-4}	5.269×10^{-4}	79.9	3.304	3.314	7.2	72.7

RX = 0.1 M Et_4NPi in DMSO

Molarity (DMSO)	Molarity (DMF)	E_{cell} (mV)	pa_{Na} (DMSO)	pa_{Na} (DMF)	E_{conc} (mV)	E'_{cell} (mV)
2.631×10^{-2}	2.634×10^{-2}	63.5	1.769	1.788	4.7	58.8
2.631×10^{-3}	2.634×10^{-3}	64.3	2.633	2.655	6.6	57.7
2.105×10^{-3}	2.107×10^{-3}	64.6	2.725	2.745	6.7	57.9
1.052×10^{-3}	1.054×10^{-3}	66.0	3.013	3.026	6.8	59.2
5.262×10^{-4}	5.269×10^{-4}	66.3	3.304	3.314	7.2	59.1

RX = 0.1 M Et_4NClO_4 in DMSO

Molarity (DMSO)	Molarity (DMF)	E_{cell} (mV)	pa_{Na} (DMSO)	pa_{Na} (DMF)	E_{conc} (mV)	E'_{cell} (mV)
2.631×10^{-2}	2.634×10^{-2}	70.6	1.769	1.788	4.7	65.9
2.631×10^{-3}	2.634×10^{-3}	72.5	2.633	2.655	6.6	65.9
2.105×10^{-3}	2.107×10^{-3}	73.1	2.725	2.745	6.7	66.4
1.052×10^{-3}	1.054×10^{-3}	74.9	3.013	3.026	6.8	68.1
5.261×10^{-4}	5.269×10^{-4}	72.7	3.304	3.314	7.2	65.5

Table 12

E.m.f. Values of Cell IX in the PC-DMSO System. (Sleeve-Type) 25.00°C.

Solvent I = DMSO Solvent II = PC

RX = 0.1 M TABBPh$_4$ in DMSO

Molarity (DMSO)	Molarity (PC)	E_{cell} (mV)	pa_{Na} (DMSO)	pa_{Na} (PC)	E_{conc} (mV)	E'_{cell} (mV)
1.029×10^{-2}	1.030×10^{-2}	313.7	2.087	2.050	-7.3	321.0
1.029×10^{-3}	1.030×10^{-3}	321.7	3.022	3.008	-8.4	330.1
8.232×10^{-4}	8.240×10^{-4}	322.4	3.115	3.103	-8.5	330.9
4.116×10^{-4}	4.120×10^{-4}	323.8	3.407	3.399	-9.0	332.8
2.058×10^{-4}	2.060×10^{-4}	324.5	3.702	3.696	-9.6	334.1

RX = 0.1 M Et$_4$NPi in DMSO

Molarity (DMSO)	Molarity (PC)	E_{cell} (mV)	pa_{Na} (DMSO)	pa_{Na} (PC)	E_{conc} (mV)	E'_{cell} (mV)
1.029×10^{-2}	1.030×10^{-2}	309.0	2.087	2.050	-7.3	316.3
1.029×10^{-3}	1.030×10^{-3}	312.7	3.022	3.008	-8.4	321.1
8.232×10^{-4}	8.240×10^{-4}	319.7	3.115	3.103	-8.5	328.2
4.116×10^{-4}	4.120×10^{-4}	314.3	3.407	3.399	-9.0	323.3
2.058×10^{-4}	2.060×10^{-4}	314.7	3.702	3.696	-9.6	324.3

RX = 0.1 M Et$_4$NClO$_4$ in DMSO

Molarity (DMSO)	Molarity (PC)	E_{cell} (mV)	pa_{Na} (DMSO)	pa_{Na} (PC)	E_{conc} (mV)	E'_{cell} (mV)
1.029×10^{-2}	1.030×10^{-2}	304.7	2.087	2.050	-7.3	312.0
1.029×10^{-3}	1.030×10^{-3}	311.1	3.022	3.008	-8.4	319.5
8.232×10^{-4}	8.240×10^{-4}	314.4	3.115	3.103	-8.5	322.9
4.116×10^{-4}	4.120×10^{-4}	313.3	3.407	3.399	-9.0	322.3
2.058×10^{-4}	2.060×10^{-4}	315.1	3.702	3.696	-9.6	324.7

Table 13

E.m.f. Values for Cell IX in the PC-DMF System. (Sleeve-Type) 25.00°C.

Solvent I = DMF Solvent II = PC

RX = 0.1 M $TABBPh_4$ in DMF

Molarity (DMF)	Molarity (PC)	E_{cell} (mV)	pa_{Na} (DMF)	pa_{Na} (PC)	E_{conc} (mV)	E'_{cell} (mV)
1.008×10^{-2}	9.943×10^{-3}	268.4	2.064	2.136	-14.1	282.5
1.008×10^{-3}	9.943×10^{-4}	264.5	3.024	3.045	-25.2	289.7
8.064×10^{-4}	7.954×10^{-4}	257.9	3.118	3.137	-26.1	284.0
4.032×10^{-4}	3.977×10^{-4}	235.0	3.414	3.426	-29.1	264.1
RX = 0.1 M Et_4NPi in DMF						
1.026×10^{-2}	1.022×10^{-2}	269.2	2.129	2.053	-22.6	291.8
1.026×10^{-3}	1.022×10^{-3}	258.9	3.038	3.012	-27.8	286.7
8.208×10^{-4}	8.176×10^{-4}	266.0	3.130	3.106	-28.5	294.5
4.104×10^{-4}	4.088×10^{-4}	240.3	3.418	3.402	-30.6	270.9
RX = 0.1 M Et_4NClO_4 in DMF						
1.026×10^{-2}	1.022×10^{-2}	253.3	2.129	2.053	-22.6	275.9
1.026×10^{-3}	1.022×10^{-3}	240.8	3.038	3.012	-27.8	268.6
8.208×10^{-4}	8.176×10^{-4}	242.6	3.130	3.106	-28.5	271.1
4.104×10^{-4}	4.088×10^{-4}	243.9	3.418	3.402	-30.6	274.5

Table 14

E.m.f. Values for Cell IX in the NMF-MeCN System.

(Sleeve-Type) 25.00°C.

RX = 0.1 M $TABBPh_4$ in MeCN

Molarity (MeCN)	Molarity (NMF)	E_{cell} (mV)	pa_{Na} (MeCN)	pa_{Na} (NMF)	E_{conc} (mV)	E'_{cell} (mV)
1.042×10^{-2}	1.155×10^{-2}	234.9	2.128	1.952	10.1	224.8
1.042×10^{-3}	1.155×10^{-3}	238.4	3.033	2.942	5.2	233.2
8.333×10^{-4}	9.240×10^{-4}	237.1	3.125	3.039	4.9	232.2
RX = 0.1 M Et_4NPi in MeCN						
1.042×10^{-2}	1.155×10^{-2}	243.0	2.128	1.952	10.1	232.9
1.042×10^{-3}	1.155×10^{-3}	251.3	3.033	2.942	5.2	246.1
8.333×10^{-4}	9.240×10^{-4}	247.6	3.125	3.039	4.9	242.7
RX = 0.1 M Et_4NClO_4 in MeCN						
1.042×10^{-2}	1.155×10^{-2}	238.0	2.128	1.952	10.1	227.9
1.042×10^{-3}	1.155×10^{-3}	241.2	3.033	2.942	5.2	236.0
8.333×10^{-4}	9.240×10^{-4}	230.7	3.125	3.039	4.9	225.8

Table 15

Values of $\frac{E'_{cell}(mV)}{59.16}$ Using Various Salt-Bridge Electrolytes.

	$\frac{E'_{cell}(mV)}{59.16}$ (Measure of log $_{m}\gamma_{Na}$)		
Solvent I = MeCN			Solvent II = DMSO
Approximate Molarity of $NaBPh_4$	$TABBPh_4$	Et_4NPi	Et_4NClO_4
1×10^{-2}	-5.90, -5.98	-5.83, -5.81	-5.73, -5.70
1×10^{-3}	-6.15, -6.10	-5.95, -6.00	-5.87, -5.93
8×10^{-4}	-6.16	-5.98	-5.97
4×10^{-4}	-6.14, -6.22	-6.07	-6.05
	$\bar{x}$ = -6.09±.10	$\bar{x}$ = -5.94±.09	$\bar{x}$ = -5.88±.12
Solvent I = MeCN			Solvent II = DMF
1×10^{-2}	-4.93	-5.07	-4.94
1×10^{-3}	-5.19	-5.18	-5.05
8×10^{-4}	-5.24	-5.20	-5.07
4×10^{-4}	-5.25	-	-5.12
2×10^{-4}	-5.22	-5.32	-
	$\bar{x}$ = -5.17±.12	$\bar{x}$ = -5.19±.09	$\bar{x}$ = -5.05±.07
Solvent I = MeCN			Solvent II = PC
1×10^{-2}	-	-0.36	-0.40
1×10^{-3}	-0.54	-0.47	-0.55
8×10^{-4}	-0.53	-0.41	-0.55
4×10^{-4}	-0.55	-0.39	-0.59
2×10^{-4}	-0.51	-0.47	-
	$\bar{x}$ = -0.53±.01	$\bar{x}$ = -0.42±.04	$\bar{x}$ = -0.52±.07

Table 15 (continued)

Solvent I = DMSO Solvent II = DMF

Approximate Molarity of $NaBPh_4$	$TABBPh_4$	Et_4NPi	Et_4NClO_4
1×10^{-2}	1.15	0.99	1.11
1×10^{-3}	1.15	0.98	1.11
8×10^{-4}	1.16	0.98	1.12
4×10^{-4}	1.15	1.00	1.15
2×10^{-4}	1.23	1.00	1.11
	$\bar{x}$ = 1.16±.04	$\bar{x}$ = .99±.01	$\bar{x}$ = 1.12±.02
Solvent I = DMSO			Solvent II = PC
1×10^{-2}	5.43	5.35	5.27
1×10^{-3}	5.58	5.43	5.40
8×10^{-4}	5.59	5.55	5.46
4×10^{-4}	5.63	5.46	5.45
2×10^{-4}	5.64	5.48	5.49
	$\bar{x}$ = 5.57±.08	$\bar{x}$ = 5.45±.07	$\bar{x}$ = 5.41±.08
Solvent I = DMF			Solvent II = PC
1×10^{-2}	4.78	4.93	4.66
1×10^{-3}	4.90	4.85	4.54
8×10^{-4}	4.80	4.98	4.58
4×10^{-4}	4.46	4.58	4.64
	$\bar{x}$ = 4.74±.17	$\bar{x}$ = 4.84±.15	$\bar{x}$ = 4.60±.05
Solvent I = MeCN			Solvent II = NMF
1×10^{-2}	-3.80	-3.94	-3.85
1×10^{-3}	-3.94	-4.16	-3.99
8×10^{-4}	-3.92	-4.10	-3.82
	$\bar{x}$ = -3.89±.06	$\bar{x}$ = -4.07±.09	$\bar{x}$ = -3.89±.07

Liquid Junction Potentials.

As we have previously discussed, if the values of the liquid-junction potential across the interface between two media are known, transfer activity coefficients of single ions to which the measuring electrode responds can be calculated. Consider Cell IX, with $NaBPh_4$ as the source of Na^+ ions:

$$\text{Na-electrode} \left| \begin{matrix} Na^+ \text{ solution} \\ \text{(Solvent I)} \end{matrix} \right| \begin{matrix} RX \\ 0.1M\text{(Solvent I)} \end{matrix} \left| \begin{matrix} Na^+ \text{ solution} \\ \text{(Solvent II)} \end{matrix} \right| \text{Na-electrode}$$

(Cell IX)

The liquid-junction potential of this cell is represented by:

$$E_j(\text{mv}) = -(t_{Na} - t_{BPh_4})\ (59.16)\ \log \frac{{}_{S_2}a_{NaBPh_4}}{{}_{S_1}a_{NaBPh_4}} - (59.16)$$

$$[t_{Na} \log {}_m\gamma_{Na} - t_{BPh_4} \log {}_m\gamma_{BPh_4} + t_R \log {}_m\gamma_R$$

$$- t_X \log {}_m\gamma_X] + E_{j\text{solvent}} \qquad (60)$$

where a_{NaBPh_4} is the conventional activity of the $NaBPh_4$ solutions. The liquid-junction potential is due to the transport of all species across the interface:

$$E_j = \underset{\text{ions}}{-\Sigma}\ t_i \Delta G_{\text{ions}} + \underset{i}{\Sigma} \Delta G_{i\text{solvent molecules}} \qquad (35)$$

or simply:

$$E_j = E_j' + E_{j\text{solvent}} \qquad (38)$$

where E_j' represents all the terms due to the transport of ions across the interface, (i.e., all but the last term in Equation 60). It is worth repeating that the movement of ions and solvent molecules across an interface between two solvents is mutually interdependent and, thus, the division of E_j into E_j' and $E_{j\text{solvent}}$ is strictly formal. E_j' can be calculated from the transference numbers, t_i, and transfer activity coefficients of the single ions in solution if those data are available.

Since the values of transference numbers of these ions in the solvents of interest are not always known, transference numbers in our system were estimated based on the limiting ionic conductance, λ_o, and concentration of those ions in solution. Table 16 contains values for the limiting conductances of ions in several dipolar aprotic solvents. All of these values were obtained from the literature, except that of the picrate ion, Pi^-, in PC which was calculated from experimental data of the limiting conductance of KPi obtained in this study. Table 17 lists values for the limiting conductances and concentrations of KPi in propylene carbonate. A value of 24.7 for Λ_o of KPi in propylene carbonate was determined by plotting Λ versus $\sqrt{c}$. The correlation coefficient, R, for this plot is .966.

Transference numbers for ions in a solvent were calculated by:

$$t_i = \frac{C_i\lambda_{oi}}{\sum_i C_i\lambda_{oi}} \qquad (61)$$

where C_i is the concentration of ion, i, and λ_{oi} is the limiting conductance of that ion in solution. The quantity $C_i\lambda_{oi}$ is an estimate of the mobility of ion i in the solvent. Tables 18-20 list the calculated transference numbers for these ions in various solvents, using different salt bridge electrolytes. Values of these calculated transference numbers in the solvents of interest were averaged and used as the approximation of the transference number in Equation 60. They are listed in Tables 21-23.

As can easily be seen from Tables 18-23, the tranference number of Na^+ and BPh_4^- ions are not significant at $NaBPh_4$ concentrations below 10^{-2}M (except, of course, for the BPh_4^- ion with $TABBPh_4$ as salt bridge, where the salt bridge contributes significantly to the BPh_4^- ion concentration). Thus, the first two bracketed terms in Equation 60 can be neglected if the concentration ratio of salt bridge electrolyte RX to $NaBPh_4$ is at least a hundredfold.

Values of transfer activity coefficients for single ions were obtained from the literature (1,10) or from data experimentally determined by the author. Table 24 lists values of log ${}_m\gamma_i$ (molar scale) referred to water for the single ions of interest. The value of log ${}^{H_2O}_{m}\gamma^{MeCN}_{Na}$ is different than that reported in Reference 1, because a value of $pK_{sp}NaCl$ in acetonitrile based on a solubility determination

(48) was used here rather than one determined from a conductometric titration of a halide in a saturated solution (10).

Table 25 lists values of log ${}^{S_R}_{m}\gamma^{S}_{i}$ for single ions to be substituted into Equation 60 for calculation of E'_j. S_R and S refer to the reference solvent and solvent of interest, respectively. Transfer activity coefficients for the TAB^+ ion in all solvent pairs and of Pi^- ion in solvent pairs containing DMSO were not available in the literature; nor could they be determined from experimental measurements due to the extreme solubility of electrolytes containing these ions in the solvents of interest. Transfer activity coefficient data in solvent pairs involving NMF are not available in the literature.

E'_j was calculated using Equation 60 for cells using Et_4NClO_4 as a salt-bridge electrolyte for all solvent systems and for cells using Et_4NPi as salt bridge electrolyte in all solvent pairs not involving DMSO. Tables 26-27 list values for the calculated E'_j and $E'_{cell}-E'_j$.

If we assume that the $E_{j\,solvent}$ term in Equation 60 is negligible, transfer activity coefficients for the sodium ion, log ${}_{m}\gamma_{Na}$ can be calculated from:

$$\log {}_{m}\gamma_{Na} = \frac{E'_{cell} - E'_j}{59.16} \qquad (62a)$$

Values of log ${}_{m}\gamma_{Na}$ obtained from Equation 62a are listed in Tables 26-27.

It is possible to calculate $E_{j\ \text{solvent}}$ by using Equation 47:

$$E_{j\ \text{solvent}} = E_{\text{cell}} - E_{j\ A} - \frac{1}{F}[t_Z \Delta G_t^\circ(MZ) - t_R(\Delta G_t^\circ(RX) - \Delta G_t^\circ(RX) - \Delta G_t^\circ(MX) + t_X \Delta G_t^\circ(MX)] \qquad (47)$$

but the calculation of the transfer activity coefficient and $E_{j\ \text{solvent}}$ contain a term involving the e.m.f. of the cell, E'_{cell}. If we want to calculate $\log {}_m\gamma_{Na}$ in Cell IX by:

$$\log {}_m\gamma_{Na} = \frac{E'_{\text{cell}} - E'_j - E_{j\ \text{solvent}}}{59.16} \qquad (62b)$$

we end up subtracting E'_{cell} from itself. Thus, we are forced to obtain a value of $E_{j\ \text{solvent}}$ independently or make some approximation as to its value when calculating the transfer activity coefficient.

Parker, et. al. (17) based on their studies of the correlation of heats of solution and cell potentials, concluded that the $E_{j\ \text{solvent}}$ term between dipolar aprotic solvents is small and can be neglected. Hence, as a first approximation, $E_{j\ \text{solvent}}$ will be considered negligible in the dipolar aprotic systems.

Table 16

Limiting Equivalent Conductances of Ions.

λ_o

Ion	DMF	DMSO	MeCN	PC
Na^+	29.9 (32)	13.5 (35)	76.6 (40)	10.2 (44)
Li^+	25.0 (32)	11.4 (36,37)	69.3 (41)	7.3 (45)
Et_4N^+	35.4 (33)	17.1 (9)	85.1 (9)	14.4 (46)
TAB^+		11.0 (38)	57.7 (42)	
Ag^+	35.2 (32)	15.9 (39)	86.0 (33)	
Ph_4As^+	31.0 (34)			
Pi^-	37.5 (9)	17.3 (9)	77.3 (9)	12.7[a]
ClO_4^-	52.4 (32)	24.6 (9)	103.4 (40)	18.3 (45)
BPh_4^-		11.0 (35)	57.7 (43)	7.8 (47)

[a] This work.

Table 17

Conductances of KPi in Propylene Carbonate at 25.00°C.

10^3C, M	Λ
4.055	21.04
4.583	20.79
5.481	20.27
62.41	19.47
11.71	18.37

Table 18

Transference Numbers of Et_4NClO_4 & $NaBPh_4$ in Individual Solvents.

Et_4NClO_4 Salt Bridge Concentration = .1 M

Solvent: DMF

C_{NaBPh_4}

	10^{-2}	10^{-3}	8×10^{-4}	4×10^{-4}
t_{Na}	.032	.003	.002	.001
t_{BPh_4}	.033	.004	.003	.001
t_{Et_4N}	.377	.400	.401	.402
t_{ClO_4}	.588	.593	.594	.595

Solvent: DMSO

	10^{-2}	10^{-3}	8×10^{-4}	4×10^{-4}
t_{Na}	.031	.003	.003	.001
t_{BPh_4}	.025	.003	.002	.001
t_{Et_4N}	.387	.408	.408	.409
t_{ClO_4}	.557	.586	.587	.589

Solvent: MeCN

	10^{-2}	10^{-3}	8×10^{-4}	4×10^{-4}
t_{Na}	.038	.004	.003	.002
t_{BPh_4}	.029	.003	.002	.001
t_{Et_4N}	.421	.448	.449	.450
t_{ClO_4}	.512	.545	.545	.547

Table 18 (continued)

Solvent: PC

	C_{NaBPh_4}			
	10^{-2}	10^{-3}	8×10^{-4}	4×10^{-4}
t_{Na}	.029	.003	.002	.002
t_{BPh_4}	.023	.002	.001	.001
t_{Et_4N}	.417	.438	.439	.439
t_{ClO_4}	.530	.557	.558	.558

Table 19

Transference Numbers of Et_4NPi & $NaBPh_4$ in Individual Solvents.

Et_4NPi Salt Bridge Concentration = .1 M

Solvent: DMF

	C_{NaBPh_4}			
	10^{-2}	10^{-3}	8×10^{-4}	4×10^{-4}
t_{Na}	.038	.004	.003	.002
t_{BPh_4}	.039	.004	.003	.002
t_{Et_4N}	.448	.482	.482	.484
t_{Pi}	.475	.510	.511	.512

Solvent: DMSO

t_{Na}	.037	.004	.003	.002
t_{BPh_4}	.030	.003	.003	.002
t_{Et_4N}	.464	.494	.494	.495
t_{Pi}	.469	.499	.500	.501

Solvent: MeCN

t_{Na}	.044	.005	.004	.002
t_{BPh_4}	.033	.004	.003	.002
t_{Et_4N}	.484	.510	.521	.522
t_{Pi}	.440	.472	.473	.474

Table 19 (continued)

Solvent: PC

	C_{NaBPh_4}			
	10^{-2}	10^{-3}	8×10^{-4}	4×10^{-4}
t_{Na}	.044	.005	.004	.002
t_{BPh_4}	.033	.004	.003	.002
t_{Et_4N}	.484	.520	.521	.523
t_{Pi}	.440	.472	.473	.474

Table 20

Transference Numbers of $TABBPh_4$ & $NaBPh_4$ in Individual Solvents.

$TABBPh_4$ Salt Bridge Concentration = .1 M

Solvent: DMF

	C_{NaBPh_4}			
	10^{-2}	10^{-3}	8×10^{-4}	4×10^{-4}
t_{Na}	.044	.005	.005	.003
t_{BPh_4}	.500	.500	.500	.501
t_{TAB}	.456	.495	.495	.497

Solvent: DMSO

	10^{-2}	10^{-3}	8×10^{-4}	4×10^{-4}
t_{Na}	.056	.005	.005	.003
t_{BPh_4}	.500	.500	.500	.501
t_{TAB}	.443	.495	.495	.497

Solvent: MeCN

	10^{-2}	10^{-3}	8×10^{-4}	4×10^{-4}
t_{Na}	.046	.005	.005	.003
t_{BPh_4}	.500	.500	.500	.501
t_{TAB}	.454	.495	.495	.497

Solvent: PC

	10^{-2}	10^{-3}	8×10^{-4}	4×10^{-4}
t_{Na}	.057	.006	.002	.002
t_{BPh_4}	.494	.500	.499	.499
t_{TAB}	.448	.494	.499	.499

Table 21

Average Transference Numbers for Et_4NClO_4 & $NaBPh_4$ in Solvent Pairs.

Et_4NClO_4 Salt Bridge Concentration = .1 M

Solvent System: DMF-MeCN

	C_{NaBPh_4}			
	10^{-2}	10^{-3}	8×10^{-4}	4×10^{-4}
t_{Na}	.035	.004	.003	.002
t_{BPh_4}	.031	.004	.002	.001
t_{Et_4N}	.399	.424	.425	.426
t_{ClO_4}	.535	.569	.570	.571

Solvent System: DMSO-MeCN

t_{Na}	.034	.004	.002	.002
t_{BPh_4}	.028	.003	.002	.002
t_{Et_4N}	.404	.428	.428	.428
t_{ClO_4}	.535	.566	.566	.566

Solvent System: PC-MeCN

t_{Na}	.034	.004	.002	.002
t_{BPh_4}	.026	.002	.002	.002
t_{Et_4N}	.419	.443	.444	.444
t_{ClO_4}	.521	.551	.552	.552

Table 21 (continued)

Solvent System: DMF-DMSO

C_{NaBPh_4}

	10^{-2}	10^{-3}	8×10^{-4}	4×10^{-4}
t_{Na}	.032	.003	.002	.002
t_{BPh_4}	.029	.003	.002	.002
t_{Et_4N}	.382	.404	.405	.405
t_{ClO_4}	.557	.590	.591	.591
Solvent System: PC-DMF				
t_{Na}	.030	.003	.002	.002
t_{BPh_4}	.028	.003	.002	.002
t_{Et_4N}	.447	.419	.420	.420
t_{ClO_4}	.544	.575	.576	.576
Solvent System: PC-DMSO				
t_{Na}	.030	.003	.002	.002
t_{BPh_4}	.024	.002	.002	.002
t_{Et_4N}	.402	.423	.424	.424
t_{ClO_4}	.544	.572	.572	.572

Table 22

Average Transference Numbers for Et_4NPi & $NaBPh_4$ in Solvent Pairs.

Et_4NPi Salt Bridge Concentration = .1 M

C_{NaBPh_4}

Solvent System: DMF-MeCN

	10^{-2}	10^{-3}	8×10^{-4}	4×10^{-4}
t_{Na}	.041	.004	.004	.002
t_{BPh_4}	.036	.004	.003	.002
t_{Et_4N}	.466	.501	.501	.504
t_{Pi}	.458	.491	.492	.494

Solvent System: DMSO-MeCN

	10^{-2}	10^{-3}	8×10^{-4}	4×10^{-4}
t_{Na}	.041	.004	.004	.002
t_{BPh_4}	.032	.004	.003	.001
t_{Et_4N}	.474	.507	.507	.510
t_{Pi}	.454	.486	.486	.488

Solvent System: PC-MeCN

	10^{-2}	10^{-3}	8×10^{-4}	4×10^{-4}
t_{Na}	.040	.004	.003	.003
t_{BPh_4}	.031	.004	.003	.003
t_{Et_4N}	.491	.524	.525	.525
t_{Pi}	.440	.469	.470	.470

Table 22 (continued)

Solvent System: DMF-DMSO

C_{NaBPh_4}

	10^{-2}	10^{-3}	8×10^{-4}	4×10^{-4}
t_{Na}	.038	.004	.003	.003
t_{BPh_4}	.034	.004	.003	.003
t_{Et_4N}	.456	.488	.489	.489
t_{Pi}	.472	.504	.505	.505

Solvent System: PC-DMF

t_{Na}	.036	.004	.003	.003
t_{BPh_4}	.034	.003	.002	.002
t_{Et_4N}	.473	.505	.506	.506
t_{Pi}	.457	.488	.489	.489

Solvent System: PC-DMSO

t_{Na}	.036	.004	.003	.003
t_{BPh_4}	.029	.003	.003	.003
t_{Et_4N}	.481	.511	.512	.512
t_{Pi}	.454	.482	.482	.482

Table 23

Average Transference Numbers for $TABBPh_4$ & $NaBPh_4$ in Solvent Pairs.

$TABBPh_4$ Salt Bridge Concentration = .1 M

Solvent System: DMF-MeCN

C_{NaBPh_4}

	10^{-2}	10^{-3}	8×10^{-4}	4×10^{-4}
t_{Na}	.045	.005	.005	.003
t_{BPh_4}	.500	.500	.500	.501
t_{TAB}	.455	.495	.495	.497

Solvent System: DMSO-MeCN

t_{Na}	.051	.005	.005	.003
t_{BPh_4}	.500	.500	.500	.501
t_{TAB}	.449	.495	.495	.497

Solvent System: PC-MeCN

t_{Na}	.051	.005	.005	.003
t_{BPh_4}	.497	.500	.500	.501
t_{TAB}	.452	.495	.495	.497

Solvent System: DMSO-DMF

t_{Na}	.050	.005	.005	.003
t_{BPh_4}	.500	.500	.500	.501
t_{TAB}	.450	.495	.495	.496

Table 23 (continued)

Solvent System: PC-DMF

	C_{NaBPh_4}			
	10^{-2}	10^{-3}	8×10^{-4}	4×10^{-4}
t_{Na}	.050	.005	.005	.003
t_{BPh_4}	.497	.500	.500	.500
t_{TAB}	.453	.495	.495	.497

Solvent System: PC-DMSO

	10^{-2}	10^{-3}	8×10^{-4}	4×10^{-4}
t_{Na}	.056	.005	.005	.003
t_{BPh_4}	.497	.500	.500	.500
t_{TAB}	.447	.495	.495	.497

Table 24

Values of Transfer Activity Coefficients, log ${}^{H_2O}_{m}\gamma_i$,
for Single Ions (molar scale-water reference). (1)

Ion	MeCN	DMSO	DMF	PC
Na^+	3.0 (48)	-2.4	-1.6	2.7
Et_4N^+	-1.7	-2.2	-1.5	-0.9
TAB^+	-	-	-	-
Ag^+	-3.8	-5.9	-3.0	2.9
Pi^-	-0.3	-	-1.7	-1.6
ClO_4^-	0.8	-0.2	0.1	-0.3
BPh_4^-	-5.9	-6.5	-6.7	-6.1

Table 25

Values of Transfer Activity Coefficients, log ${}^{S_1}_{m}\gamma^{S_2}_{i}$, for Single Ions (molar scale). (1,10)

Ion	DMF-MeCN (MeCN-ref.)	DMSO-MeCN (MeCN-ref.)	PC-MeCN (MeCN-ref.)
Na^+	-4.6	-5.4	-0.3
Et_4N^+	0.2	-0.5	0.8
TAB^+	-	-	-
Ag^+	0.8	-2.1	6.7
Pi^-	-1.4	-	-1.3
ClO_4^-	-0.7	-1.0	-1.1
BPh_4^-	-0.8	-0.6	-0.2

Ion	DMF-DMSO (DMSO-ref.)	PC-DMF (DMF-ref.)	PC-DMSO (DMSO-ref.)
Na^+	0.8	4.3	5.1
Et_4N^+	0.7	0.6	1.3
TAB^+	-	-	-
Ag^+	2.9	5.9	8.8
Pi^-	-	0.1	-
ClO_4^-	0.3	-0.4	-0.1
BPh_4^-	-0.2	0.6	0.4

Table 26

Calculated Liquid-Junction Potentials, E_j' & log ${}_m\gamma_{Na}$, Using Cells with Et_4NClO_4 as a Salt Bridge.

DMF-MeCN

Approximate Concentration $NaBPh_4$	E'_{cell} (mV)	E_j' (mV)	$E'_{cell} - E_j'$ (mV)	$\log {}^{MeCN}_{m}\gamma^{DMF}_{Na}$
1×10^{-2}	-292.0	-18.8	-273.2	-4.62
1×10^{-3}	-298.8	-27.7	-271.1	-4.58
8×10^{-4}	-300.0	-27.9	-272.1	-4.60
2×10^{-4}	-303.0	-27.9	-275.1	-4.65

$$\log {}^{MeCN}_{m}\gamma^{DMF}_{Na} \ (\bar{x}) = -4.61 \pm .03$$

$$\log {}^{MeCN}_{m}\gamma^{DMF}_{Na} = -4.6$$

(based on literature data in Table 25)

DMSO-MeCN

Approximate Concentration $NaBPh_4$	E'_{cell} (mV)	E_j' (mV)	$E'_{cell} - E_j'$ (mV)	$\log {}^{MeCN}_{m}\gamma^{DMSO}_{Na}$
1×10^{-2}	-338.9,-337.1	-9.8	-329.1,-327.3	-5.56,-5.53
1×10^{-3}	-347.4,-351.1	-19.7	-327.7,-331.4	-5.54,-5.60
8×10^{-4}	-353.0	-20.3	-332.7	-5.62
4×10^{-4}	-339.5,-357.7	-20.3	-319.2,-337.4	-5.40,-5.70

$$\log {}^{MeCN}_{m}\gamma^{DMSO}_{Na} \ (\bar{x}) = -5.56 \pm .08$$

$$\log {}^{MeCN}_{m}\gamma^{DMSO}_{Na} = -5.4$$

(based on literature data in Table 25)

Table 26 (continued)

PC-MeCN

Approximate Concentration $NaBPh_4$	E'_{cell} (mV)	E'_j (mV)	$E'_{cell} - E'_j$ (mV)	$\log {}^{\mathrm{MeCN}}_{\mathrm{m}}\gamma^{\mathrm{PC}}_{\mathrm{Na}}$
1×10^{-2}	- 23.6	-53.0	29.4	.50
1×10^{-3}	- 32.8	-56.7	23.9	.40
8×10^{-4}	- 32.6	-56.8	24.2	.41
4×10^{-4}	- 35.0	-56.8	21.8	.37

$$\log {}^{\mathrm{MeCN}}_{\mathrm{m}}\gamma^{\mathrm{PC}}_{\mathrm{Na}} \ (\bar{x}) = .42 \pm .05$$

$$\log {}^{\mathrm{MeCN}}_{\mathrm{m}}\gamma^{\mathrm{PC}}_{\mathrm{Na}} = -0.3$$

(based on literature data in Table 25)

DMF-DMSO

Approximate Concentration $NaBPh_4$	E'_{cell} (mV)	E'_j (mV)	$E'_{cell} - E'_j$ (mV)	$\log {}^{\mathrm{DMSO}}_{\mathrm{m}}\gamma^{\mathrm{DMF}}_{\mathrm{Na}}$
1×10^{-2}	65.9	- 7.8	73.7	1.25
1×10^{-3}	65.9	- 6.4	72.3	1.22
8×10^{-4}	66.9	- 6.4	73.3	1.24
4×10^{-4}	68.1	- 6.4	74.5	1.26
2×10^{-4}	65.5	- 6.4	71.9	1.22

$$\log {}^{\mathrm{DMSO}}_{\mathrm{m}}\gamma^{\mathrm{DMF}}_{\mathrm{Na}} \ (\bar{x}) = 1.24 \pm .02$$

$$\log {}^{\mathrm{DMSO}}_{\mathrm{m}}\gamma^{\mathrm{DMF}}_{\mathrm{Na}} = 0.8$$

(based on literature data in Table 25)

Table 26 (continued)

PC-DMF

Approximate Concentration $NaBPh_4$	E'_{cell} (mV)	E'_j (mV)	$E'_{cell} - E'_j$ (mV)	$\log {}^{DMF}_{m}\gamma^{PC}_{Na}$
1×10^{-2}	275.9	-35.0	310.9	5.26
1×10^{-3}	268.6	-29.1	297.7	5.03
8×10^{-4}	271.1	-29.0	300.1	5.07
4×10^{-4}	274.5	-29.0	303.5	5.13

$$\log {}^{DMF}_{m}\gamma^{PC}_{Na}\ (\bar{x}) = 5.12 \pm .08$$

$$\log {}^{DMF}_{m}\gamma^{PC}_{Na} = 4.3$$

(based on literature data in Table 25)

PC-DMSO

Approximate Concentration $NaBPh_4$	E'_{cell} (mV)	E'_j (mV)	$E'_{cell} - E'_j$ (mV)	$\log {}^{DMSO}_{m}\gamma^{PC}_{Na}$
1×10^{-2}	312.0	-42.3	354.3	5.99
1×10^{-3}	319.5	-36.7	356.2	6.02
8×10^{-4}	322.9	-36.6	359.5	6.08
4×10^{-4}	322.3	-36.6	358.9	6.07
2×10^{-4}	324.7	-36.6	361.3	6.11

$$\log {}^{DMSO}_{m}\gamma^{PC}_{Na}\ (\bar{x}) = 6.05 \pm .04$$

$$\log {}^{DMSO}_{m}\gamma^{PC}_{Na} = 5.1$$

(based on literature data in Table 25)

Table 27

Calculated Liquid-Junction Potentials, E'_j & log ${}_{m}\gamma_{Na}$, Using Cells with Et_4NPi as a Salt Bridge.

DMF-MeCN

Approximate Concentration $NaBPh_4$	E'_{cell} (mV)	E'_j (mV)	$E'_{cell} - E'_j$ (mV)	log ${}^{MeCN}_{m}\gamma^{DMF}_{Na}$
1×10^{-2}	-299.7	-34.0	-265.7	-4.49
1×10^{-3}	-306.3	-45.7	-260.6	-4.41
8×10^{-4}	-307.8	-45.7	-262.1	-4.43
2×10^{-4}	-314.5	-45.8	-268.7	-4.54

$$\log {}^{MeCN}_{m}\gamma^{DMF}_{Na} \ (\bar{x}) = -4.47 \pm .05$$

$$\log {}^{MeCN}_{m}\gamma^{DMF}_{Na} = -4.6$$

(based on literature data in Table 25)

PC-MeCN

Approximate Concentration $NaBPh_4$	E'_{cell} (mV)	E'_j (mV)	$E'_{cell} - E'_j$ (mV)	log ${}^{MeCN}_{m}\gamma^{PC}_{Na}$
1×10^{-2}	-21.3	-56.3	35.0	.59
1×10^{-3}	-27.6	-60.8	33.3	.56
8×10^{-4}	-24.0	-60.9	36.9	.62
4×10^{-4}	-22.8	-60.9	38.1	.64
2×10^{-4}	-28.0	-60.9	32.9	.56

$$\log {}^{MeCN}_{m}\gamma^{PC}_{Na} \ (\bar{x}) = .60 \pm .03$$

$$\log {}^{MeCN}_{m}\gamma^{PC}_{Na} = -0.3$$

(based on literature data in Table 25)

Table 27 (continued)

PC-DMF

Approximate Concentration $NaBPh_4$	E'_{cell} (mV)	E'_j (mV)	$E'_{cell} - E'_j$ (mV)	$\log {}^{PC}_{m}\gamma^{DMF}_{Na}$
1×10^{-2}	291.8	-21.6	313.4	5.29
1×10^{-3}	286.7	-15.7	302.4	5.11
8×10^{-4}	294.5	-15.7	310.2	5.24
4×10^{-4}	270.9	-15.7	286.6	4.84

$$\log {}^{PC}_{m}\gamma^{DMF}_{Na}\ (\bar{x}) = 5.12 \pm .17$$

$$\log {}^{PC}_{m}\gamma^{DMF}_{Na} = 4.3$$

(based on literature data in Table 25)

Comparison of Calculated Transfer Activity Coefficients with Literature Values.

Table 28 contains data comparing the average values of log $_m\gamma_{Na}$ calculated by Equation 61 with literature values. As can easily be seen, there is excellent agreement between the literature values based on the Ph_4AsBPh_4 assumption and those obtained using Equation 61 for systems involving measurements between acetonitrile, dimethylsulfoxide, and dimethylformamide. However, transfer activity coefficients between propylene carbonate and other solvents disagree with the literature data by an almost constant amount of 0.8 log $_m\gamma$ units.

To what can we attribute the large discrepancy in the transfer activity coefficient involving propylene carbonate and the relative smaller differences in the other solvents? Possible uncertainties in the literature values for log $_m\gamma_i$ for the single ions and experimental error are not sufficient to explain this problem. The answer seems to lie with our assumption of negligible $E_{jsolvent}$ in Equation 60.

Acetonitrile, dimethylsulfoxide, and dimethylformamide have similar values for dielectric constants and dipole moments (49). However, the dielectric constant and dipole moment of propylene carbonate are much higher than the other solvents mentioned. Table 29 lists values of the dielectric constant and dipole moment of these solvents (50). The $E_{jsolvent}$ term can be considered small (within experimental error) for measurements between similar solvents. However,

$E_{j\ \mathrm{solvent}}$ cannot be neglected in measurements of junctions between propylene carbonate and acetonitrile, dimethylsulfoxide, and dimethylformamide. These conclusions were drawn based on the tetraphenylborate assumption for transfer activity coefficients of single ions.

The value of $E_{j\ \mathrm{solvent}}$ can be approximated from:

$$\Delta = E_{j\ \mathrm{solvent}} = \log\ {}_{m}\gamma_{Na}\ (\mathrm{lit.}) - \log\ {}_{m}\gamma_{Na}\ (\mathrm{cal.}) \qquad (63)$$

These values are also listed in Table 28.

Table 28

Calculated and Literature Values of Transfer Activity Coefficients of the Sodium Ion, log ${}^{S_1}_{m}\gamma^{S_2}_{Na}$.

	log ${}^{S_1}_{m}\gamma^{S_2}_{Na}$				
S_2 : S_1	Literature (Table 25)	Et_4NClO_4 (This Work)	Δ*	Et_4NPi This Work	Δ*
DMSO : MeCN	-5.4	-5.56	0.2	-	-
DMF : MeCN	-4.6	-4.61	0.0	-4.47	-0.1
DMF : DMSO	0.8	1.41	-0.3	-	-
PC : MeCN	-0.3	0.42	-0.7	0.60	-0.9
PC : DMF	4.3	5.12	-0.8	5.12	-0.8
PC : DMSO	5.1	6.05	-0.9	-	-

*Δ = log ${}_{m}\gamma_{Na}$ (lit.) - log ${}_{m}\gamma_{Na}$ (this work)

S_1 = Reference Solvent

Table 29.

Dielectric Constants and Dipole Moments of Solvents (50)

Solvent	Dielectric Constant	Dipole Moment
MeCN	35.6	3.92
DMF	36.7	3.86
DMSO	46.7	3.96
PC	64.4	4.98

Calculation of Transfer Activity Coefficients for TAB^+ and Pi^- Ions.

Transfer activity coefficients for the picrate ion between dimethylsulfoxide and any of the other solvents of interest are not available due to the extreme solubility of picrates in dimethylsulfoxide. For the same reason, solubility data of electrolytes containing TAB^+ ion in dipolar aprotic solvents are not available in the literature. However, transfer activity coefficients of the above ions can be calculated from the measured e.m.f. of Cell IX and known values of log ${}_m\gamma$ for the other ions in solution.

By rearranging terms in Equation 60 and recalling that:

$$\log {}_m\gamma_{Na} = \frac{E'_{cell} - E_j}{0.05916} \quad \text{at } 25°C \qquad (49a)$$

we obtain when using $TABBPh_4$ as salt bridge electrolyte in Cell IX:

$$\log {}_m\gamma_{TAB} = \frac{(1-t_{Na})}{t_{TAB}} \log {}_m\gamma_{Na} - \frac{E'_{cell}(mV)}{(59.16)(t_{TAB})} - \frac{(t_{Na} - t_{BPh_4})}{t_{TAB}} \log \frac{S_2 a_{NaBPh_4}}{S_1 a_{NaBPh_4}} + \frac{t_{BPh_4}}{t_{TAB}} \log {}_m\gamma_{BPh_4} + \frac{E_j \text{ solvent (mV)}}{(59.16)(t_{TAB})} \qquad (64)$$

Similarly, when using Et_4NPi as salt bridge, we can express:

$$\log {}_m\gamma_{Pi} = \frac{E'_{cell}(mV)}{(59.16)(t_{Pi})} + (t_{Na} - t_{BPh_4}) \log \frac{S_2 a_{NaBPh_4}}{S_1 a_{NaBPh_4}} -$$

$$\frac{(1-t_{Na})}{t_{Pi}} \log {}_m\gamma_{Na} - \frac{t_{BPh_4}}{t_{Pi}} \log {}_m\gamma_{BPh_4} +$$

$$\frac{t_{Et_4N}}{t_{Pi}} \log {}_m\gamma_{Et_4N} + \frac{E_{j\ solvent}\ (mV)}{(59.16)(t_{Pi})}$$

Calculated values of $\log {}_m\gamma_{Pi}$ and $\log {}_m\gamma_{TAB}$ are listed in Table 30. Only values of E'_{cell} for Cell IX for $NaBPh_4$ concentrations below 10^{-2}M were used in the calculation of $\log {}_m\gamma_{TAB}$ and $\log {}_m\gamma_{Pi}$ using Equations 64 and 65, to minimize the contributions due to the ions other than those of the salt bridge electrolyte.

Values of the transfer activity of picrate ion in DMSO referred to water were calculated by:

$$\log {}^{H_2O}_{m}\gamma^{DMSO}_{Pi} = \log {}^{H_2O}_{m}\gamma^{S}_{Pi} - \log {}^{S}_{m}\gamma^{DMSO}_{Pi} \qquad (66)$$

with S being either acetonitrile, dimethylformamide or propylene carbonate. The average value of $\log {}^{H_2O}_{m}\gamma^{DMSO}_{Pi}$ was found to be -1.8 units.

Table 30

Transfer Activity Coefficients for TAB$^+$ and Pi$^-$ Ions in Dipolar Aprotic Solvents.

S_2 : S_1	$\log {}^{S_1}_{m}\gamma^{S_2}_{TAB}$	$\log {}^{S_1}_{m}\gamma^{S_2}_{Pi}$
DMSO : MeCN	0.5	-1.3
DMF : MeCN	0.5	
PC : MeCN	-1.5	
PC : DMSO	-2.4	0.3
PC : DMF	-2.1	
DMF : DMSO	-0.1	0.2

S_1 = Reference Solvent

Calculation of Transfer Activity Coefficients for Ag^+ Ion Using Parker's Cell.

Transfer activity coefficients for the Ag^+ ion can be obtained from measurements of Parker's Cell (Cell V) if the liquid-junction potentials are known:

$$\begin{array}{c|c|c|c|c} \mathrm{Ag} & \begin{matrix}\mathrm{AgClO_4}\ (0.01\ \mathrm{M})\\ \text{Reference Solvent}\end{matrix} & \begin{matrix}\mathrm{Et_4NPi}\ (0.1\ \mathrm{M})\\ \text{Reference Solvent}\end{matrix} & \begin{matrix}\mathrm{AgClO_4}\ (0.01\ \mathrm{M})\\ \mathrm{S}\end{matrix} & \mathrm{Ag} \end{array} \tag{Cell V}$$

The liquid-junction potential, E_j, can be calculated from:

$$E_j = -59.16[t_{Ag} \log {}_m\gamma_{Ag} - t_{ClO_4} \log {}_m\gamma_{ClO_4} + t_{Et_4N} \log {}_m\gamma_{Et_4N} - t_{Pi} \log {}_m\gamma_{Pi}] + E_{j\,solvent} \tag{67}$$

Parker (9) reports the e.m.f. of Cell V, using acetonitrile as reference solvent, to be -152 mV when S is DMSO and 40 mV when S is DMF. These voltages correspond to values of $\log {}^{MeCN}_{m}\gamma^{DMSO}_{Ag} = -2.6$ and $\log {}^{MeCN}_{m}\gamma^{DMF}_{Ag} = 0.7$.

Assuming $E_{j\,solvent}$ to be negligible between these solvents, as in our previous discussion, E_j can be calculated from transference numbers and transfer activity coefficients for the ions in solution. Transference numbers, t_i, are calculated as done previously (Equation 61) and are listed in Table 31. Values of transfer activity coefficients for the ions of interest can be found in Tables 25 and 30. E_j for Cell V was calculated to be -18 mV and -47 mV when S was DMSO and DMF, respectively. Transfer activity coefficients were then calculated using Equation 49. Table 32 compares values of log ${}_m\gamma_{Ag}$ with the literature.

Table 31

Transference Numbers of $AgClO_4$ and Et_4NPi.

0.01 M $AgClO_4$ & 0.1 M Et_4NPi

	Solvents				
	MeCN	DMSO	DMF	DMSO-MeCN	DMF-MeCN
t_{Ag}	.047	.041	.043	.044	.045
t_{ClO_4}	.057	.064	.064	.060	.060
t_{Et_4N}	.469	.445	.434	.457	.452
t_{Pi}	.426	.450	.459	.438	.443

Table 32

Comparison of Values of Transfer Activity Coefficients for the Silver Ion, log ${}^{\mathrm{MeCN}}_{\mathrm{m}}\gamma_{\mathrm{Ag}}$ (MeCN-reference).

	Parker, et. al. Negligible E_j	Calculated E_j (This Work)	Literature(1)
log ${}^{\mathrm{MeCN}}_{\mathrm{m}}\gamma^{\mathrm{DMSO}}_{\mathrm{Ag}}$	-2.6	-2.3	-2.1
log ${}^{\mathrm{MeCN}}_{\mathrm{m}}\gamma^{\mathrm{DMF}}_{\mathrm{Ag}}$	0.7	1.5	0.8

Studies Using Hydrogen (Glass) Electrodes.

Additional e.m.f. studies in dipolar aprotic solvents were made using hydrogen glass electrodes in Cell X.

$$\text{H-glass electrode}\left|\begin{array}{c}pa^*_H\text{-buffer}\\ \text{Solvent(I)}\end{array}\right|\begin{array}{c}0.1\ M\ RX\\ \text{Solvent(I)}\end{array}\left|\begin{array}{c}pa^*_H\text{-buffer}\\ \text{Solvent(II)}\end{array}\right|\text{H-glass electrode}$$

(Cell X)

Buffer solutions of known pa^*_H-values in these solvents were prepared based on the literature data (25, 26, 50). Combinations of different concentrations of picric acid and tetrabutylammonium picrate were used to prepare buffers in acetonitrile (26). Similar mixtures of 2,6-dinitrophenol and tetraethylammonium 2,6-dinitrophenolate were used in dimethylformamide (25). Buffers in dimethylsulfoxide were solutions of picric acid, salicylic acid and sodium salicylate or benzoic acid and lithium benzoate (50). Results of measurements of Cell X can be found in Tables 33-34.

The term $E_{cell}/59.16 + \Delta pa^*_H$ is a measure of the transfer activity coefficient for the hydrogen ion and the liquid-junction potential, E_j:

$$\frac{E_{cell}}{59.16} + \Delta pa^*_H = \log {}_m\gamma_H + \frac{E_j}{59.16} \qquad (68)$$

Values of this term are also listed in Tables 33-34. The precision of these measurements is about 0.2 units except for the 0.5 value in the DMSO-MeCN system with $TABBPh_4$ as salt bridge. However, the accuracy of the value of $E_{cell}/59.16 + \Delta pa^*_H$ is questionable because of the large uncertainty of the K_a values of these buffers in these solvents which, in certain cases, are reported to be one significant figure only and, consequently, the pa^*_H values of the standard buffer are uncertain.

Table 33

E.m.f. Values for Cell X in the DMF-MeCN System.

(Sleeve-type) 25.00°C.

Solvent I = MeCN

Solvent II = DMF

RX = 0.1 M TABBPh₄ in MeCN

pa^*_H (DMF)	pa^*_H (MeCN)	E_{cell}	Δpa^*_H	$\frac{E_{cell}}{59.16}$	$\frac{E_{cell}}{59.16} + \Delta pa^*_H$
5.2	10.4	-395.7	-5.2	-6.69	-11.9
5.2	11.8	-318.0	-6.6	-5.38	-12.0
5.2	10.1	-411.0	-4.9	-6.95	-11.9
5.8	10.4	-432.0	-4.6	-7.30	-11.9
5.8	11.8	-366.0	-6.0	-6.19	-12.2
5.8	10.1	-459.0	-4.3	-7.76	-12.1

$\bar{x} = -12.0 \pm 0.1$

Table 34

E.m.f. Values for Cell X in the DMSO-MeCN System. (Sleeve-type) 25.00°C.

Solvent I = MeCN Solvent II = DMSO

RX = 0.1 M TABBPh$_4$ in MeCN

pa_H^* (DMSO)	pa_H^* (MeCN)	E_{cell}	Δpa_H^*	$\frac{E_{cell}}{59.16}$	$\frac{E_{cell}}{59.16} + \Delta pa_H^*$
10.4	10.1	-744.3	0.3	-12.58	-12.3
6.4	10.1	-503.7	-3.7	- 8.51	-12.2
10.4	10.4	-715.3	0.0	-12.09	-12.1
6.4	10.4	-547.7	-4.0	-9.26	-13.3
1.9	10.4	-258.5	-8.5	- 4.37	-12.9
1.9	11.8	-187.3	-9.9	- 3.17	-13.1
					$\bar{x}$ = -12.7±0.5

RX = 0.1 M Et$_4$NPi in MeCN

pa_H^* (DMSO)	pa_H^* (MeCN)	E_{cell}	Δpa_H^*	$\frac{E_{cell}}{59.16}$	$\frac{E_{cell}}{59.16} + \Delta pa_H^*$
6.4	10.4	-530.3	-4.0	- 8.96	-13.0
1.9	10.4	-252.6	-8.5	- 4.27	-12.8
1.9	11.8	-180.4	-9.9	- 3.05	-13.0
6.4	11.8	-462.3	-5.4	- 7.81	-13.2
10.4	11.8	-698.0	-1.4	-11.80	-13.2
					$\bar{x}$ = -13.1±0.1

Table 34 (continued)

RX = 0.1 M Et_4NClO_4 in MeCN

pa^*_H (DMSO)	pa^*_H (MeCN)	E_{cell}	Δpa^*_H	$\frac{E_{cell}}{59.16}$	$\frac{E_{cell}}{59.16} + \Delta pa^*_H$
10.4	10.4	-769.7	0.0	-13.01	-13.0
6.4	10.4	-523.0	-4.0	- 8.84	-12.8
1.9	10.4	-245.3	-8.5	- 4.15	-12.7
10.4	11.8	-703.3	-1.4	-11.89	-13.3
6.4	11.8	-460.3	-5.4	- 7.78	-13.2
1.9	11.8	-181.4	-9.9	- 3.07	-13.0
10.4	10.1	-798.0	0.3	-13.49	-13.2
6.4	10.1	-556.3	-3.7	- 9.40	-13.1
1.9	10.1	-277.2	-8.2	- 4.69	-12.9

$\bar{x} = -13.0 \pm 0.2$

Transfer Activity Coefficients of the Hydrogen Ion in Dipolar Aprotic Solvents.

The transfer activity coefficient of the hydrogen ion can be calculated from the e.m.f. of Cell X by:

$$\log {}_{m}\gamma_{H} = \frac{E_{cell} - E_{j}}{59.16} + \Delta pa_{H}^{*} \tag{68a}$$

The liquid-junction potential, E_j, of this cell cannot be calculated precisely because of the lack of information as to the transfer activity coefficients of the ions in the pa_H^* buffers used. In addition, the buffer ions are, in some cases, of equal concentration to that of the salt bridge electrolyte, thus significantly contributing to ion transport across the interface and the liquid-junction potential. However, some estimation of E_j is possible by assuming that only the salt bridge ions contribute significantly to transport across the solvent-solvent interface.

Table 35 list estimated values of E_j based on transport of salt bridge ions only. Values of $\log {}_{m}\gamma_{H}$ calculated by Equation 68a using these calculated E_j values are also listed in Table 35. By subtracting the estimated value of E_j from the $E_{cell}/59.16 + \Delta pa_H^*$ term, the estimated value of $\log {}_{m}\gamma_{H}$ approaches the literature value, although it does not exactly match it. It is important to reiterate at this point that the accuracy of the values of $E_{cell}/59.16 + \Delta pa_H^*$ term is suspect because of the large uncertainty of the K_a values of the buffers in these solvents.

Table 35

Estimated Values of E_j and Transfer Activity Coefficients of the Hydrogen Ion in Cell X

Salt Bridge (MeCN)	$\frac{E_{cell}\,(mV)}{59.16} + \Delta pa^*_H$ (Table 33)	$\frac{E_j\ (mV)}{59.16}$	$\log {}^{MeCN}_{\ \ m}\gamma^{DMSO}_H$
$TABBPh_4$	-0.6	-12.7	-12.1
Et_4NPi	-0.4	-13.1	-12.7
Et_4NClO_4	-0.1	-13.0	-12.9

$\log {}^{MeCN}_{\ \ m}\gamma^{DMSO}_H\ (1) = -11.2$

Salt Bridge	$\frac{E_{cell}\,(mV)}{59.16} + \Delta pa^*_H$ (Table 34)	$\frac{E_j\ (mV)}{59.16}$	$\log {}^{MeCN}_{\ \ m}\gamma^{DMF}_H$
$TABBPh_4$	-0.7	-12.0	-11.3

$\log {}^{MeCN}_{\ \ m}\gamma^{DMF}_H\ (1) = -10.4$

Summary of Studies in Dipolar Aprotic Solvents.

In summary, measurements of e.m.f. cells with liquid junction between solvent pairs were made. The use of three different electrolytes as salt bridges was studied. Equations for the calculation of the liquid-junction potential, E_j, of these cells were developed and values of E_j were calculated.

Transfer activity coefficients for the sodium and hydrogen ions were calculated from the measured e.m.f. of the cell and the calculated liquid-junction potential, E_j, and were compared to literature values obtained by other methods. In addition, the transfer activity coefficients of TAB^+ ion between various solvents and Pi^- ion for solvent systems involving DMSO, which are not accessible via other methods, were calculated. The transfer activity coefficient of Ag^+ ion was determined using literature data on the e.m.f. of cells with liquid junction by calculating the E_j and correcting for it.

The $E_{j\text{solvent}}$ term in the liquid-junction potential equations can be assumed to be negligible between acetonitrile, dimethylformamide, and dimethylsulfoxide while, in measurements between propylene carbonate and these other solvents, $E_{j\text{solvent}}$ was significant. These conclusions were drawn based on the tetraphenylborate assumption for transfer activity coefficients of single ions.

Alcohol-Water Mixtures.

Introduction.

As we have discussed previously, the liquid-junction potential between two solvents is primarily due to the transport of ions and solvent molecules that are transported in the solvation sphere of the ions across the interface. The liquid-junction potential, E_j, can be represented by:

$$E_j = E_j' + E_{j\,\text{solvent}} \tag{38}$$

where E_j' accounts for all terms due to the transport of ions across the interface and $E_{j\text{solvent}}$ involves the transport of solvent molecules across the interface. While E_j' can only be calculated using extrathermodynamic data for transfer activity coefficients of single ions, $E_{j\text{solvent}}$ can be calculated from e.m.f. measurements of cells with and without salt bridges and other thermodynamic data. For example, for Cell VII, a cell without a salt bridge:

$$\text{Ag, AgZ(s)} \;\Big|\; \begin{array}{c}\text{MZ}\\(\text{H}_2\text{O})\end{array} \;\Big|\; \begin{array}{c}\text{MZ}\\(\text{S})\end{array} \;\Big|\; \text{AgZ(s), Ag} \qquad \text{(Cell VII)}$$

$E_{j\text{solvent}}$ is calculated from:

$$E_{j\text{solvent}} = E_{\text{cell}} - \frac{t_M}{F}\Delta G_t^\circ(\text{MZ}) \tag{37}$$

and for a cell with a salt bridge (Cell VIII):

$$\text{M} \;\Big|\; \begin{array}{c}\text{MZ}\\ \text{S}_1\end{array} \;\Big|\; \begin{array}{c}\text{RX}\\ \text{S}_1\end{array} \;\Big|\; \begin{array}{c}\text{MZ}\\ \text{S}_2\end{array} \;\Big|\; \text{M} \qquad \text{(Cell VIII)}$$

$$E_{j\text{solvent}} = E_{\text{cell}} - \frac{1}{F}[t_Z \Delta G_t^\circ(MZ) - t_R(\Delta G_t^\circ(RX) - \Delta G_t^\circ(MX)] + t_X \Delta G_t^\circ(MX) \tag{47a}$$

Although we can evaluate $E_{j\text{solvent}}$, we are faced with a dilemma: both the calculation of the transfer activity coefficient and $E_{j\text{solvent}}$ contain a term for the e.m.f. of the measured cell, E_{cell}. The calculation of the transfer activity coefficient involves subtracting the liquid-junction potential from E_{cell}:

$$\log {}_m\gamma_M = \frac{E_{\text{cell}} - E_j}{0.05916} \tag{49}$$

Since

$$E_j = E_j' + E_{j\text{solvent}}, \tag{38}$$

we are in reality subtracting the value of E_{cell} from E_{cell} and are left with a useless identity, $\log {}_m\gamma_M = \log {}_m\gamma_M$. Thus, if we chose to evaluate the transfer activity coefficients for single ions, $E_{j\text{solvent}}$ must be obtained from an independent source or by some approximation.

In our study of dipolar aprotic media, where many of the values of transfer activity coefficients are questionable, we chose to evaluate $\log {}_m\gamma_i$ rather than $E_{j\text{solvent}}$. However, in methanol-water mixtures, transfer activity coefficients are known with good precision and accuracy based on the tetraphenylborate assumption. Therefore, we studied the $E_{j\ \mathrm{solvent}}$ term of the liquid-junction potential between aqueous and methanol-water mixtures. In addition, existing literature data on cells with liquid junction in methanol-water and ethanol-water media are interpreted.

Previous Studies Evaluating $E_{jsolvent}$.

Alfenaar, Deligny and Reminjse (22) evaluated E_j' and $E_{jsolvent}$ in Cell VII:

$$\text{Ag, AgZ} \left| \begin{array}{c} \text{MZ} \\ (H_2O) \end{array} \right| \begin{array}{c} \text{MZ} \\ (S) \end{array} \Big| \text{AgZ, Ag} \qquad \text{(Cell VII)}$$

for 2 x 10^{-5} mole fraction MZ solutions in water and methanol-water solvent where MZ was one of seven alkali halides. $E_{j\ solvent}$ was calculated by:

$$E_{jsolvent} = E_{cell} - \frac{t_M}{F}\Delta G_t^\circ(MZ) \qquad (37)$$

They found that the value of $E_{jsolvent}$ increased steadily with the percentage of methanol in solvent, S, for all the electrolytes studied. $E_{jsolvent}$, also, varied a few millivolts depending on the nature of electrolyte MZ.

Murray and Aikens (51) measured $E_{jsolvent}$ in cells similar to Cell VII with junctions between water and methanol, ethanol, acetone, acetonitrile, and propylene carbonate solutions and for some junctions between pairs of nonaqueous solutions. Their cell (Cell XI),

$$\text{M(s), MX(s)} \;\Big|\; \text{NX(sat., } S_1) \;\Big|\; \text{NX(sat., } S_2) \;\Big|\; \text{MX(s), M} \qquad \text{(Cell XI)}$$

consists of two saturated solutions of NX in two different solvents, S_1 and S_2, with M representing some metal with a sparingly soluble salt, MX.

The e.m.f. of this cell can be represented by:

$$E_{cell} = \frac{t_N}{F}\Delta G_t^{\circ}(NX) + E_{jsolvent} \qquad (69)$$

As discussed, in the absence of any crystal solvates, the (partial molar) free energies of any two saturated solutions of a solute, $\underline{i}$, are equal. Thus, the free energies of the two saturated solutions of NX in solvents S_1 and S_2 must be equal and $\Delta G_t^{\circ}(NX)$ is equal to zero, leaving

$$E_{cell} = E_{jsolvent} \qquad (70)$$

Murray and Aikens (51) found a strong dependence of $E_{jsolvent}$ on the nature of current-carrying species, N^+ and X^-. In addition, the value of $E_{jsolvent}$ in Cell XI with saturated KCl as NX between water and methanol is nearly three times smaller than $E_{jsolvent}$ reported by Alfenaar, et. al. (22) between 2×10^{-5} mole fraction KCl in water and methanol. They state that "...the value of $E_{jsolvent}$ depends not only on the nature, but also on the concentration of the current-carrying species present" (51). They concluded that the solvent contribution to the liquid-junction potential is due to the transfer of solvated ions across the solvent-solvent interface, which in turn is a consequence of the difference in the chemical potential of the solvent species. In other words, the ions themselves have no tendency to diffuse in Cell XI, since they are at equal chemical potentials; however, the solvent molecules will tend to diffuse and carry solvated ions with them across the interface. Differences in transport of solvated ions across the interface cause the liquid-junction potential.

Outline of the Present Work.

In our present work, we have derived equations evaluating $E_{j\ \mathrm{solvent}}$ in cells with liquid junction between water and methanol-water solvents. Four different e.m.f. cells:

$$\mathrm{Hg, Hg_2Cl_2} \left| \begin{array}{c} \mathrm{NaCl} \\ (\mathrm{H_2O}) \end{array} \right. \vdots \begin{array}{c} \mathrm{NaCl} \\ (\mathrm{S}) \end{array} \left| \mathrm{Hg_2Cl_2, Hg} \right. \qquad \text{(Cell XII)}$$

$$\text{Na-glass} \left| \begin{array}{c} \mathrm{NaCl} \\ (\mathrm{H_2O}) \end{array} \right. \vdots \begin{array}{c} \mathrm{NaCl} \\ (\mathrm{S}) \end{array} \left| \text{Na-glass} \right. \qquad \text{(Cell XIII)}$$

$$\mathrm{Hg, Hg_2Cl_2} \left| \begin{array}{c} \mathrm{NaCl} \\ (\mathrm{H_2O}) \end{array} \right| \begin{array}{c} \mathrm{KCl(sat.)} \\ (\mathrm{H_2O}) \end{array} \vdots \begin{array}{c} \mathrm{NaCl} \\ (\mathrm{S}) \end{array} \left| \mathrm{Hg_2Cl_2, Hg} \right. \qquad \text{(Cell XIV)}$$

$$\text{Na-glass} \left| \begin{array}{c} \mathrm{NaCl} \\ (\mathrm{H_2O}) \end{array} \right| \begin{array}{c} \mathrm{KCl(sat.)} \\ (\mathrm{H_2O}) \end{array} \vdots \begin{array}{c} \mathrm{NaCl} \\ (\mathrm{S}) \end{array} \left| \text{Na-glass} \right. \qquad \text{(Cell XV)}$$

were studied at various concentrations of NaCl from saturated to 3×10^{-3} M. These potentials were measured with solutions at different percentages of methanol for solvent S.

Derivations of Equations for $E_{j\,solvent}$ in Cells XII-XV.

The e.m.f. of Cells XII and XIV are equal to:

$$E_{(Cell\ XII)} = E_{(Cell\ XIV)} = E_A - \frac{RT}{F} \log {}_m\gamma_{Cl} + E_j \qquad (71)$$

where $E_A = -\frac{RT}{F} \log \frac{a_2}{a_1}$ where a_1 and a_2 are the conventional activities of NaCl solutions in solvents S_1 and S_2, respectively. Similarly,

$$E_{(Cell\ XIII)} = E_{(Cell\ XV)} = E_A + \frac{RT}{F} \log {}_m\gamma_{Na} + E_j \qquad (72)$$

The liquid-junction potentials, E_j, in Cells XII and XIII are the same (same solutions, only different electrodes). Thus,

$$E_{j(Cell\ XII)} = E_{j(Cell\ XIII)} = -\frac{RT}{F}[t_{Na} \log {}_m\gamma_{Na} - t_{Cl} \log {}_m\gamma_{Cl}] + E_{j\,solvent} \qquad (73)$$

The sum of transport numbers of all ions in solution is equal to unity:

$$t_{Na} + t_{Cl} = 1 \qquad (74)$$

Thus,

$$t_{Na} = 1 - t_{Cl} \qquad (74a)$$

and

$$t_{Cl} = 1 - t_{Na} \qquad (74b)$$

Substituting Equation 74b into Equation 73 yields:

$$E_{j(\text{Cell XII})} = \frac{RT}{F}[t_{Na} \log {}_m\gamma_{NaCl} - \log {}_m\gamma_{Cl}] + E_{j\text{solvent}} \qquad (75)$$

Substituting Equation 75 into Equation 71 and rearranging terms yields an expression for $E_{j\text{solvent}}$ for Cell XII in terms of measurable quantities:

$$E_{j\text{solvent}(\text{Cell XII})} = E_{(\text{Cell XII})} + \frac{RT}{F} \log {}_m\gamma_{NaCl} - E_A \qquad (76)$$

Similarly, substituting Equation 74a into Equation 73 yields:

$$E_{j(\text{Cell XIII})} = [\frac{RT}{F} \log {}_m\gamma_{Na} - t_{Cl} \log {}_m\gamma_{NaCl}] + E_{j\text{solvent}} \qquad (77)$$

Substituting Equation 77 into Equation 72 and rearranging terms yields an expression for $E_{j\text{solvent}}$ for Cell XIII in terms of measurable quantities:

$$E_{j\text{solvent}(\text{Cell XIII})} = E_{(\text{Cell XIII})} - \frac{RT}{F} \log {}_m\gamma_{NaCl} - E_A \qquad (78)$$

For Cells XIV and XV, the liquid-junction potentials are equal to:

$$E_{j(\text{Cell XIV})} = E_{j(\text{Cell XV})} = \frac{RT}{F}[t_{Na} \log {}_m\gamma_{Na} - t_{Cl} \log {}_m\gamma_{Cl} + t_K \log {}_m\gamma_K] + E_{j\text{solvent}} \qquad (79)$$

The sum of transport numbers of the ions:

$$t_{Na} + t_{Cl} + t_{K} = 1 \tag{80}$$

Thus,

$$t_{Na} = 1 - t_{Cl} - t_{K} \tag{80a}$$

and

$$t_{Cl} = 1 - t_{Na} - t_{K} \tag{80b}$$

Substituting Equation 80b into Equation 79 yields:

$$E_{j(\text{Cell XIV})} = -\frac{RT}{F}[t_{Na} \log {}_{m}\gamma_{NaCl} + t_{K} \log {}_{m}\gamma_{KCl} - \log {}_{m}\gamma_{Cl}] + E_{j\text{solvent}} \tag{81}$$

Substituting Equation 81 into Equation 71 and rearranging terms yields:

$$E_{j\text{solvent}(\text{Cell XIV})} = E_{(\text{Cell XIV})} + \frac{RT}{F}[t_{Na} \log {}_{m}\gamma_{NaCl} + t_{K} \log {}_{m}\gamma_{KCl}] - E_{A} \tag{82}$$

At low concentrations of NaCl in comparison to the KCl concentration, t_{Na} can be considered negligible and Equation 81 reduces to:

$$E_{j\text{solvent}(\text{Cell XIV})} = E_{(\text{Cell XIV})} + \frac{RT}{F}[t_{K} \log {}_{m}\gamma_{KCl}] - E_{A} \tag{83}$$

Similarly, substituting Equation 80a into Equation 79 and recalling that:

$$\log {}_m\gamma_K - \log {}_m\gamma_{Na} = \log {}_m\gamma_{KCl} - \log {}_m\gamma_{NaCl} \qquad (84)$$

yields:

$$E_{j(\text{Cell XV})} = -\frac{RT}{F}[t_K(\log {}_m\gamma_{KCl} - \log {}_m\gamma_{NaCl}) - t_{Cl} \log {}_m\gamma_{NaCl} + \log {}_m\gamma_{Na}] + E_{j\text{solvent}} \qquad (85)$$

Substituting Equation 85 into Equation 72 and rearranging terms yields:

$$E_{j\text{solvent}(\text{Cell XV})} = E_{(\text{Cell XV})} - \frac{RT}{F}[t_K(\log {}_m\gamma_{KCl} - \log {}_m\gamma_{NaCl}) - t_{Cl} \log {}_m\gamma_{NaCl}] - E_A \qquad (86)$$

At low concentrations of NaCl, we can assume t_{Na} to be zero and $t_K = t_{Cl} = 0.5$ and Equation 86 reduces to:

$$E_{j\text{solvent}(\text{Cell XV})} = E_{(\text{Cell XV})} - \frac{RT}{F}[\log {}_m\gamma_{NaCl} - 0.5 \log {}_m\gamma_{KCl}] - E_A \qquad (87)$$

In review, Equations 76, 78, 82, and 86 evaluate $E_{j\text{solvent}}$ in Cell XII-XV in terms of the measured e.m.f. of these cells and other thermodynamic data.

Present Work in Evaluating $E_{j\text{solvent}}$.

$E_{j\text{solvent}}$ was calculated for Cell XII-XV by using the appropriate equation derived for each cell. Cell XII and XIII contain exactly the same solvent and electrolyte compositions except that calomel electrodes are used in Cell XII and sodium glass electrodes are used in Cell XIII. Thus, the value of $E_{j\text{solvent}}$ should be the same for these cells. Similarly, Cell XIV and XV differ only as to the electrodes used to measure the cell potential. Hence, $E_{j\text{solvent}}$ should be the same in Cell XIV and Cell XV.

Transfer activity coefficients for electrolytes, NaCl and KCl, in various methanol-water mixtures studied were calculated from literature data (52). These values are listed in Table 36 and plotted in Figures 5 and 6. Transference numbers for Na^+ and Cl^- ions used in the equations for $E_{j\text{solvent}}$ in Cells XII and XIII were assumed to be approximately equal based on literature data in methanol (53), so,

$$t_{Na} = t_{Cl} = 0.5 \qquad (88)$$

The transference of Na^+ ion was assumed to be negligible in Cells XIV and XV if the KCl/NaCl concentration ratio was more than a hundred to one, thus,

$$t_K = t_{Cl} = 0.5 \qquad (89)$$

Conventional salt-effect activities for all the unsaturated solutions were calculated by the Debye-Hückel equation. Debye-Hückel constants, A and B, for methanol-water solvents are listed in Appendix 2.

Measurements of the e.m.f. of Cells XII-XV were made between solutions of equal concentration in water and in the methanol-water solvent at concentrations of 3×10^{-2} M, 3×10^{-3} M and saturated NaCl. $E_{j\text{solvent}}$ was calculated using equations derived for each cell:

for Cell XII,

$$E_{j\text{solvent}} = E_{\text{cell}} + \frac{RT}{F} \log {}_m\gamma_{\text{NaCl}} - E_A \tag{76}$$

for Cell XIII,

$$E_{j\text{solvent}} = E_{\text{cell}} - \frac{RT}{F} \log {}_m\gamma_{\text{NaCl}} - E_A \tag{78}$$

for Cell XIV,

$$E_{j\text{solvent}} = E_{\text{cell}} + \frac{RT}{F}[t_K \log {}_m\gamma_{\text{KCl}}] - E_A \tag{83}$$

and for Cell XV,

$$E_{j\text{solvent}} = E_{\text{cell}} - \frac{RT}{F}[\log {}_m\gamma_{\text{NaCl}} - 0.5 \log {}_m\gamma_{\text{KCl}}] - E_A \tag{87}$$

Recalling that the free energies of saturated solutions of a solute in different solvents are equal, it follows that the potential of cells of the type of Cells XII and XIII should be zero. The reason why it is not zero is attributed to the existence of $E_{j\text{solvent}}$. Therefore, for Cells XII and

and XIII containing saturated solutions, we recall that

$$E_{jsolvent} = E_{cell} \tag{70}$$

as in the work of Murray and Aikens (51). Table 37 lists values for $E_{jsolvent}$ calculated from the above equations for each cell studied. The e.m.f. of Cells XII-XV containing saturated NaCl solutions are listed in Table 38.

As previously stated, the value of $E_{jsolvent}$ should be the same when calculated in Cells XII and XIII and, similarly, in Cells XIII and XIV, because the liquid-junction potential in each of these cases is between the same solutions. As can be seen from Table 37, there is excellent agreement (±3 mV) between $E_{jsolvent}$ values calculated from Cell XII and Cell XIII, with the best agreement at NaCl concentrations other than saturated (±2 mV). $E_{jsolvent}$ values calculated for Cells XIV and XV are in good agreement with each other (±5 mV) but poorer than for Cell XII-XIII, which may be attributed to our approximations of transport numbers in these cells.

In our previous study in dipolar aprotic solvents, $E_{jsolvent}$ was found to be significant for junctions between propylene carbonate and acetonitrile, dimethylformamide, and dimethylsulfoxide and negligible for junctions between the other solvents. This was attributed to propylene carbonate's dissimilarity with the other solvents in terms of their dielectric constants and dipole moments. As the percentage of methanol increases in the nonaqueous solvent in Cells

XII-XV, the solvent becomes less similar to that of the reference, water. For example, the dielectric constant of methanol-water solvents decreases with increasing methanol content. Figure 7 shows a plot of $E_{jsolvent}$ for 3×10^{-2} M NaCl solutions in Cells XII and XIII vs. wt. % methanol and Figure 8 plots $E_{jsolvent}$ for 3×10^{-2} M NaCl solutions in Cells XIV and XV. As can easily be seen from these plots, $E_{jsolvent}$ tends to increase with increasing wt. % methanol.

From Table 37, we can see that, as the concentration of NaCl decreases, $E_{jsolvent}$ generally increases. The value of $E_{jsolvent}$ for saturated solutions of NaCl is appreciably lower than values determined at the other concentrations studied. For example, for a junction between 90 wt. % methanol and water, $E_{jsolvent}$ for saturated NaCl solutions in Cell XII is 14 mV compared to 45 mV for solutions of 3×10^{-3} M NaCl. Similarly, an $E_{jsolvent}$ value of 57.8 mV for a junction between 2×10^{-5} mole fraction NaCl solutions in water and 87.68 wt. % methanol was calculated from experimental measurements of Alfenaar, et. al. (22), using a value of log ${}_{m}\gamma_{NaCl}$ from Reference 52. Although this measurement was made at 87.68 wt. % methanol rather than at 90% methanol, it seems to indicate a trend toward larger values of $E_{jsolvent}$ with decreasing concentration of NaCl. The dependence of $E_{jsolvent}$ on the concentration of the charge-carrying species was also observed by Murray and Aikens (51). Reasons as to why $E_{jsolvent}$ should vary with concentration are open to conjecture.

For liquid-junctions between aqueous solutions, the liquid-junction potential, E_j, has been decreased experimentally by including concentrated (relative to the other ions present) salt bridges containing ions of equal mobility between the two half cells. Although the E_j for junctions between two dissimilar solvents cannot be simply suppressed by addition of a salt bridge due to the dependence of E_j' on the transfer activity coefficients of all the ions in solution, it is of interest to see the effect of the addition of a concentrated aqueous KCl salt bridge between NaCl solutions in water and methanol-water solvents. In addition, most pa_H measurements in alcohol-water media make use of a calomel electrode containing a saturated aqueous solution of KCl as salt bridge electrolyte (54).

The e.m.f.'s of Cells XII-XV are determined by the same NaCl solutions except that Cell XIV and XV contain saturated aqueous KCl solutions as salt bridges. As can easily be seen from Table 37, without exception, the values of $E_{jsolvent}$ in Cells XIV and XV (with salt bridges) are appreciably lower than those in the cells without the salt bridge present. This may, in part, be due to the dependence of $E_{jsolvent}$ on the concentration of the ionic species in solution, which we discussed earlier. $E_{jsolvent}$ tends to be smaller at high concentration of the current-carrying ions in solution.

To summarize, $E_{jsolvent}$ was calculated independently for two different cells with a junction between the same solutions but with different pairs of indicator electrodes. The values of $E_{jsolvent}$ were within good-to-excellent agreement with each other. $E_{jsolvent}$ values between aqueous and methanol-water solvents were found to increase with increasing methanol content (increasing dissimilarity of the solvents). $E_{jsolvent}$ showed inverse dependence on the concentration of the charge-carrying species in solution. In addition, values of $E_{jsolvent}$ were lowered by addition of saturated aqueous KCl salt bridges between the NaCl solutions.

Table 36

Transfer Activity Coefficients of NaCl and KCl in Methanol-Water Solvents (Water reference-molar scale) (52).

Wt. % Methanol	log ${}_m\gamma_{NaCl}$	log ${}_m\gamma_{KCl}$
100	3.81	3.87
90	3.37	3.64
80	2.91	3.06
70	2.48	2.55
60	2.05	2.10
50	1.70	1.70
40	1.31	1.32
30	0.97	0.97
20	0.65	0.64
10	0.32	0.31
0	0.00	0.00

Figure 5

Transfer Activity Coefficients of NaCl in Methanol-Water Solvents (molar scale)

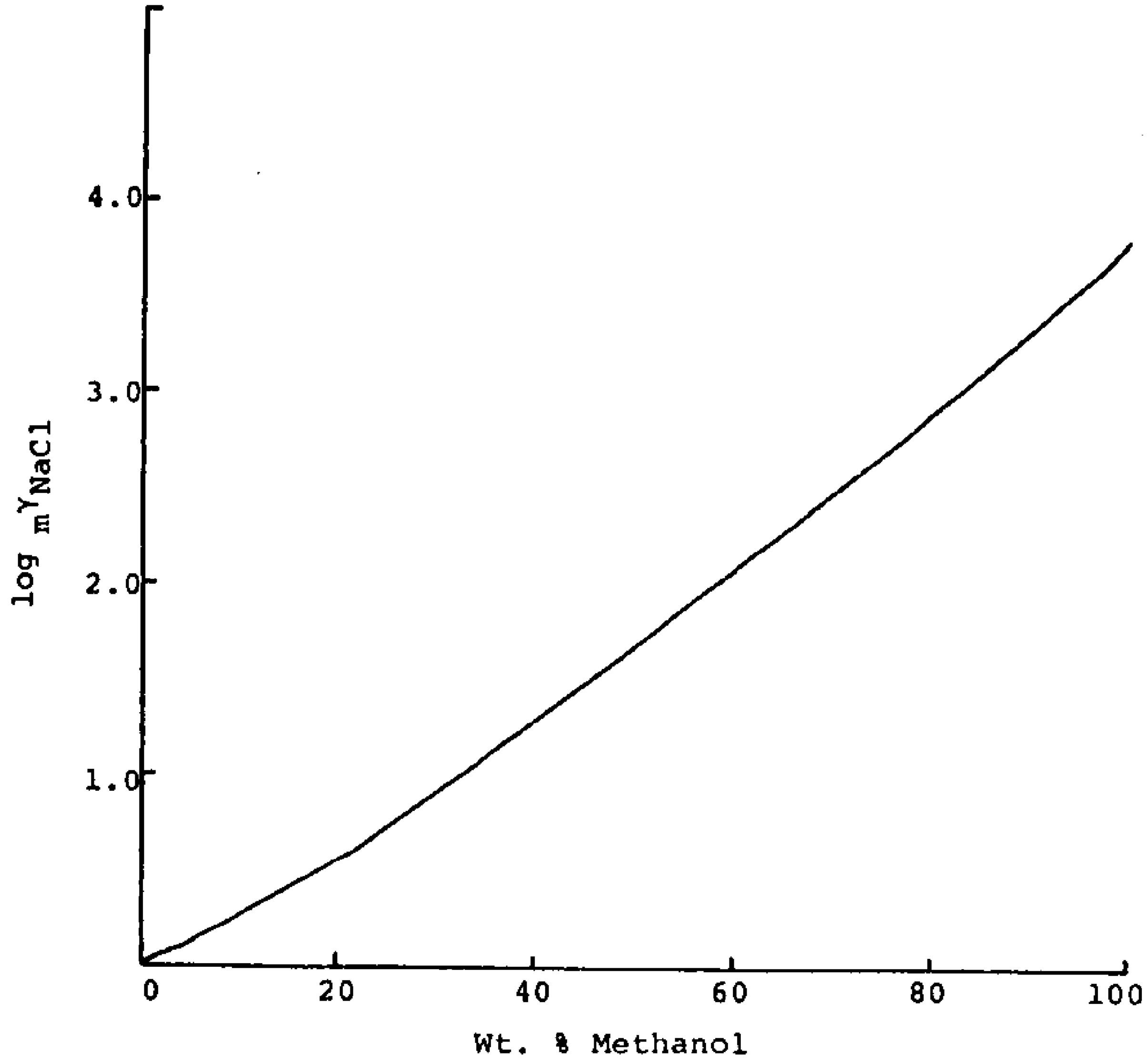


Figure 6

Transfer Activity Coefficients of KCl in Methanol-Water Solvents (molar scale)

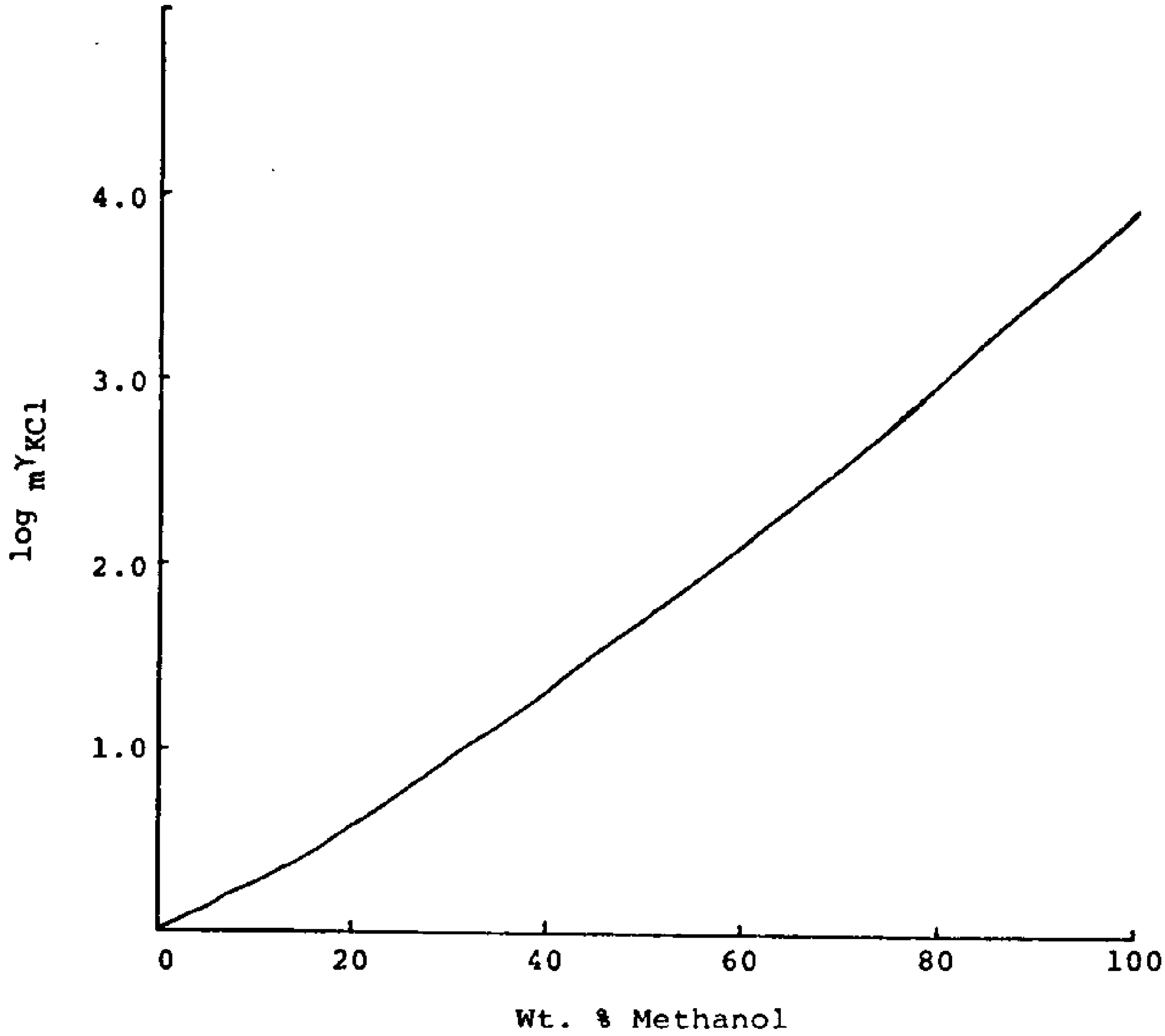


Table 37

Calculated $E_{j\ solvent}$ Values for Cell XII-XV.

$E_{j\ solvent}$

90% MeOH

Approximate NaCl Conc.	Cell XII	Cell XIII	Cell XIV	Cell XV
sat.	14	18		
3×10^{-2}	40±1	37±2	23±2	16±3
3×10^{-3}	45±1	45±2	28±5	24±5

80% MeOH

Approximate NaCl Conc.	Cell XII	Cell XIII	Cell XIV	Cell XV
sat.	7	12		
3×10^{-2}	32±0	30±4	14±1	14±1
3×10^{-3}	39±2	36±2	15±1	20±1

70% MeOH

Approximate NaCl Conc.	Cell XII	Cell XIII	Cell XIV	Cell XV
sat.	7	11		
3×10^{-2}	26±1	26±3	10±2	11±1
3×10^{-3}	32±1	32±1	5±1	17±1

50% MeOH

Approximate NaCl Conc.	Cell XII	Cell XIII	Cell XIV	Cell XV
sat.	2	7		
3×10^{-2}	21±0	23±1	7±2	11±2
3×10^{-3}	20±4	26±1	5±2	13±2

Figure 7

$E_{j\ solvent}$ of Cells XII-XIII in Methanol-Water Solvents

(3 x 10^{-2} M NaCl)

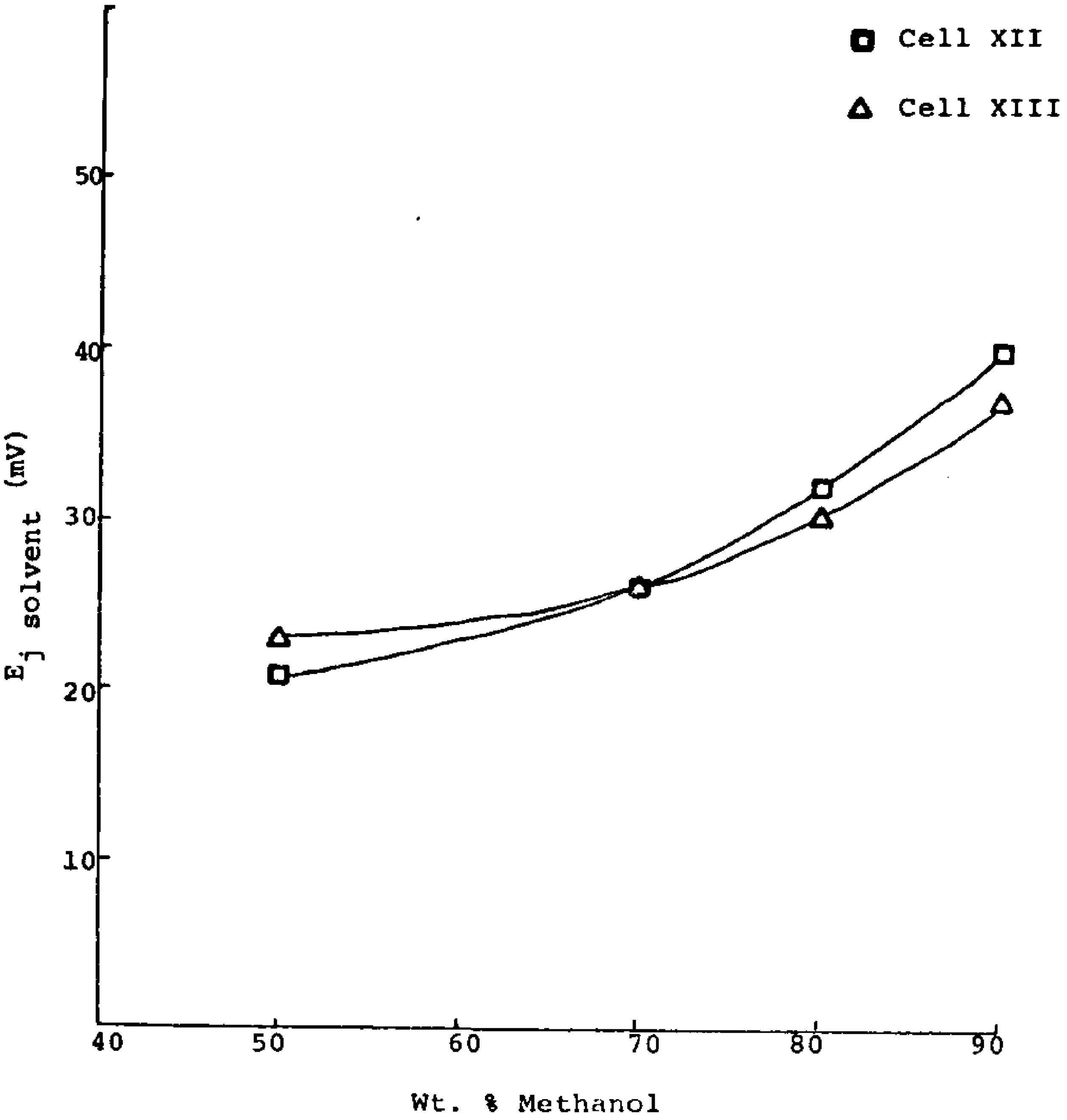


Figure 8

$E_{j\ solvent}$ of Cells XIV-XV in Methanol-Water Solvents

(3×10^{-2} M NaCl)

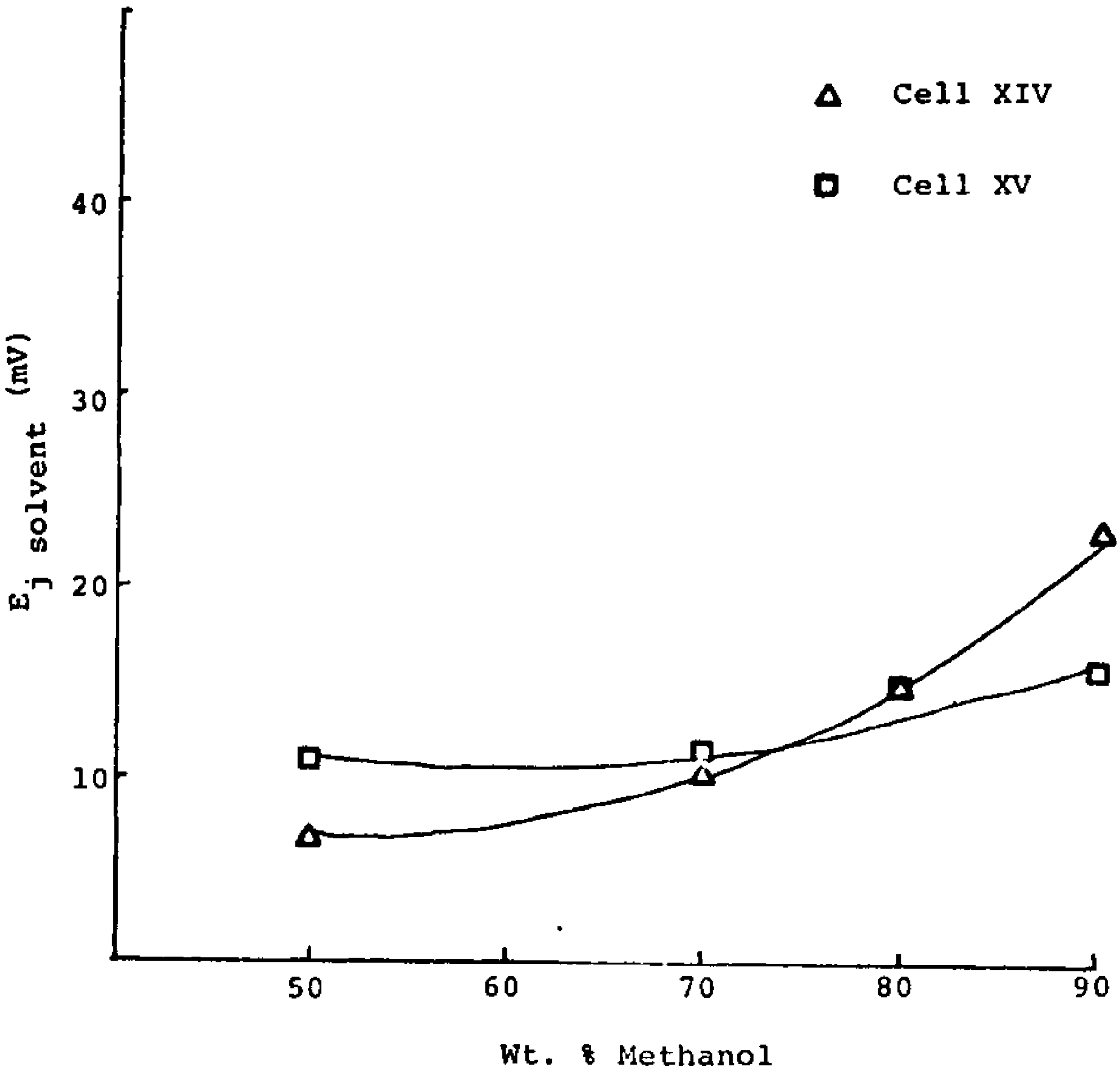


Table 38

E.m.f. of Cell XII-XV for Saturated NaCl Solutions in Water and Methanol-Water Solvents.

	E.m.f. (mV)			
Wt. % MeOH	Cell XII	Cell XIII	Cell XIV	Cell XV
90	14	18	8	16
80	7	12	10	13
70	7	11	2	7
50	2	7	7	8

Measurements Using pH-Cells in Alcohol-Water Media.

The normal operation of a pH cell (Cell XVI)

$$\mathrm{Hg, Hg_2Cl_2(s)} \,\Big|\, \mathrm{KCl(conc\ \ aq)} \,\Big|\, \mathrm{Buffer} \,\Big|\, \mathrm{H\text{-}electrode} \qquad \text{(Cell XVI)}$$

involves the standardization of the electrodes with buffers of known pa_H and, then, comparing the potential difference in the unknown solution to that of the standard with the assumption that the liquid-junction potential is the same in the unknown solution as in the standard buffer. This works well for aqueous solutions. However, if we measure the e.m.f. of a nonaqueous buffer in Cell XVI and standardize the electrodes with aqueous buffers, the pa_H will be:

$$pa_H = pa_H^* - \log {}_m\gamma_H + E_j \qquad (90)$$

where pa_H and pa_H^* refer to the aqueous and nonaqueous conventional activities, respectively.

Bates, Paabo and Robinson (54), in their studies of Cell XVI, determined values of δ defined as:

$$\delta \equiv E_j - \log {}_m\gamma_H \qquad (91)$$

for dilute buffer solutions in ethanol-water and methanol-water solvents in contact with 3.5 M aqueous KCl. Popovych, Gibofsky and Berne (11) calculated the liquid-junction potential, E_j, by adding values of $\log {}_m\gamma_H$ based on the Ph_4AsBPh_4 assumption to the δ's determined by Bates, et. al.

(54). These values of E_j and log ${}_m\gamma_H$ are listed in Table 39. Similarly, values of E_j in Cell XVI can be calculated for junctions between buffers in methanol-water solvents and concentrated KCl by using values of log ${}_m\gamma_H$ (55) based on the tetraphenylborate assumption. Values of E_j and log ${}_m\gamma_H$ for methanol-water solvents are listed in Table 40.

The liquid-junction potential can be written as:

$$E_j = E_j' + E_{j\text{solvent}} \tag{38}$$

Thus, if the value of E_j' is known, $E_{j\text{solvent}}$ can be obtained:

$$E_{j\text{solvent}} = E_j - E_j' \tag{38a}$$

Since, in Cell XVI, the concentration of KCl is at least one-hundred times greater than the concentration of the ions in the buffer solutions, the contributions of the buffer ions to the liquid-junction potential can be considered negligible. Thus, E_j' can be approximated by:

$$E_j' = -\frac{1}{F}[t_K \log {}_m\gamma_K - t_{Cl} \log {}_m\gamma_{Cl}] \tag{92}$$

Values of the transfer activity coefficients for K^+ and Cl^- ions based on the Ph_4AsBPh_4 assumption were used to calculate E_j' in ethanol-water solvents (11) and in methanol-water solvents (55) and are listed in Tables 39 and 40, respectively. E_j' and $E_{j\text{solvent}}$ for Cell XVI are listed in Table 39 for ethanol-water solvents and Table 40 for methanol-water solvents. Figure 9 shows values of E_j' vs. wt. % ethanol and Figure 10 displays variation of E_j' vs. wt. % methanol.

Values of $E_{j\ solvent}$ vs. wt. % ethanol are plotted in Figure 11. A good correlation exists between the $E_{j\ solvent}$ values from the work of Bates, et. al. (54) and those calculated from Cells XIV-XV for 3×10^{-2} M NaCl solutions in water and methanol-water solvents with saturated KCl as salt bridge. This can be seen in Figure 12. Values of $E_{j\ solvent}$ for junctions between concentrated aqueous KCl and dilute solutions of ions in methanol-water solvents may be approximated from Figure 12.

Table 39

Values of δ, E_j, E_j', $E_{j\ \mathrm{solvent}}$, and Transfer Activity Coefficients of K^+, H^+, and Cl^- Ions in Ethanol-Water Solvents.

Wt. % EtOH	(a) δ(53) (pH units)	(interpolated) $\log {}_m\gamma_H$ (11)	(b) E_j (mV)	(interpolated) $\log {}_m\gamma_K$	(interpolated) $\log {}_m\gamma_{Cl}$	E_j' (mV)	E_j solvent (mV)
0.0	0.000	0.00	0	0.00	0.00	0	0
16.2	0.003	0.08	-5	0.34	0.16	-5	0
33.2	0.086	-0.12	2	0.46	0.56	3	-1
52.0	0.221	-0.68	27	0.67	1.28	18	9
73.4	0.196	-0.83	37	1.12	2.10	29	8
85.4	-0.032	-0.53	33	1.70	2.60	27	6
100.0	-2.91	1.68	73	2.67	3.45	23	50

(a) $\delta \equiv E_j - \log {}_m\gamma_H$

(b) sign changed to conform to H_2O reference

Table 40

Values of δ, E_j, E'_j, $E_{j\ \text{solvent}}$, and Transfer Activity Coefficients of K^+, H^+, and Cl^- Ions in Methanol-Water Solvents.

Wt. % MeOH	(a) δ (53) (pH units)	(interpolated) $\log {}_m\gamma_H$ (11)	(b) E_j (mV)	(interpolated) $\log {}_m\gamma_K$	(interpolated) $\log {}_m\gamma_{Cl}$	E'_j (mV)	E_j solvent (mV)
0.0	0.000	0.00	0	0.00	0.00	0	0
8.1	0.002	0.02	1	0.18	0.08	3	2
16.3	0.004	0.06	4	0.38	0.12	8	4
33.3	0.051	0.06	7	0.74	0.31	13	6
52.1	0.130	0.12	1	1.02	0.67	12	11
68.1	0.121	0.16	-2	1.29	1.06	7	9

(a) $\delta \equiv E_j - \log {}_m\gamma_H$

(b) sign changed to conform to H_2O reference

Figure 9

E_j' of Cell XVI in Ethanol-Water Solvents

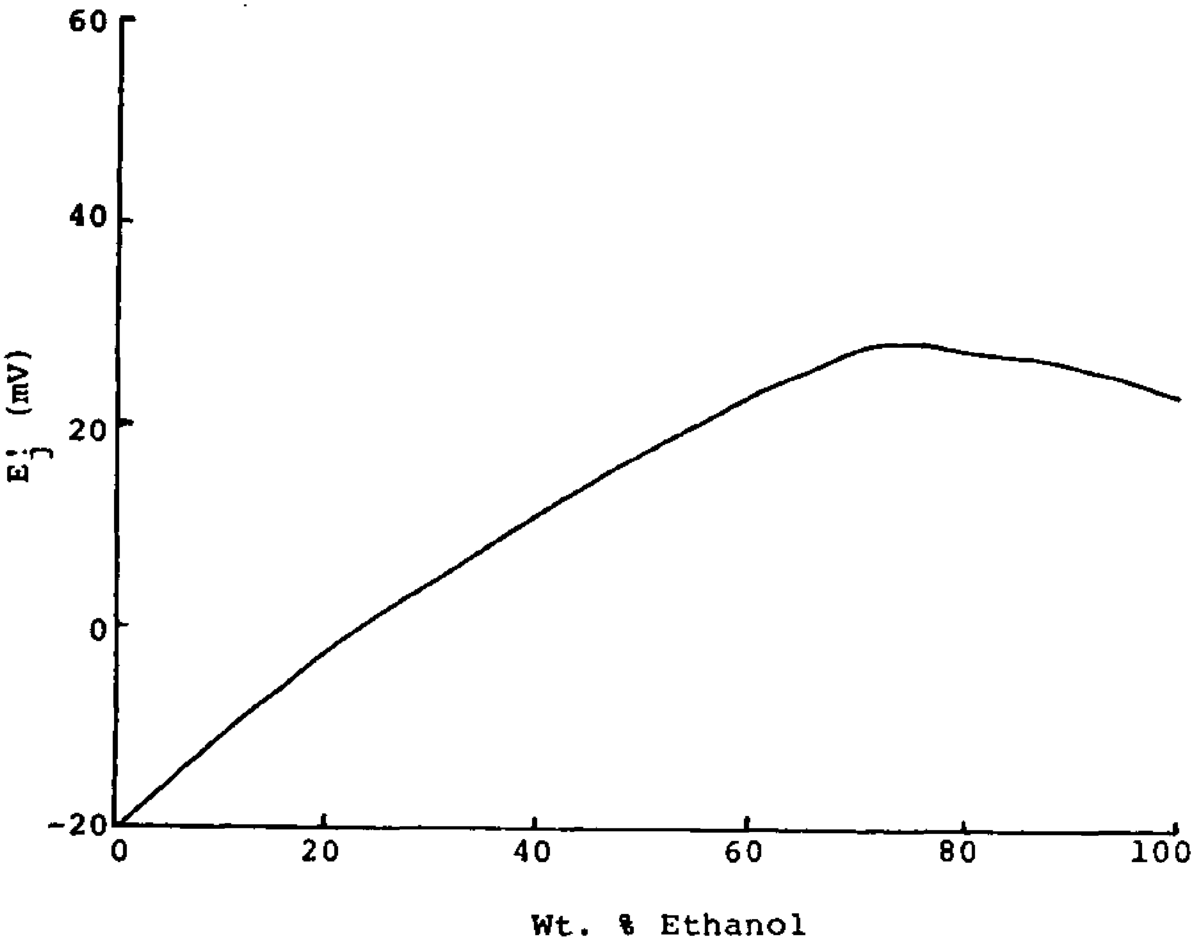


Figure 10

E_j' of Cell XVI in Methanol-Water Solvents

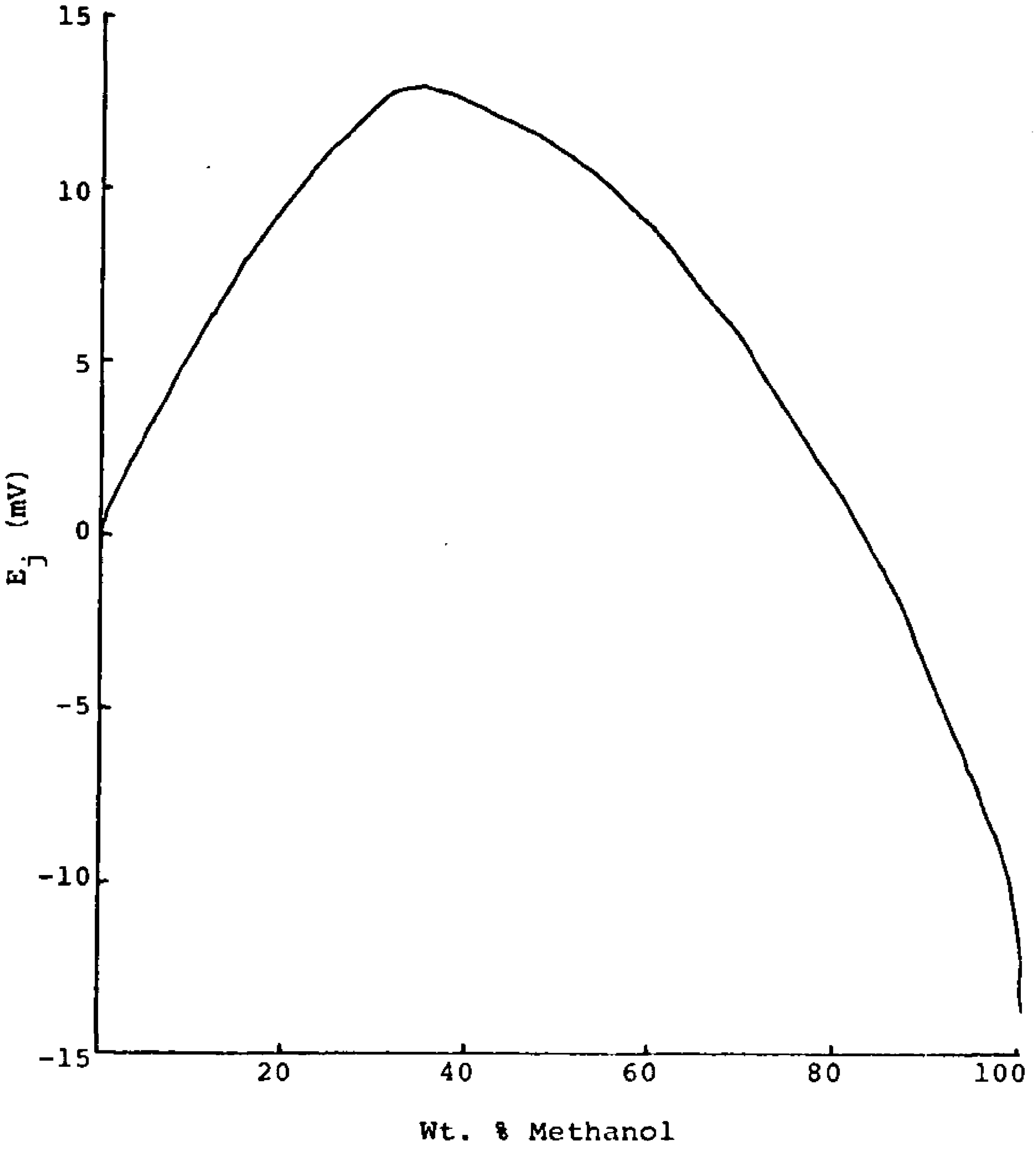


Figure 11

$E_{j\ solvent}$ in Cell XVI in Ethanol-Water Solvents

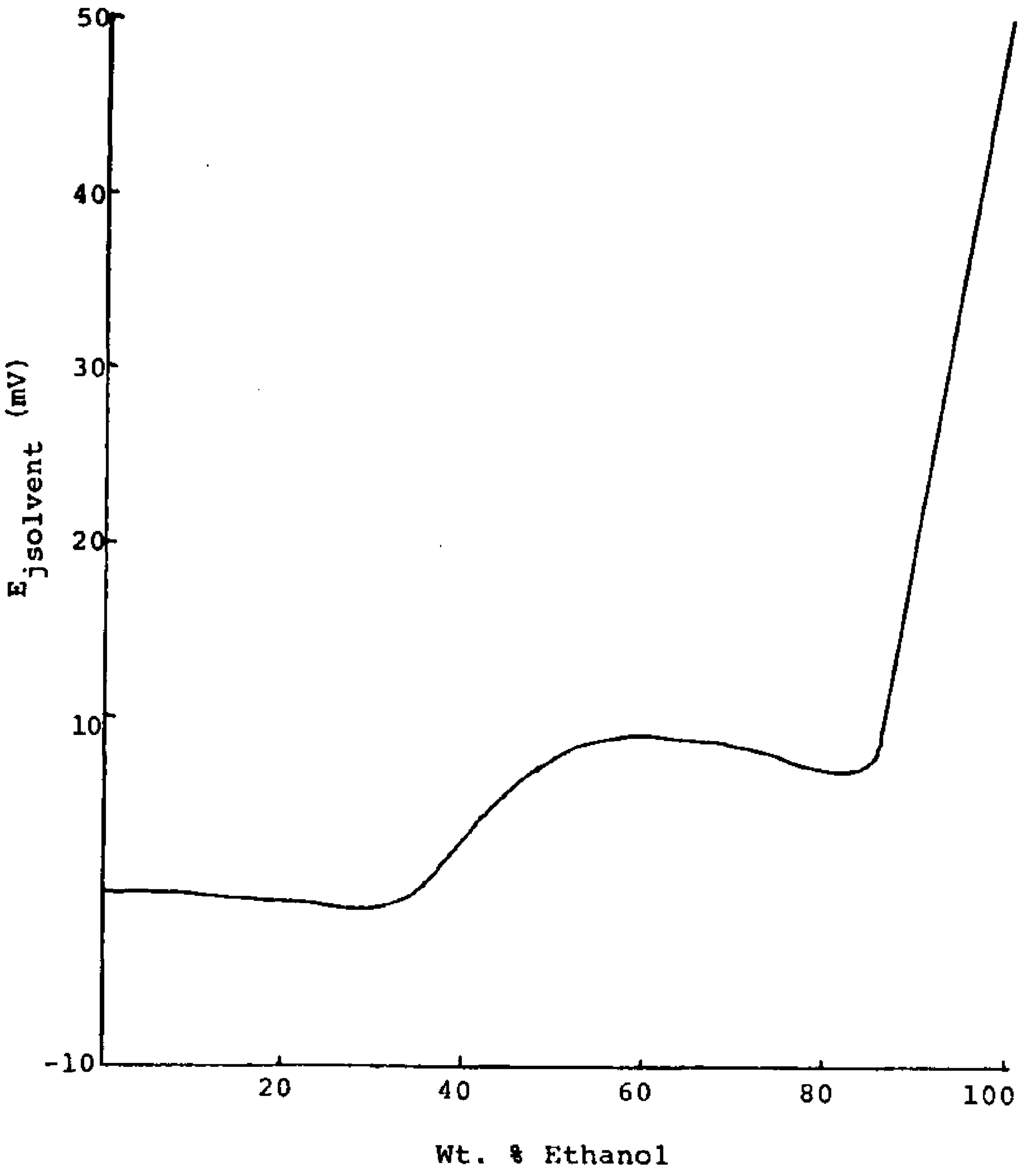
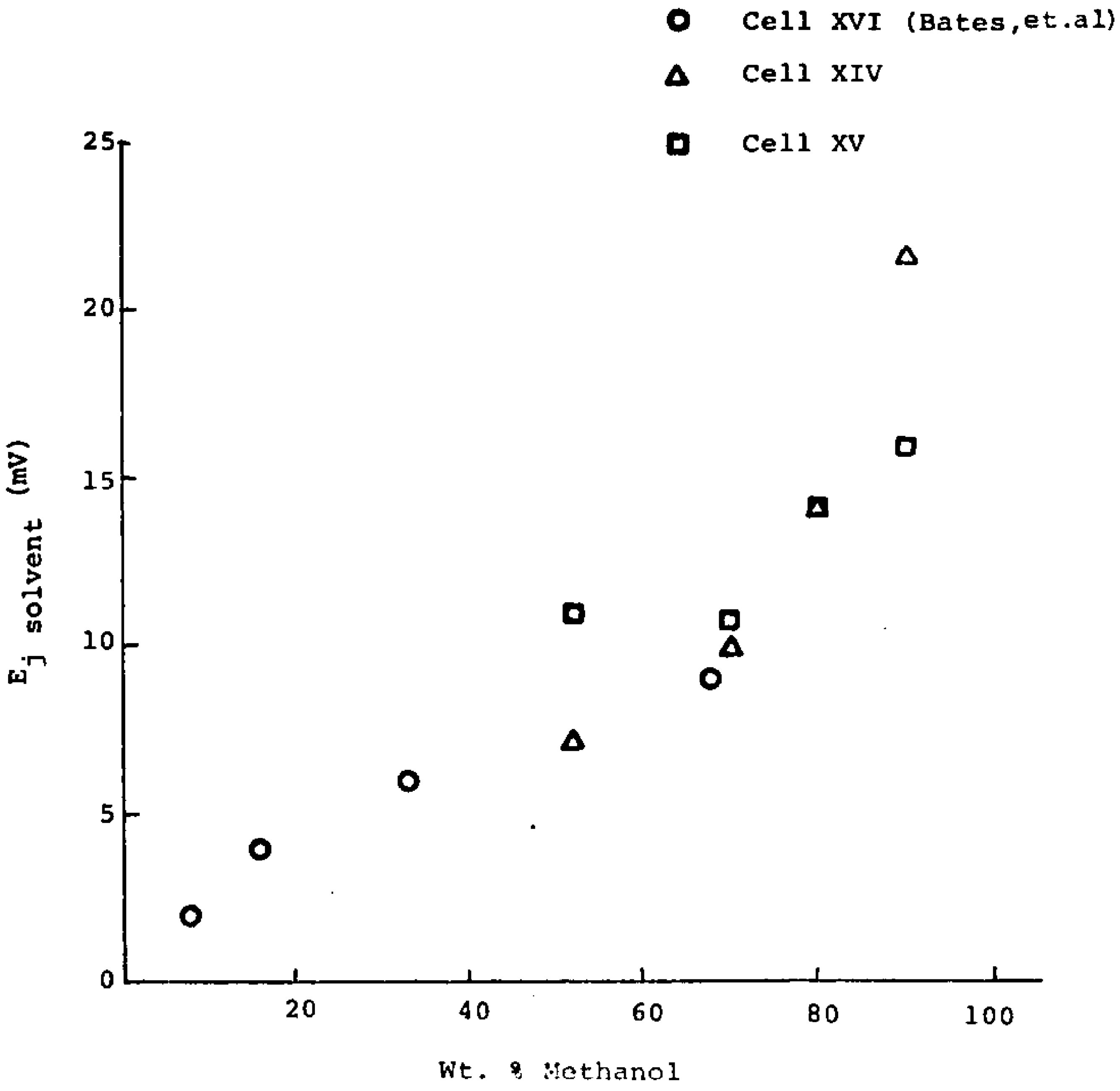


Figure 12

$E_{j\ solvent}$ in Cells XIV-XVI in Methanol Water Solvents



Iterative Methods for the Determination of Transfer Activity Coefficients of Single Ions.

As we have discussed previously, it is possible to calculate transfer activity coefficients of single ions from the e.m.f. of cells with junctions between different solvents if the liquid-junction potential is known.

Consider Cell XVII,

$$\text{H-electrode}\left|\begin{matrix}\text{HCl}\\ H_2O\end{matrix}\right|\begin{matrix}\text{KCl(conc)}\\ H_2O\end{matrix}\left|\begin{matrix}\text{HCl}\\ \text{S}\end{matrix}\right|\text{H-electrode}$$

(Cell XVII)

The transfer activity coefficients of the hydrogen ions are obtained from:

$$\log {}_m\gamma_H = \frac{(E_{cell} - E_j)}{59.16} \qquad \text{at } 25.0° \text{ C} \qquad (93)$$

The liquid-junction potential, E_j, is calculated from:

$$E_j = -\ 59.16[t_H \log {}_m\gamma_H - t_{Cl} \log {}_m\gamma_{Cl} + t_K \log {}_m\gamma_K] + E_{jsolvent} \qquad (94)$$

Since the concentration of KCl in the salt bridge is much greater than the HCl concentration, t_H can be assumed to be negligible and $t_K = t_{Cl} = 0.5$, yielding

$$E_j = -\ 59.16[.5 \log {}_m\gamma_K - .5 \log {}_m\gamma_{Cl}] + E_{jsolvent} \qquad (95)$$

By substituting values of the transfer activity coefficients of the K^+ and Cl^- ions based on the Ph_4AsBPh_4 assumption and approximating the value of $E_{j\,solvent}$, the liquid-junction potential can be calculated. Substituting the E_j and e.m.f. of the cell into Equation 93 yields the transfer activity coefficient of the hydrogen ion.

In the early stages of this work, it was thought that better values of transfer activity coefficients for single ions could be obtained by a series of iterations. Recalling that

$$\log {}_m\gamma_{Cl} = \log {}_m\gamma_{HCl} - \log {}_m\gamma_H \tag{96a}$$

and

$$\log {}_m\gamma_K = \log {}_m\gamma_{KCl} - \log {}_m\gamma_{Cl} \tag{96b}$$

new "corrected" values of log ${}_m\gamma_{Cl}$ and log ${}_m\gamma_K$ can be obtained by substituting a new value for log ${}_m\gamma_H$ (not necessarily that based on the Ph_4AsBPh_4 assumption). These new "corrected" values for log ${}_m\gamma_{Cl}$ and log ${}_m\gamma_K$ would be substituted into Equation 95, yielding a new estimate of the liquid-junction potential. E_j would then be resubstituted into Equation 93 and log ${}_m\gamma_H$ re-evaluated. This process would be repeated until the values of the transfer activity coefficients converged.

However, this plan proved impractical because of the nature of transfer activity coefficients and of the E_j equation. Since transfer activity coefficients of electrolytes are constant values and

$$\log {}_m\gamma_{\text{cation}} + \log {}_m\gamma_{\text{anion}} = \log {}_m\gamma_{\text{electrolyte}} \qquad (97)$$

any increase in the value of log ${}_m\gamma_{\text{cation}}$ must be matched by a corresponding decrease in the value of log ${}_m\gamma_{\text{anion}}$. Thus, if log ${}_m\gamma_H$ is increased by 1.0 log ${}_m\gamma$ units, log ${}_m\gamma_{Cl}$ must decrease by a corresponding 1.0 log ${}_m\gamma$ units. In addition, values of transfer activity coefficients for all other cations must increase by 1.0 units and values for all other anions must decrease by 1.0 units:

$$\log {}_m\gamma_M = \log {}_m\gamma_{MCl} - \log {}_m\gamma_{Cl} \qquad (98a)$$

$$\log {}_m\gamma_X = \log {}_m\gamma_{HX} - \log {}_m\gamma_H \qquad (98b)$$

Thus, log ${}_m\gamma_K$ will increase by 1.0 log ${}_m\gamma$ units.

With this in mind, if we substitute the new values of log ${}_m\gamma_K$ and log ${}_m\gamma_{Cl}$ into Equation 95, the bracketed term will increase by 1.0 log ${}_m\gamma$ units and E_j will decrease by 59.16 mV (1.0 log ${}_m\gamma$ units). When the new E_j is substituted into Equation 93, it, in turn, causes log ${}_m\gamma_H$ to increase, restarting the cycle. The value of log ${}_m\gamma_H$ will change unidirectionally with every iteration and no convergence will occur.

While this kind of iteration for the purpose of obtaining convergence of transfer activity coefficients and E_j values proved impossible, it is possible to use such a process to make a single correction in the values of the transfer activity coefficient of the measured ion. Consider

Oiwa's cell (Cell IV)

$$\begin{array}{l|c|c|l} \mathrm{Pt,\ H_2(g)} & \mathrm{HCl} & \mathrm{KCl(sat.\ aq.)} & \mathrm{Hg_2Cl_2(s),\ Hg} \\ & \mathrm{MeOH{-}H_2O} & & \end{array}$$

(Cell IV)

If we subtract the e.m.f. of Cell IV from the e.m.f. of the same cell where $C_{MeOH} = 0$, it would be equivalent to measuring the e.m.f. of Cell XVII:

$$\begin{array}{l|c|c|c|l} \mathrm{H\text{-}electrode} & \mathrm{HCl} & \mathrm{KCl(sat.\ aq.)} & \mathrm{HCl} & \mathrm{H\text{-}electrode} \\ & \mathrm{(H_2O)} & & \mathrm{S} & \end{array}$$

(Cell XVII)

The E_j of Cell XVII can be calculated from Equation 95 with the value of $E_{j\ solvent}$ approximated from Figure 12 (previous section). Values of transfer activity coefficients of single ions (55) based on the Ph_4AsBPh_4 assumption are used to calculate E_j. The E_j is then substituted into Equation 93 to calculate new values of log ${}_m\gamma_H$. Values of E_j', $E_{j\ solvent}$, E_{cell}, and transfer activity coefficients of single ions as well as the "new" values of log ${}_m\gamma_H$ are listed in Table 41 at different wt. % methanol.

Table 41

Values of E_j', $E_{j\ solvent}$, E(Cell XVII) and Transfer Activity Coefficients Used in Iterations of log ${}_m\gamma_H$.

90% MeOH

E(Cell XVII) = 18.5

log ${}_m\gamma_{KCl}$ = 3.45

E_j' (Equation 94) = 9 mV

log ${}_m\gamma_{HCl}$ = 1.83

$E_{j\ solvent}$(Figure 12) = 22 mV

	Initial Values	Iterated Values
log ${}_m\gamma_H$	-0.02	-0.20
log ${}_m\gamma_{Cl}$	1.87	2.05
log ${}_m\gamma_K$	1.58	1.40

60% MeOH

E(Cell XVII) = -11.7 mV

log ${}_m\gamma_{KCl}$ = 2.00

E_j' (Equation 94) = -9 mV

log ${}_m\gamma_{HCl}$ = 0.69

$E_{j\ solvent}$(Figure 12) = 10 mV

	Initial Values	Iterated Values
log ${}_m\gamma_H$	-0.15	-0.21
log ${}_m\gamma_{Cl}$	0.85	0.90
log ${}_m\gamma_K$	1.15	1.10

Table 41 (continued)

40% MeOH

$E(\text{Cell XVII}) = -7.1$ mV

$\log {}_m\gamma_{KCl} = 1.26$

E_j' (Equation 94) $= -12$ mV

$\log {}_m\gamma_{HCl} = 0.43$

$E_{j\ \text{solvent}}$ (Figure 12) $= 8$ mV

	Initial Values	Iterated Values
$\log {}_m\gamma_H$	0.02	0.19
$\log {}_m\gamma_{Cl}$	0.42	0.24
$\log {}_m\gamma_K$	0.84	1.02

Recommendations for Future Studies.

Further studies of e.m.f. cells with liquid junctions between different solvents would increase our understanding of the nature of liquid-junction potentials in these cells. Knowledge of transfer activity coefficients for salt-bridge ions in dipolar aprotic solvents (e.g., NMF) would help us determine log $_m\gamma$ values for ions of interest, using these cells. Transfer activity coefficients of ions unattainable by other methods (similar to the previous studies with TAB^+ and Pi^- ions) can be obtained. Studies of e.m.f. cells without salt bridges between solutions of electroactive ions in different solvent media would also be of interest.

Additional studies of the dependence of $E_{j\ solvent}$ on the physico-chemical properties (dielectric constant, dipole moment, polarizability, hydrogen bonding, etc.) of the solvents in the cell would help us elucidate the nature of this term. For example, studies of cells containing dissimilar solvents, e.g., formamide (very high dielectric constant) and DMF (low dielectric constant), and similar solvents might help us develop a better theory of explaining the $E_{j\ solvent}$ term. Methods of prediction of when $E_{j\ solvent}$ can be considered a negligible contribution to E_j need to be found. The significance of this research is dependent on possible errors in the value of E_j and on the propagation of these errors in subsequent calculations.

Measurements of cells containing solutions of ions of unequal transference and solvation numbers and of different polarizabilities (e.g., potassium, nitrate, bromide, and iodide) should be carried out to test further the validity of our equations. Commercial ion-selective electrodes are available to perform these measurements. An explanation of the inverse relationship of the value of $E_{j\ solvent}$ with the concentration of ions present in solution is needed. It would be of great value if one could develop a method for measuring or calculating $E_{j\ solvent}$ which would not depend on e.m.f. measurements of cells with liquid junction, of which $E_{j\ solvent}$ is a component. Analysis of the solvent composition at the interphase region between the two solvents by chromatography or refractometry could, possibly, be used.

Appendix 1

Densities of Methanol-Water Solvents at 25°C (24).

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 2

Debye-Hückel Coefficients for Various Solvents at 25°C (molar scale) (24, 49).

Solvent	A	B
DMF	1.59	.481
DMSO	1.11	.439
MeCN	1.64	.486
PC	.686	.363
NMF	.144	.215
100% MeOH	1.90	.509
90% MeOH	1.52	.473
80% MeOH	1.28	.446
70% MeOH	1.10	.424
60% MeOH	.956	.405
50% MeOH	.839	.388
H_2O	.509	.329

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