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Electrochemical studies of nonaqueous solutions

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ELECTROCHEMICAL STUDIES OF NONAQUEOUS SOLUTIONS

by

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Abstract

Electrochemical studies of Nonaqueous Solutions

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The liquid-junction potential, E_j, in cells with junctions between two solvents is attributed to the transport of solvated ions across the solvent-solvent interface. The E_j is formally divided into $E_{j,ion}$ and $E_{j,s}$ components, which account, respectively, for the transport of the ions and the solvent molecules across the interface. The $E_{j,ion}$ values between electrolyte solutions in water and methanol-water (MeOH/H_2O), ethanol-water (EtOH/H_2O), acetonitrile-water (AN/H_2O), dimethylformamide-water (DMF/H_2O) and dimethylsulfoxide-water (DMSO/H_2O) solvent systems were calculated using both the old equation from the literature and a new formulation developed in our laboratory by Anna Berne [4]. The new formulation for $E_{j,ion}$ accounts for the variation of the transport numbers and the chemical potentials of the ions crossing the boundary with the solvent composition across the diffusion layer.

Conductance measurements were carried out in methanol-water mixtures to obtain the limiting equivalent conductance of sodium chloride. Using these data and available literature values, the limiting transport numbers of sodium, chloride and hydrogen ions were calculated for NaCl and HCl solutions over the entire range of methanol-water solvents.

Transfer activity coefficients for the nitrate ion in acetonitrile-water mixtures, required for the E_j calculation, were determined by

using the solubility method and from the e.m.f. of cells with liquid junction.

Comparison of the $E_{j,ion}$ calculations from both the old equation and the new equation were carried out for the above systems. For HCl in MeOH-water, EtOH-water, DMF-water and DMSO-water and for $AgNO_3$ in AN-water solvent systems, large differences in the $E_{j,ion}$ values between the old and the new equations were observed because of the transport numbers and transfer activity coefficients of ions go through a very pronounced minimum or a maximum. The difference in $E_{j,ion}$ values were appreciable for the solvent compositions where a maximum or a minimum was observed for the transfer activity coefficients or transport numbers.

$E_{j,s}$ has been described in general terms as that components of E_j which is determined by the passage of solvent molecules rather than ions, across the junction. The term $E_{j,s}$ depends on the two solvents forming the junction, but there is no formula from which it can be calculated. Here, the $E_{j,s}$ was estimated from the experimental e.m.f.'s of cells with liquid junction between pairs of solutions mentioned above and the calculated $E_{j,ion}$. The $E_{j,s}$ values were higher than the $E_{j,ion}$ values for the dipolar aprotic systems, whereas the reverse was true for the protic systems.

To my parents and brothers.

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Table of Contents

List of Tables

List of Figures

INTRODUCTION

Presentation of the Problem.

Introduction.

Electrochemical cells with liquid junctions between different solvents have found wide application both in practical electroanalytical measurements and in theoretical studies of ion-solvent interactions.

Anyone who has had occasion to determine electrometric pH values, or perform potentiometric titrations or voltammetric measurements in nonaqueous or mixed solvents, most likely has used a liquid junction between the test solution of nonaqueous media and a concentrated aqueous KCl solution as a salt bridge. At the boundaries of two aqueous electrolyte solutions, a saturated aqueous KCl salt bridge solution is known to minimize or even render negligible the liquid-junction potentials, E_j. However, this is not generally true for the interfaces of KCl with nonaqueous solutions, including mixed solutions. The E_j values are now known to attain the order of magnitude of 100 mV at aqueous/nonaqueous interfaces, thus introducing large and often unknown errors in the ionic activities and the measured potentials determined on their basis. Similarly, it is recognized that appreciable E_j values often arise at the interface of two nonaqueous solutions as well. As a result, it has become imperative to study and evaluate all the factors that determine the magnitude of E_j at the interface of electrolyte solutions in different solvent media, in order to make the E_j corrections in electrochemical data, or to tailor-make salt bridges that would tend to minimize the Ej.

The main objective of this study was to test a new equation for

the E_j at the junction of electrolyte solutions in different media. Interpretation of the E_j between aqueous solutions and those in methanol-water ($MeOH/H_2O$), ethanol-water ($EtOH/H_2O$), acetonitrile-water (AN/H_2O), dimethylformamide-water (DMF/H_2O) and dimethylsulfoxide-water ($DMSO/H_2O$) media were the objectives for this study. Literature data required for my calculations were used whenever possible, but additional experimental work was also performed.

Another objective of this research was to determine the transfer activity coefficient of the nitrate ion, in order to calculate the $E_{j,ion}$ for $AgNO_3$ junctions in acetonitrile-water solvents.

In addition, calculations were carried out to determine $E_{j,s}$, the solvent contribution to the liquid-junction potential. The $E_{j,s}$ can be estimated for junctions between water and the above mixed solvents by combining the measured e.m.f. of cells with liquid junctions and the calculated values of the $E_{j,ion}$.

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

Types of E.M.F. Cells.

Generally in this work, two types of cells with liquid junction are used: (I) without a salt bridge, and (II) with a salt bridge. The first type of cell consists of two identical electrodes, reversible to either a cation M^+, or an anion X^-, added to solution in the form of the electrolyte MX. For example, if the electrodes are reversible to the cation M^+ :

$$\begin{array}{c} M\,(S)\ |\ MX\ |\ MX\ |\ M\,(S) \\ \qquad S_1 \quad\ S_2 \\ \qquad\ E_j \end{array} \qquad (I)$$

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

The presence of a salt bridge between the half-cells in the two different solvents is the difference between the second type of cell and the first cell. The electrolyte RZ constitutes a salt-bridge solution which is at a high concentration relative to the electroactive electrolyte MX in solvent S_3 that is not necessarily the same as either of the electrode solvents:

$$\begin{array}{c} M\,(S)\ |\ MX\ |\ RZ\ |\ MX\ |\ M\,(S) \\ \qquad S_1 \quad\ S_3 \quad\ S_2 \\ \qquad\ E_{j1} \quad\ E_{j2} \end{array} \qquad (II)$$

Two liquid junctions are present in cell (II), one on each side of the salt bridge, giving rise to two liquid-junction potentials, E_{j1} and

E_{j2}, respectively.

The potential of either cell (I) or (II) is a sum of two terms: E_l and E_j, which is the sum of all liquid-junction potentials in a given cell. E_l is the value that the potential of the cell would assume in the absence of a liquid junction. It can be simply expressed by the difference between the Nernst equations for the two electrodes, so that for the cell with electrodes reversible to the cation M^+ and at 25° C we have, in millivolts:

$$E_l = {}_2E_M^o + 59.16 \log {}_2a_+ - {}_1E_M^o - 59.16 \log {}_1a_+ \qquad (1)$$

The ${}_1a_+$ and ${}_2a_+$ stand for the molar ionic activities of the ion M^+ in the solvents S_1 and S_2 respectively. The ${}_1E_M^o$ and ${}_2E_M^o$ refer to the standard electrode potentials for the half-cell reaction in solvent S_1 and S_2, respectively.

To compare the activities of a solute or in order to correlate the electrochemical series in different solvents, we must use a single standard state. Usually, water is chosen as a reference solvent. The problem is reduced to one of evaluating the difference between the standard free energy of the solute i in the given solvent and in a reference solvent. This difference is often termed the <u>standard free energy of transfer</u> from the reference medium to the medium in which the property is determined. The transfer free energy, $\Delta G_t^o(i)$, and the transfer activity coefficient (medium effect), ${}_m\gamma_i$, are defined as follows:

$$\Delta G_t^o(i) \equiv {}_SG_i^o - {}_WG_i^o \equiv RT \ln {}_m\gamma_i \qquad (2)$$

where ${}_SG_i^o$ and ${}_WG_i^o$ are the (partial molal) standard free energies of

the solute i in the nonaqueous solvent and in water, respectively. Of course, the above transfer process can be defined also with respect to reference solvents other than water.

Using the definition of ${}_m\gamma$ from Equation (2) as well as the relationship $\Delta G^o = - n F \Delta E^o$, where in reference to cells (I) and (II), $\Delta E^o = {}_2E_M^o - {}_1E_M^o$, we obtain the following relationship for the e.m.f., E_1:

$$E_1 = 59.16 \log {}_m\gamma_M + 59.16 \log({}_2a_+ / {}_1a_+) \qquad (3a)$$

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

If the electrodes in cells (I) and (II) are reversible to the anion X^-, an analogous equation can be written. In that case:

$$E_1 = -59.16 \log {}_m\gamma_X - 59.16 \log({}_2a_- / {}_1a_-) \qquad (3b)$$

By using Equations (3a) or (3b), the values of E_1 which account for the difference in the Nernstian responses of the two electrodes, in cell (I) or cell (II) can be obtained. That difference is a function of two parameters only:

1. The transfer activity coefficients, ${}_m\gamma$, of the ion to which the electrodes are reversible.
2. The activity of the ion in each of the solvents.

The Existing Formulations of the E_j Between Different Solvents.

The theory relevant to these studies has been reviewed very lucidly by Murray and Aikens [1]. The present formulation of the E_j is essentially that of Alfenaar, De Ligny and Reminjse [2], only extended here to include the salt-bridge electrolyte. It incorporates the well-accepted [3], formal division of the E_j into its components due to the passage of ions, $E_{j,ion}$, and the solvent molecules, $E_{j,s}$ across the junction.

$$E_j = E_{j,ion} + E_{j,s} \tag{4}$$

This division is also of practical importance, because at the present time we have equations from which to calculate the $E_{j,ion}$, but not the $E_{j,s}$.

The most general expression for the $E_{j,ion}$ term at a junction of two electrolyte solutions in solvents S_1 and S_2 is:

$$E_{j,ion} = -\frac{1}{F}\sum_i \int_{s_1}^{s_2} \frac{t_i}{Z_i} dG_i \tag{5}$$

where t_i, Z_i and G_i are the transport number, charge and chemical potential of each ionic species, i, and F is the Faraday. When the junction is formed between two different solvent media, it is useful to expand Equation (5) into:

$$E_{j,ion} = -\frac{1}{F}\sum_i \int_{S_1}^{S_2} \frac{t_i}{Z_i} dG_i^o - \frac{RT}{F}\int_{S_1}^{S_2} \frac{t_i}{Z_i} d\ln a_i \qquad (6)$$

so as to consider separately the effect of changes in the standard chemical potentials, G_i^o, and the activities of ions, a_i.

In e.m.f. cells containing the same solvent on both sides of the junction, the first term in Equation (6) is zero and the $E_{j,ion}$ is determined by the second term, which is referred to as the Henderson term, $E_{j,H}$:

$$E_{j,H} = -\frac{RT}{F}\sum_i \int_{S_1}^{S_2} \frac{t_i}{Z_i} d\ln a_i \qquad (7)$$

In our studies, the $E_{j,H}$ term has been minimized in two ways:

1. The concentrations of MX in each solution were chosen to be low and as close to each other as possible in cell (I).
2. A salt bridge of a suitable concentrated electrolyte was used in junction with the equal low concentrations of MX in both solvents in cell (II).

The expression for the $E_{j,H}$ for cell (II) is given below:

$$E_{j,H}(II) = (-RT/F)(t_R - t_Z)\ln({}_2a_{\pm}/{}_1a_{\pm}) \qquad (8)$$

It is clear that $E_{j,H}$ will be equal to zero when $t_R = t_Z$. The small $E_{j,H}$ corrections can always be calculated, but they are usually negligible compared to the solvent effects, and will be omitted from

our subsequent equations. Very recently a new equation was reported by Izutsu [5] to calculate $E_{j,H}$ by assuming that both the ionic transport numbers and the electrolyte activity varied linearly in the interface region.

When the junction is formed between different solvent media, the E_j is determined primarily by the Gibbs transfer free energies and the transport numbers of the ions crossing the junction, a combination we call $E_{j,G}$:

$$E_{j,G} = -\frac{1}{F}\sum_i \int_{s_1}^{s_2} \frac{t_i}{Z_i} dG_i^o \qquad (9)$$

If we make the common assumption prevalent in the literature that the t_i's are solvent-independent, then for a simple junction present in cell (I), $E_{j,G}$ is equal to:

$$E_{j,G} = -(1/F)\,[\, t_M \Delta G_t^o(M) - t_X \Delta G_t^o(X)\,] \qquad (10a)$$

When either junction present in cell (II) (with a salt-bridge) is considered, $E_{j,G}$ is equal to:

$$E_{j,G} = -(1/F)[t_M \Delta G_t^o(M) - t_X \Delta G_t^o(X) + t_R \Delta G_t^o(R) - t_Z \Delta G_t^o(Z)] \qquad (10b)$$

In Equations (10a) and (10b), the t's and the ΔG_t^o's are respectively the Hittorf transference numbers and the transfer free energies of the ions M^+, X^-, R^+ and Z^- as noted. The transfers are defined here as occurring from solvent S_1 to S_2.

We have already seen that E_j between two different solvents has three components:

$$E_j = E_{j,G} + E_{j,H} + E_{j,S} \qquad (11)$$

Upon omission of the $E_{j,H}$, the expression for E_j, in cell (II) becomes:

$$E_j = -(1/F)[t_M \Delta G_t^o(M) - t_X \Delta G_t^o(X) + t_R \Delta G_t^o(R) - t_Z \Delta G_t^o(Z)] + E_{j,S} \qquad (12)$$

Comparing Equations (4) and (12) the expression for $E_{j,ion}$ in cell (II) becomes simply the $E_{j,G}$ expressed by Equation (10b).

In Equation (12), we used the average transport numbers for each ion computed for the solvents S_1 and S_2. While this was an improvement over the assumption prevailing in the literature that the $\underline{t}$ values could be taken as solvent-independent, averaging was still an approximation. A precise formulation of the $E_{j,ion}$ would require knowing the functional dependence of the transference numbers of each ion on the mixed-solvent composition in the diffusion layer.

Anna Berne [4] has derived such a precise expression for the $E_{j,ion}$ term by taking into account the solvent-dependence of the transference numbers $\underline{t}_i$ and of the standard chemical potentials G_i^o. In the new formulation, it is assumed that the composition of the solvent in the diffusion layer changes continuously from S_1 to S_2 in a single-valued manner and that the variation of t_i and G_i^o with the solvent composition is described by the functions t_i (s) and G_i^o(s), respectively. Thus, we can write for the contribution of each ion:

$$E_{j,ion} = -\frac{1}{F}\int_{s_1}^{s_2} \frac{t_i(s)}{Z_i}\frac{dG^o(s)}{ds}ds \qquad (13)$$

where ds represents an infinitesimal change in the solvent composition. Equation (13) can be rewritten as:

$$E_{j,ion} = -\frac{1}{FZ_i}\int_{s_1}^{s_2} \frac{d[t_i(s)\,G^{o}(s)]}{ds}\,ds + \frac{1}{FZ_i}\int_{s_1}^{s_2} \frac{G_i^{o}(s)\,dt_i(s)}{ds}\,ds \qquad (14)$$

Both Equations (13) and (14) represent the new, more precise, formulations of the first term of Equation (6). By using Equation (13), the $E_{j,ion}$ can be calculated simply by the summation for each ion of the terms $[t_i(s)\,\Delta G_i^{o}(s)/\Delta s]$. The first term of the Equation (14) can be calculated exactly if the standard solvation energies, G_i^{o}, which can be calculated by using Eqn.(2) from knowledge from the literature of hydration energies and the transfer free energies of each ion, and the transference numbers, t_i, are known in the two end solutions, i.e. in solvents S_1 and S_2. It is simply:

$$(-1/F\,Z_i)\,[t_i(s_2)\,G_i^{o}(s_2) - t_i(s_1)\,G_i^{o}(s_1)] \qquad (15)$$

The second integral in Eqn. (14) can be evaluated as the summation of $[G_i^{o}(s)\,\Delta t_i(s)/\Delta s]$. The $E_{j,ion}$ is then calculated as the sum of these two terms.

If we use Equation (13), we do not need the values of ionic hydration energies from the literature and require only transfer free energies and transference numbers of each ion to calculate $E_{j,ion}$. This is one advantage to using Equation (13) over Equation (14), because hydration energies enter indirectly in both RHS terms of Equation (14). Furthermore, if there are any sharp changes, such as a

maximum or a minimum in the graph of transport numbers vs. wt% of any solvent system, the $[\Delta t_i(s)/\Delta s]$ term can be avoided by using Equation (13). In such a case, Eqn. (13) is preferable for $E_{j,ion}$ calculations. On the other hand, for systems showing a maximum or a minimum in the graph of transfer free energies vs. wt% solvents, the $[\Delta G_t^o(s)/\Delta s]$ term can be avoided by using Equation (14). If this is the situation, Eqn. (14) may be preferred to calculate $E_{j,ion}$. The results of these $E_{j,ion}$ calculations, using both Equations (13) and (14) are discussed later.

Methods of Determination of Thermodynamic Transfer Activity Coefficients.

While the transfer activity coefficients of single ions can be determined only with the aid of extrathermodynamic assumptions, the transfer activity coefficients of uncharged molecules, complete electrolytes and electroneutral combinations of ions can be calculated from experimental data. The most common methods for the determination of thermodynamic transfer activity coefficients are discussed below.

Solubility Method.

Generally, in determining thermodynamic transfer activity coefficients, the most widely used method is the solubility method. The free energies of the saturated solutions are shown in Equations (16) and (17):

$$G(i, H_2O) = {}_WG_i^o + RT \ln (a_i)_{sat} \quad (16)$$

$$G(i, S) = {}_SG_i^o + RT \ln (a_i^*)_{sat} \quad (17)$$

When an aqueous and a nonaqueous solution are saturated with the compound of interest, their free energies will be equal if the solid crystals in contact with them are identical. It follows from Equations (16) and (17) that:

$${}_SG_i^o - {}_WG_i^o = RT \ln (a_i)_{sat} / (a_i^*)_{sat} \quad (18)$$

It can be seen that by measuring the solubilities of an uncharged molecular substance in the two solvents, its medium effect can be determined from Equation (19):

$$\log {}_m\gamma_i = \log (a_i)_{sat} / (a_i^*)_{sat} \qquad (19)$$

where $(a_i)_{sat}$ and $(a_i^*)_{sat}$ are the activities of the saturated solutions in water and the nonaqueous solvent, respectively.

For an electrolyte, the transfer activity coefficient (medium effect) can be determined by determining its solubility products in the solvents of interest. The transfer activity coefficients for a given electrolyte can be calculated using Equation (20), when the solubility products are known for it in water and various nonaqueous solvents. Substituting ion-activity products, K_{sp} , for activities and rearranging Equation (19), we get:

$$\log {}_m\gamma_i = pK_{sp\,(i\,,\,S)} - pK_{sp\,(i\,,\,H_2O)} \qquad (20)$$

While the estimation of transfer activity coefficients of single ions requires some extrathermodynamic assumptions, it is possible to utilize that concept in formulating expression for transfer activity coefficients for electroneutral combinations of ions. For example;

$$\log {}_m\gamma_{Cl^-} - \log {}_m\gamma_{Br^-} = \log {}_m\gamma_{AgCl} - \log {}_m\gamma_{AgBr} \qquad (21)$$

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

$$\log {}_m\gamma_{(electrolyte)} = \log {}_m\gamma_{\pm}^2 = (\log {}_m\gamma_+ + \log {}_m\gamma_-) \qquad (22)$$

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

E.m.f. Method.

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

$$G_i^o = -nFE_i^o \qquad (23)$$

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

$$\Delta E_i^o = -(RT/nF) \ln {}_m\gamma_i \qquad (24)$$

In actuality, the conventional standard potential of any electrode is equal to the potential difference between the given standard electrode and a standard hydrogen electrode in the solvent of interest. Thus, the standard potential difference 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 (III) represents a hydrogen-silver-silver chloride cell:

$$Pt\ ;\ H_2\ (g)\ |\ HCl\ (a=1)\ |\ AgCl\ (s)\ ;\ Ag\ (s) \qquad (III)$$

The value of E^o_{AgCl} is simply equal to the standard potential of cell (III). In water and nonaqueous solvents, the difference between the standard potential of the silver-silver chloride electrode is related to $\log_m \gamma_{HCl}$:

$$\log_m \gamma_{HCl} = (\log_m \gamma_H + \log_m \gamma_{Cl})$$
$$= [\ {}_W E^o_{AgCl} - {}_S E^o_{AgCl}\ ]/\ 59.16 \qquad (25)$$

Similarly, a measure of the difference of the transfer activity coefficient between the metal ion and the hydrogen ion is given by the difference between the standard potentials of any metal-metal ion electrode between water and the given nonaqueous solvent:

$$\log_m \gamma_M - \log_m \gamma_H = [\ {}_S E^o_M - {}_W E^o_M\ ]/\ 59.16 \qquad (26)$$

Thus, only transfer activity coefficients for electroneutral combinations of ions are thermodynamically determinable. In Eqns. (25) and (26) the potentials are in millivolts.

Distribution Method.

The use of the distribution method for the determination of transfer activity coefficients is quite limited. In cases where two solvents are totally immiscible, the values 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 neglecting the uncertain corrections for salt-effect activity coefficients and the degree of dissociation required in the solubility method. However, in practice, this method for determining transfer activity coefficients has not been too useful because most solvents of interest are miscible with one another.

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 between e.m.f. and pH scales in different solvents. The key to the correlation of e.m.f. scales, universal ion-activity scale and the evaluation of liquid-junction potentials lies in knowledge of transfer activity coefficients of single ions. Since these quantities are not thermodynamically attainable, various extrathermodynamic methods have been developed to determine them. Comprehensive critical reviews of these methods were published by Popovych [6,7].

The Reference-Electrolyte Method.

A 1:1 electrolyte composed of large ions as identical as possible in size, geometry, and other physico-chemical properties which determine interactions with solvents is referred to as a reference electrolyte. In this method the basic assumption is that the transfer

activity coefficients for the electrolyte can be divided equally between the anion and the cation:

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

Fuoss and Hirsch [8] proposed the use of tetrabutylammonium tetraphenylborate and Coetzee and Cunningham [9] used tetraisoamylammonium tetraisoamylborate as the reference electrolyte in the evaluation of single-ion conductivities in solvents where accurate transference data were not available.

The estimation of transfer free energies for ions using the reference electrolyte was first reported in 1960. To estimate free-energy changes for the transfer of single ions between dioxane-water mixtures, tetraphenylphosphonium tetraphenylborate (Ph_4PBPh_4). was used by Grunwald, Baughman and Kohnstam [10]. Popovych [11] used triisoamyl-n-butylammonium tetraphenylborate ($TABPh_4$) to determine transfer activity coefficients in methanol and the ASTM mixture, consisting of 50% toluene, 49.5% isopropanol and 0.5% water, by volume. Popovych and Dill [7] used the same reference electrolyte in ethanol-water mixtures, to determine transfer activity coefficients. Currently, the reference-electrolyte of choice is tetraphenylarsonium tetraphenylborate (Ph_4AsBPh_4) [6,7,12-16]. The transfer activity coefficient of the complete electrolyte is divided equally between its ions, when the Ph_4AsBPh_4 assumption is applied:

$$\log_m \gamma_{Ph_4As} = \log_m \gamma_{BPh_4} = (1/2) \log_m \gamma_{Ph_4AsBPh_4} \qquad (27a)$$

The values of $\log_m \gamma$ for all single ions can be calculated from

available data, when the transfer activity coefficient is available for one ion. For example:

$$\log {}_m\gamma_K = \log {}_m\gamma_{KBPh_4} - \log {}_m\gamma_{BPh_4} \quad (27b)$$

$$\log {}_m\gamma_{Cl} = \log {}_m\gamma_{KCl} - \log {}_m\gamma_K \quad (27c)$$

$$\log {}_m\gamma_H = \log {}_m\gamma_{HCl} - \log {}_m\gamma_{Cl} \quad (27d)$$

$$\log {}_m\gamma_{NO_3} = \log {}_m\gamma_{Ph_4PNO_3} - \log {}_m\gamma_{Ph_4P} \quad (27e)$$

Because of the extremely low solubility of Ph_4AsBPh_4 in water (the most popular reference solvent), the transfer activity coefficient of Ph_4AsBPh_4 is difficult to determine directly, but the transfer activity coefficient of Ph_4AsBPh_4 can be calculated from $\log {}_m\gamma$ values of other electrolytes, e.g.:

$$\log {}_m\gamma_{Ph_4AsBPh_4} = \log {}_m\gamma_{Ph_4AsPi} + \log {}_m\gamma_{KBPh_4} - \log {}_m\gamma_{KPi} \quad (27f)$$

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

Existing Potentiometric Methods.

Potentiometry using e.m.f. cells with liquid junction is the only experimental method which can provide direct estimation for the transfer activity coefficients of single ions.

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

$$\begin{array}{c} M(S) \mid MX \mid RZ \mid MX \mid M(S) \\ H_2O \quad H_2O \quad S \end{array} \qquad (II)$$

If, for the sake of simplification, the activity of M^+ ions, added to solution in the form of electrolyte MX, is adjusted to be equal in the two solvents, the potential of cell (II) is given by:

$$E^o(II) = {}_sE^o_M - {}_wE^o_M + E_j \qquad (28)$$

where E_j is the liquid-junction potential at the interface of the two solvents. Recalling the definition of ${}_m\gamma$ from Equation (24) as well as the relationship $\Delta G^o = -nF\Delta E^o$, it follows that at 25°C:

$$E^o(II) = 59.16 \log {}_m\gamma_M + E_j \qquad (29)$$

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

Methods Assuming Negligible Liquid-Junction Potential.

An early example of the application of this assumption to the estimation of transfer activity coefficients of single ions was the use of cell (IV) by Bjerrum and Larsson [17]:

$$\underset{H_2O}{Pt\,(s)\,;\,H_2\,(g)\;|\;a_H=1} \;\underset{E_{j1}}{|\;3.5\;M\;KCl\;|}\; \underset{H_2O}{a_H=1\;|\;H_2\,(g)\,;\,Pt\,(s)} \qquad (IV)$$

They [17] estimated the values of transfer activity coefficients of the hydrogen ion in ethanol-water media from the e.m.f. measurements of cells composed of hydrogen electrodes in the nonaqueous media and 3.5 N aqueous calomel electrodes as the reference by assuming that the E_j between the ethanol-water solutions and the aqueous KCl bridge solution could be neglected.

Actually, the potential of cell (IV) is a measure of the combination of the transfer activity coefficient of the hydrogen ion and the liquid-junction potential:

$$E(IV) = 59.16 \log {}_m\gamma_H + E_{j1} + E_{j2} \qquad (30)$$

While Bjerrum and Larsson [17] made several erroneous assumptions in their calculations, such as neglecting the incomplete dissociation of the electrolyte in ethanol-water solvents, and using a cube root formula, $\log f = -KC^{1/3}$, for estimating activity coefficients, their most significant error was the assumption of negligible E_j.

In 1957, Oiwa [18] estimated values for ${}_m\gamma_H$ in methanol-water mixtures by using cell (V):

$$Pt\,(s)\,;\,H_2\,(g)\;|\;HCl\;|\;KCl\,(Sat.\,aq.)\;|\;Hg_2Cl_2(s)\,,\,Hg(l) \qquad (V)$$

While he tried to account for the differences in ionic mobilities by the use of the Plank equation [19], Oiwa, like Bjerrum and Larsson, failed to consider the effect of the transfer activity coefficients on the liquid-junction potential of such a cell.

Parker and his associates [12,20-24] used cell (VI) to study the magnitude of the E_j between various solvents.

$$\underset{}{\text{Ag (s)} \mid \underset{S_1}{AgNO_3\ (0.01M)} \mid \underset{S_1 \text{ or } S_2}{Et_4NPi\ (Sat.)} \mid \underset{S_2}{AgNO_3\ (0.01M)} \mid \text{Ag (s)}} \qquad \text{(VI)}$$

The bridge solution of tetraethylammonium picrate (Et_4NPi) was contained either in the S_1 or S_2 solvent, whichever was the poorer solvator of Ag^+ ions. They chose Et_4NPi as the salt-bridge electrolyte because its ions have similar mobilities in several solvents. In addition, they claimed that neither of these 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 different solvents. By assuming that E_j in cell (VI) was negligible, the transfer activity coefficients of silver ion were calculated from Equation (31).

$$E(VI) = 59.16 \log {}_m\gamma_{Ag} + E_j \qquad (31)$$

Parker et. al. then proposed that the assumption of negligible E_j be considered valid for those pairs of solvents for which the transfer activity coefficients for silver ion thus obtained were similar to those arrived at by other method (such as the Ph_4AsBPh_4 assumption). Using those $\log {}_m\gamma_{Ag}$ values, Parker then calculated E_j via Equation (31).

Methods Using Calculated Liquid-Junction Potentials.

From the literature, we see that the transfer activity coefficients of single ions were at first obtained by neglecting or minimizing the E_j, but with time an effort was made to correct that assumption by calculating the E_j. Goldberg [25] and Goldberg and Popovych [26] have used both approaches in their study of the medium effects for Na^+ and H^+ ions between a number of dipolar aprotic solvents. The following cell was used:

$$\text{Na (glass)} \mid NaBPh_4 \mid RX = 0.1M \mid NaBPh_4 \mid \text{Na (glass)} \qquad \text{(VII)}$$

The objectives of their study were:

1. To compare the effect of the salt-bridge electrolytes ($TABBPh_4$, Et_4NPi and Et_4NClO_4) on the estimation of the transfer activity coefficients of the sodium and hydrogen ions, from the e.m.f. of cells with the assumption of negligible E_j.
2. To calculate the magnitude of E_j from Equation (12). It is important to note that the values of $E_{j,s}$ (Equation 4) which would account for the solvent contribution to E_j, were assumed to be zero in every case.

While interpreting the various results for log ${}_m\gamma_{Na}$ obtained using the three salt-bridge electrolytes, with or without corrections for E_j, Goldberg and Popovych [26] suggested a new method to determine transfer activity coefficients of ions with an independent knowledge of the values for log ${}_m\gamma_{Na}$, and either log ${}_m\gamma_R$ or $\log_m\gamma_X$ and of all the relevant transport numbers. It is possible to estimate the transfer activity coefficients of the ion X^- or R^+ (whichever is the unknown) using the new method. This method was successfully

applied by Berne and Popovych [27].

To illustrate this method of estimating transfer activity coefficients of single ions, we start with the e.m.f. of cell (VII) given by:

$$E(VII) = E_1 + E_j \qquad (31)$$

whereafter the appropriate substitutions are made with the simplifying assumption that ${}_2a_{Na}$ and ${}_1a_{Na}$ are equal, the following Equation is obtained:

$$E(VII) = 59.16 \log {}_m\gamma_{Na} - 59.16[\, t_R \log {}_m\gamma_R - t_X \log {}_m\gamma_X] \qquad (32)$$

Rearranging equation (32), an expression for $\log {}_m\gamma_R$ is obtained:

$$\log {}_m\gamma_R = (1/t_R)\,[\log {}_m\gamma_{Na} - E(VII)/59.16 - t_X \log {}_m\gamma_X] \qquad (33)$$

A similar expression can be arrived at for $\log {}_m\gamma_X$, if that is the derived quantity. This method is suitable for ions forming highly soluble electrolytes. It was used here to determine the transfer activity coefficients of the nitrate ion in acetonitrile-water solvents.

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

The liquid-junction potential between two solutions in different solvents is caused by the transport of ions as well as the solvent molecules across the interface. The liquid-junction potential, E_j, can be represented by:

$$E_j = E_{j,ion} + E_{j,s} \qquad (4)$$

where $E_{j,ion}$ accounts for all the terms caused by the transport of ions and $E_{j,s}$, caused by the transport of solvent molecules across the interface. While $E_{j,ion}$ can be calculated directly using existing equations, $E_{j,s}$ can only be estimated from e.m.f. measurements of cells with and without salt-bridges and other thermodynamic data.

Although the existence of $E_{j,s}$ was predicted theoretically by Staverman [28] as far back as 1952 and was subsequently confirmed experimentally by many workers, its nature is not yet fully understood.

In 1967, Alfenaar, de Ligny and Remijnse [2] found $E_{j,s}$ at the junction of water and methanol-water mixtures to be a function of the solvents as well as the electrolytes in the cell. The following cell was used in their study:

$$\begin{array}{l} \text{Ag , AgZ} \mid \text{MZ} \mid \text{MZ} \mid \text{AgZ , Ag} \\ \qquad\quad H_2O \quad S \end{array} \qquad \text{(VIII)}$$

where MZ was one of the seven alkali halides and the concentrations of MZ in H_2O and the methanol-water solvents were chosen to be

very low and equal, so that the e.m.f. of cell (VIII) could be written as:

$$E(VIII) = -59.16\ t_M \log_m \gamma_{MZ} + E_{j,s} \qquad (34a)$$

They found that the value of $E_{j,s}$ increased steadily with the percentage of methanol in a solvent, S, for all the electrolytes studied. $E_{j,s}$ also depended on the nature of the electrolyte MZ, as well as the two solvents.

Murray and Aikens [1] measured $E_{j,s}$ in cells similar to cell (VIII) with junctions between water and methanol, ethanol, acetone, acetonitrile and propylene carbonate solutions and for some junctions between pairs of nonaqueous solutions. Their cell (IX):

$$M\ ,\ MX\ (S)\ |\ NX\ (Satd.)\ |\ NX\ (Satd.)\ |\ MX\ (S)\ ,\ M \qquad (IX)$$

consisted 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. It can be shown [1] that in the absence of solid solvates formed by MX with either solvent, the e.m.f. of this cell is represented by the equation:

$$E(IX) = -\ (t_N/F)\ \Delta G_t(NX)\ Satd. + E_{j,s} \qquad (34b)$$

Since both solutions are saturated with NX, solid crystals of NX must be present in both solutions. If those crystals do not form a solid solvate with either solvent, then the (partial molar) free energies of any two saturated solutions of a solute, i are equal. Thus, the free energies of the two saturated solutions of NX in solvents S_1 and S_2 must be equal, $\Delta G_t(NX)$ is equal to zero, and the e.m.f. of Cell (IX) is a

direct measure of $E_{j,s}$. The following were the main conclusions in the study of Murray and Aikens [1]:

1. There is a strong dependence of $E_{j,s}$ on the nature of current-carrying species, N^+ and X^-.

2. The value of $E_{j,s}$ with saturated KCl as NX between water and methanol is nearly three times smaller than the $E_{j,s}$ reported by Alfennar [2] between $2x10^{-5}$ mole fraction KCl in water and methanol. Therefore, it appears that the value of $E_{j,s}$ depends not only on the nature, but also on the concentration of the current-carrying species present and that $E_{j,s}$ decreases significantly with increasing electrolyte concentration.

3. They concluded that the solvent contribution to the liquid-junction potential is caused by 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.

Cox, Parker and Waghorne [3] used the following cell to evaluate $E_{j,s}$. In their studies, e.m.f. cells with Et_4NPic and Bu_4NBPh_4 salt-bridges between dipolar aprotic solvents were used:

$$Ag(s) \mid AgClO_4\ (0.01M) \mid Et_4NPi\ (0.1) \mid AgClO_4\ (0.01M) \mid Ag(s) \qquad (X)$$

By assuming that the transport numbers of both Et_4N^+ and Pi^- ions are equal to each other in all the solvents used here and that the current is carried only by those two ions, the e.m.f. of cell (X) is given by:

$$E(X) = (RT/F) \ln {}_2a_{Ag}/\ {}_1a_{Ag} - (0.5/F)\ {}^1\Delta^2G^o_t(Et_4N^+) + (0.5/F)\ {}^1\Delta^2G^o_t(Pi^-) + E_{j,s} \qquad (35)$$

They further assumed that the transfer free energies of Et_4N^+ and Pi^- ions are equal for all the pairs of solvents studied and therefore any changes in the e.m.f. of cell (X) are due to changes in $E_{j,s}$. Based on these assumptions, they concluded that in the above cells, $E_{j,s}$ was small or negligible. They also found a direct correlation between the $E_{j,s}$ and the mutual heats of solution of the solvents forming the junction.

Many studies of the $E_{j,s}$ in cells with liquid junction were also carried out by Izutsu and coworkers [29-36]. The e.m.f. values of the following cells were measured while varying the solvents S_1 and S_2 and the electrolyte MX:

$$\begin{array}{l} Ag(s) \mid 10^{-3}M\ AgClO_4\ ,\ 1M\ NaClO_4 \mid 1M\ NaClO_4 \mid 0.1M\ MX \mid \\ \qquad\qquad S_1 \qquad\qquad\qquad j_1 \quad S_1 \quad J_1 \qquad J_2 \\ \mid 10^{-3}M\ Et_4NClO_4 \mid 5\times10^{-3}M\ AgClO_4\ ,\ 5\times10^{-3}M\ Et_4NClO_4 \mid Ag(s) \\ j_2\ S_2 = S_1 \text{ or } H_2O\ j_2 \quad S_2 = S_1 \text{ or } H_2O \end{array} \qquad \text{(XI)}$$

$$\begin{array}{l} aq\ SCE \mid 3M\ NaCl \mid 0.1M\ MX \mid 10^{-3}M\ Et_4NClO_4 \mid \\ \qquad j_1\ S_1{=}H_2O\ J_1 \quad S_1{=}H_2O\ J_2 \qquad S_2 \\ \qquad\quad \mid 5\times10^{-3}M\ AgClO_4\ ,\ 5\times10^{-3}M\ Et_4NClO_4 \mid Ag(s) \\ \qquad\qquad\qquad\qquad S_2 \end{array} \qquad \text{(XII)}$$

From their results, the authors concluded that the liquid-junction potential between different solvents contains a component which can be attributed to solvent-solvent interactions. When the ions are solvated weakly at the junction, the component seems to be almost independent of the types and the concentrations of these ions. But if the ions are considerably solvated, different behavior is observed.

Goldberg [25] used four different e.m.f. cells to investigate the concentration-dependence in the study of liquid-junction potentials between water and a series of methanol-water solvents.

$$\underset{\qquad\qquad\quad W \quad S}{Hg(l), Hg_2Cl_2(s) \mid NaCl \mid NaCl \mid Hg_2Cl_2(s), Hg(l)} \qquad (XIII)$$

$$\underset{\qquad\quad W \quad S}{Na\ (glass) \mid NaCl \mid NaCl \mid Na\ (glass)} \qquad (XIV)$$

$$\underset{\qquad\quad W \quad\quad W \quad\quad\quad S}{Hg(l), Hg_2Cl_2(s) \mid NaCl \mid KCl\ (Satd.) \mid NaCl \mid Hg_2Cl_2(s), Hg(l)} \qquad (XV)$$

$$\underset{\qquad\quad W \quad\quad W \quad\quad S}{Na\ (glass) \mid NaCl \mid KCl\ (Satd.) \mid NaCl \mid Na\ (glass)} \qquad (XVI)$$

He used various concentrations of NaCl from saturated to $3x10^{-3}$ M. The results showed a clear inverse dependence of $E_{j,s}$ on the concentration of the current-carrying species.

Berne [4] used eight different e.m.f. cells to study the concentration effect on liquid-junction potentials between water and a series of methanol-water solvents for NaCl and HCl. Four of the cells she used were similar to those used by Goldberg [25]. She added the following four cells:

$$\underset{\qquad\qquad\quad W \quad S}{Hg(l), Hg_2Cl_2(s) \mid HCl \mid HCl \mid Hg_2Cl_2(s), Hg(l)} \qquad (XVII)$$

$$\underset{\qquad\quad W \quad S}{H\ (glass) \mid HCl \mid HCl \mid H\ (glass)} \qquad (XVIII)$$

$$\underset{\qquad\quad W \quad\quad W \quad\quad\quad S}{Hg(l), Hg_2Cl_2(s) \mid HCl \mid KCl\ (Satd.) \mid HCl \mid Hg_2Cl_2(s), Hg(s)} \qquad (XIX)$$

$$\underset{\qquad\quad W \quad\quad W \quad\quad S}{H\ (glass) \mid HCl \mid KCl\ (Satd.) \mid HCl \mid H\ (glass)} \qquad (XX)$$

Based on Berne's study, there was enough evidence to say that at least for junctions made with strongly solvated ions, the magnitude of $E_{j,s}$ was inversely related to the concentration of the electrolyte forming the interface between the two half cells.

EXPERIMENTAL

Preparation of Solvents

Methanol (MeOH).

ACS Spectroanalyzed methanol was used as the starting material in the preparation of anhydrous methanol. Four liters of the commercial MeOH were refluxed over aluminum amalgam for 24 hours. The aluminum amalgam was prepared by mixing 25 grams of aluminum powder and 5 grams of $HgCl_2$. The methanol was then distilled through a 30-cm Vigreux column. The first and last 500 ml were discarded and the middle 3 liters were collected. The portion collected had a density of 0.7862 g/ml at 25°C, which is in favorable agreement with the literature values of 0.7866 g/ml [37].

Methanol-Water Mixtures.

The methanol-water mixtures were prepared by combining appropriate volumes of anhydrous methanol and deionized water at intervals of about 10 wt% methanol. Their densities were determined in quadruplicate with calibrated 100-ml volumetric flasks. From a large-scale graph of density vs. wt% methanol, the exact wt% of a particular mixture was read. The data plotted in the above graph were obtained from the literature [37] and are listed in Appendix 1.

Ethanol (EtOH).

U.S.P. 200 proof ethyl alcohol (Publicker Industries Co.) was used as the starting material in the preparation of 100 wt% ethanol. Five liters of the 200-proof alcohol were refluxed over magnesium

ethoxide for 24 hours. The alcohol was then distilled through a 30-cm Vigreux column. The first 1.0 liter was rejected, and the middle 2.5 liters collected. The middle fraction had a density of about 0.7850 g/ml at 25°C which compares favorably with the available literature values of 0.7850 g/ml [38] and 0.7851 g/ml [39].

Ethanol-Water Mixtures.

Purified U.S.P. 95% ethanol was used to prepare ethanol-water mixtures containing less than 90 wt% ethanol. The starting material was purified by slow distillation using a 30-cm Vigreux column. The distillation flask was charged with about five liters of the U.S.P. alcohol. The rate of distillation was about 0.2 liter/hour. The first 1.0 liter was rejected and the middle fraction (about 2.5 liters) was collected for use. The ethanol-water mixtures were prepared by combining appropriate volumes of anhydrous ethanol and deionized water at intervals of about 10 wt% ethanol. Their densities were determined in quadruplicate with calibrated 100-ml volumetric flasks. From a large-scale graph of density vs. wt% ethanol, the exact wt% of a particular mixture was read. The data plotted in the above graph were obtained from the literature [39] and are listed in Appendix 2.

Acetonitrile (AN).

Acetonitrile was purified by the method of Coetzee, et. al. [40]. 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 the decantate from

these treatments were used to charge a distillation flask. The solvent was fractionally distilled over fresh P_2O_5 using a 30-cm Vigreux column. The first and last liters were rejected and the middle fraction collected. The middle fraction had a density of 0.7768 g/ml at 25°C, which is in favorable agreement with the literature value of o.7767 g/ml [40].

Acetonitrile-Water Mixtures.

The acetonitrile-water mixtures were prepared by combining appropriate volumes of purified acetonitrile and deionized water at intervals of about 10 wt% acetonitrile. Their densities were determined in quadruplicate with calibrated 100-ml volumetric flasks. From a large-scale graph of density vs. wt% acetonitrile, the exact wt% of a particular mixture was read. The data plotted in the above graph were obtained from the literature [40] and are listed in Appendix 3.

N,N-Dimethylformamide (DMF).

Certified ACS spectroanalyzed 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. The middle fraction had a density of about 0.9438 g/ml at 25°C which compares favorably with the available literature values of 0.9439 g/ml [41].

N,N-Dimethylformamide-Water Mixtures.

The dimethylformamide-water mixtures were prepared by combining appropriate volumes of purified dimethylformamide and deionized water at intervals of about 10 wt% dimethylformamide. Their densities were determined in quadruplicate with calibrated 100-ml volumetric flasks. From a large-scale graph of density vs. wt% dimethylformamide, the exact wt% of a particular mixture was read. The data plotted in the above graph were obtained from the literature [41] and are listed in Appendix 4.

Dimethylsulfoxide (DMSO).

Certified ACS-Grade dimethylsulfoxide (Eastman) was fractionally distilled over CaH_2 under reduced pressure using a 30-cm Vigreux column. The first and last fraction of about one liter each were discarded and the middle fraction was collected for use. The middle fraction had a density of about 1.0956 g/ml at 25°C which compares favorably with the available literature values of 1.0958 g/ml [42].

Dimethylsulfoxide-Water Mixtures.

The dimethylsulfoxide-water mixtures were prepared by combining appropriate volumes of purified dimethylsulfoxide and deionized water at intervals of about 10 wt% dimethylsulfoxide. Their densities were determined in quadruplicate with calibrated

100-ml volumetric flasks. From a large-scale graph of density vs. wt% dimethylsulfoxide, the exact wt% of a particular mixture was read. The data plotted in the above graph were obtained from the literature [42] and are listed in Appendix 5.

Preparation and Purification of the Electrolytes.

KCl.

Certified ACS potassium chloride (Hall Laboratories Reagent) was purified by recrystallization from deionized water. Potassium chloride was added to boiling deionized water until the point of saturation. Upon cooling the saturated solution, crystals of KCl separated. These crystals were then collected and dried in vacuo for 24 hours at 100°C.

NaCl.

Sodium chloride (Thorn Smith Standard) was dried in a vacuum oven at 80°C overnight prior to its being used in making solutions in MeOH-water solvents.

AgCl.

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

Ph_4PNO_3.

Ph_4PNO_3 was prepared by combining a hot equimolar ethanolic solution of Ph_4PBr and an aqueous solution of $AgNO_3$. The solution of Ph_4PNO_3 separated from the yellow precipitate of AgBr. Using this solution the crystals of Ph_4PNO_3 which separated upon cooling, were washed with 1:1 ethanol-water mixture, purified by double recrystallization from ethanol-water mixtures, and dried in vacuo at 80°C for 24 hours.

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 1.012 cm^{-1}.

NaCl solutions of known concentration in the range of 10^{-3} to 10^{-2} M were prepared gravimetrically, correcting to weights in vacuo. The molarity of each solution was calculated from the weight of stock solution used and the weight of the final solution. Volumes of solutions were determined using the density of the pure solvent.

The conductance cell was repeatedly rinsed with the sample solution. The conductance cell was immersed in a water bath.The temperature of the water was controlled by a Yellow Springs proportional temperature controller (Model 72). An NBS calibrated thermometer was used to record the temperature of the bath.

Solubility Determinations.

Solubilities of solutes were determined by the analysis of saturated solutions in solvents of interest. The solubilities of Ph_4PNO_3 were determined at intervals of about 10 wt% acetonitrile in solvents ranging from 0 wt% to 100 wt% acetonitrile-water solvents. About 0.1 g of the solute was placed in each of four 100-ml volumetric flasks, about 60 ml of solvent was added to each flask and then each flask was exposed to ultrasonic waves from an ultrasonic generator (E/MC Corp., Model 450) for about 20 minutes. These solutions were then placed in a platform shaker (Lab-Line Instruments, Inc.) filled with water maintained at constant temperature of $25.00^{o} \pm 0.01C$, and agitated. The solutions reached equilibrium in about 3 days. The concentration of the saturated solutions were determined spectrophotometrically on a Perkin-Elmer Lambda 3B UV/Vis spectrophotometer. The absorbance of Ph_4PNO_3 was measured at the Ph_4P^+ absorption maxima of about 265 nm and 272 nm.

E.m.f. Measurements.

The e.m.f. of galvanic cells with liquid junction was measured with and without salt-bridge electrolytes. In this investigation, the basic e.m.f. cell used was similar to the one used earlier in our laboratory by Berne [4]. The 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 deposit 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 grayish 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.

The electrochemical cell consisted of a jacketed container (~100 ml) with a plastic (polyethylene) screw cap. The jacket allowed for circulation of water from a constant temperature water bath. The temperature of the water was kept constant at $25.00^{o} \pm 0.01^{o}C$ 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 digital ionalyzer (Orion Research, Model 701A).

RESULTS AND DISCUSSION

Studies in Aqueous Mixtures of Protic and Dipolar Aprotic Solvents.

Ion-Solvent Interactions.

The hydrogen-bond donors, e.g., water and methanol, are classified as protic solvents. Solvents with dielectric constants > 15, which, although they may contain hydrogen atoms, cannot donate suitably labile hydrogen atoms to form strong hydrogen bonds with an appropriate species, are classified as dipolar aprotic. The common dipolar aprotic solvents employed in this study are acetonitrile of dipole moment μ = 3.37, dimethylformamide μ = 3.82, and dimethylsulfoxide, μ = 4.3.

Solvents can also be described in terms of the number of sites available for specific ion-solvent interactions. Thus, acetonitrile has one site (CN), while the protic solvents H_2O, MeOH and EtOH have two sites, one for anion solvation (the OH proton), and one for cationic solvation (the OH oxygen).

Chemists need an understanding of the behavior of ions in solution and it should be emphasized that the chemistry of anions in dipolar aprotic solvents differs greatly from their chemistry in water, because anions are much less solvated in dipolar aprotic than in protic solvents.

There are four kinds of strong solvent-solute interactions: ion-dipole, dipole-dipole, π–complex forming, and hydrogen-bonding. In protic solvents, anions are solvated by ion-dipole interactions, on which are superimposed strong hydrogen bonds, which is greatest for small anions. In dipolar aprotic solvents, anions are solvated by ion-dipole interactions, on which is superimposed an interaction due to the mutual polarizability of the anion and the solvent molecule,

which is greatest for large anions. There is no significant contribution to solvation by hydrogen bonding in dipolar aprotic solvents.

Some anions are hydrogen-bond acceptors, some solvents are hydrogen-bond donors, so that relatively strong interactions take place between them, e.g., between the chloride ion and water. The magnitude of the hydrogen-bonding interaction depends on the donor strength of the solvents, e.g., HOH > EtOH > $(CH_3)_2SO$, and also the acceptor properties of the anions, e.g., $OH^-, F^- > Cl^- > Br^-$.

The solvents do not entirely retain their strong anion- or cation-solvating tendencies when mixed together. The nature of the cosolvent in the mixture modifies these changes in solvating ability. Thus, a 1:1 mixture of water with acetonitrile is a better solvator of Ag^+, by 10 kJ mol^{-1} than the corresponding mixture with ethanol, and is a better chloride-ion solvator than a 1:1 Me_2SO/H_2O mixture by 19 kJ mol^{-1}. In both cases the predominant solvator is common, MeCN for Ag^+ and H_2O for Cl^- .

The importance of interaction between the components of a mixed solvent was pointed out in the above examples. The strong hydrogen bonding between DMSO and water decreases the effectiveness of water as an anion solvator in the mixture. This was most obvious from the above examples. The relative solubilities of salts in protic and dipolar aprotic solvents are greatly influenced by the anion solvation. Potassium chloride ($\log K_s$ = -2.5) is considerably more soluble than potassium perchlorate ($\log K_s$ = -4.5) in methanol, whereas the situation is reversed in DMF. Potassium chloride is very much less soluble ($\log K_s$ = -5.4) than potassium perchlorate ($\log K_s$ = -0.1) in DMF at 25°C [43].

Parker [43] felt that these changes are often caused by anion solvation, rather than to solvation of cations or of polar molecules.

These arise because dipolar aprotic solvents have much weaker structures and are not hydrogen-bond donors whereas protic solvents have some structure and are hydrogen-bond donors and acceptors. Small anions are strong hydrogen-bond acceptors, whereas large polarizable anions are not.

Water-organic solvent mixtures are important from both a practical and a theoretical point of view because of their extensive use. Water-alcohol mixtures, in which water molecules are mixed with polar molecules that make hydrogen bonds and are capable of associating, are of particular interest. Their properties may provide conclusions to a certain extent on the structure of the liquids. The experimental data on water-alcohol mixtures are generally interpreted with regard to whether, in the given range of concentration, the alcohol stabilizes or breaks down the structure of water. It cannot be ignored, however, that in liquid mixtures containing a high concentration of alcohol, it is hardly logical to speak of water structure.

Since the component properties are similar to each other, the conditions in methanol-water mixtures are simpler than in mixtures of other aliphatic monoalcohols with water. One of the ways in which this discloses itself is that in many respects the properties of methanol-water mixtures differ considerably from those of the aqueous mixtures of other alcohols.

Calculations Based on the Old Equations and the New Formulation.

The main objective in this study is to test a new equation for $E_{j,ion}$ for the aqueous mixtures of methanol, ethanol, acetonitrile, dimethylformamide and dimethylsulfoxide. The $E_{j,ion}$ using this new formulation developed in our laboratory [4] and the old equation from the literature were used for the above solvent systems.

In order to use the old Equation (10a) and the new Equations (13) and (14) in the calculation of $E_{j,ion}$ for the junctions between water and the mixed solvents studied in this investigation, the following required parameters were either available from the literature or determined experimentally:

a). Transfer activity coefficients of

1. H^+, Na^+, and Cl^- ions between water and methanol-water solvents.
2. H^+, K^+, and Cl^- ions between water and ethanol-water solvents.
3. Ag^+ and NO_3^- ions between water and acetonitrile-water solvents.
4. H^+, K^+, Cs^+, and Cl^- ions between water and dimethylformamide-water solvents.
5. H^+, K^+, Rb^+, and Cl^- ions between water and dimethylsulfoxide-water solvents.

b). Transport numbers of all the ions in all the above solvents.

c). Hydration energies of all the ions.

The methods by which the above parameters were evaluated for the systems of interest are discussed in the following sections. Using the parameters mentioned above, the $E_{j,ion}$ values from the old equation and the new formulations were calculated and compared for junctions between electrolyte solutions in water and in all of the above solvents.

METHANOL-WATER SOLVENTS.

Transfer Activity Coefficients.

The transfer activity coefficients of the single ions needed for the present calculations, which were $\log_m \gamma_{Na}$, $\log_m \gamma_H$, and $\log_m \gamma_{Cl}$, were determined previously in this laboratory [44]. They were evaluated by the tetraphenylborate assumption. Table 1 lists the transfer activity coefficients of all the ions relevant to this study, reported at even wt% methanol and their plots are shown in Figures 1-3.

TABLE 1

Transfer Activity Coefficients of Na^+, H^+ and Cl^- Ions in Methanol-Water Solvents. (Water Reference, Molar Scale) [44].

Wt% MeOH	$\log_m \gamma_{Na}$	$\log_m \gamma_H$	$\log_m \gamma_{Cl}$
100	1.57	1.80	2.37
90	1.51	0.53	1.86
80	1.44	-0.08	1.47
70	1.35	-0.11	1.15
60	1.16	-0.10	0.88
50	1.00	-0.06	0.68
40	0.89	0.07	0.42
30	0.72	0.11	0.26
20	0.59	0.20	0.06
10	0.27	0.08	0.05

FIGURE 1

Transfer Activity Coefficients of the H^+ Ion in Methanol-Water Solvents [44].

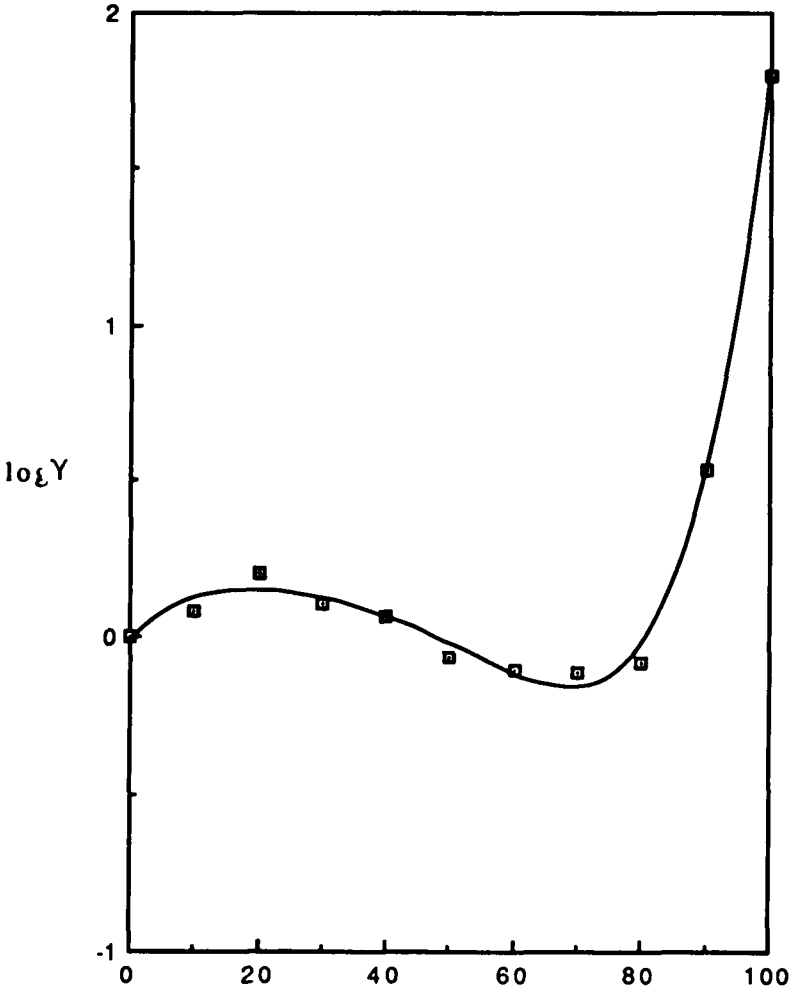


FIGURE 2

Transfer Activity Coefficients of the Na^+ Ion in Methanol-Water Solvents [44].

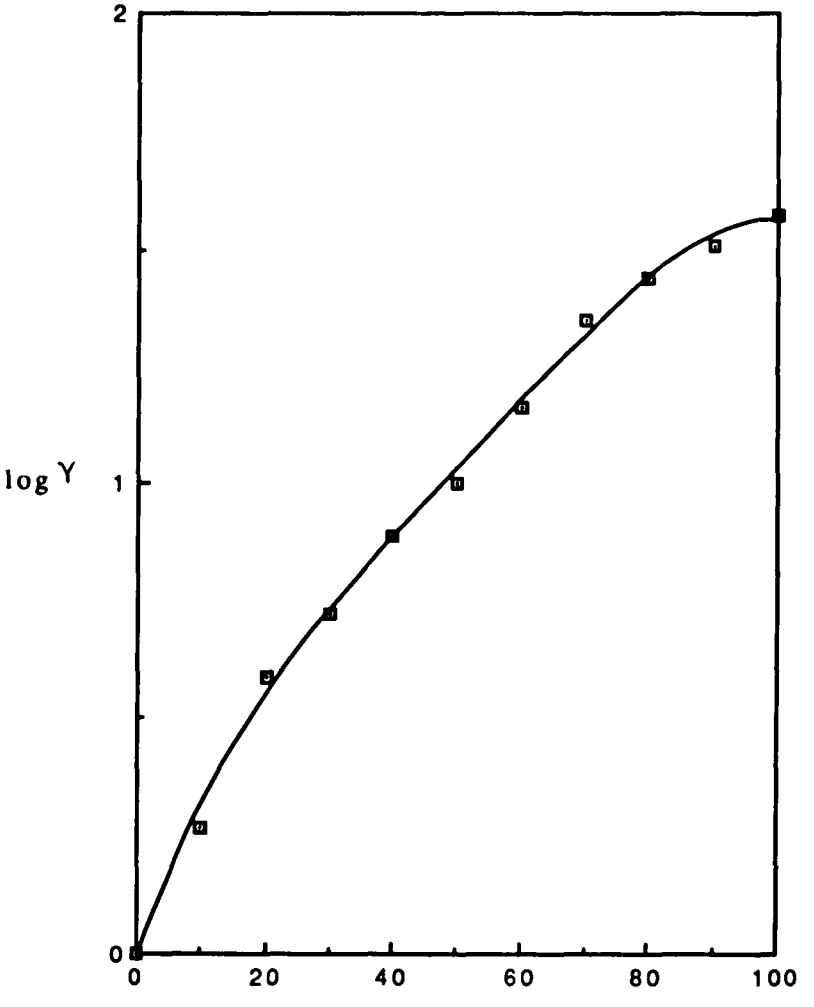
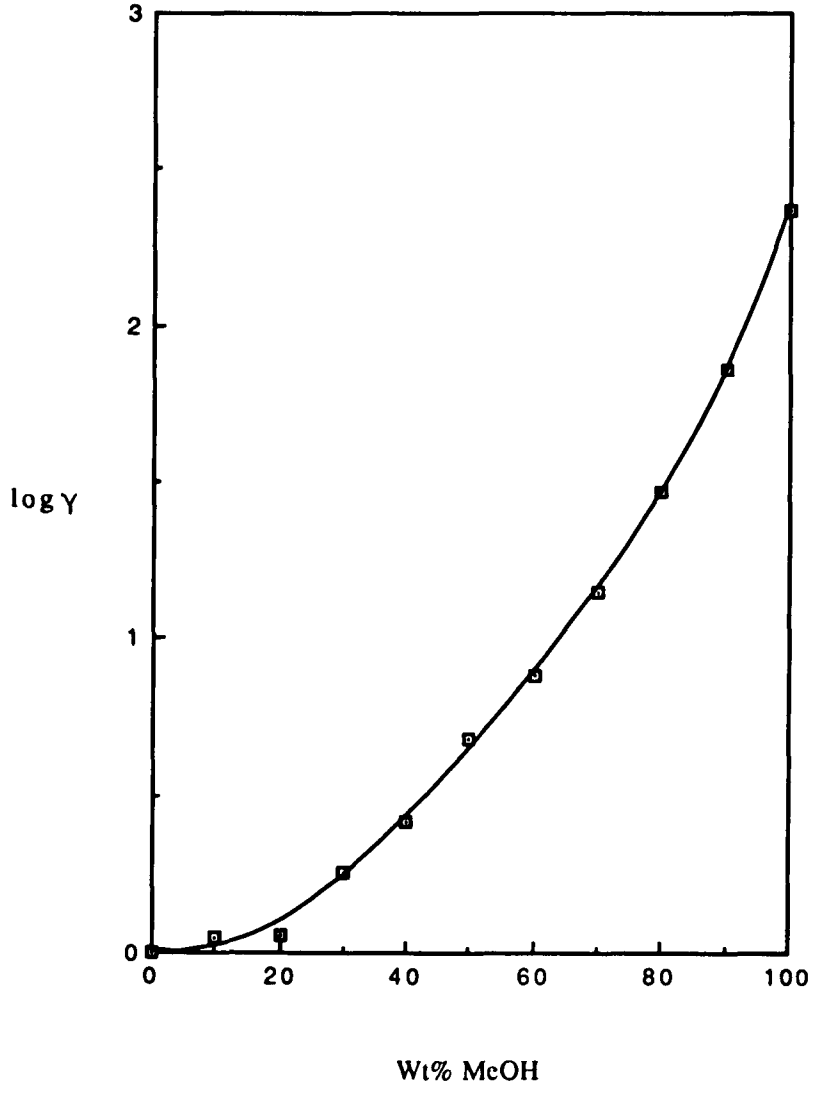


FIGURE 3

Transfer Activity Coefficients of the Cl^- Ion in Methanol-Water Solvents [44].



The variation of $\log_m \gamma_H$ upon subsequent addition of methanol (as indicated on the graph on page 52) to water was explained by Popovych [44]. Strengthening of the water structure caused by the presence of small amounts of a cosolvent is thought to be the reason why at a low concentration of alcohol there is an initial increase in transfer activity coefficients of hydrogen ions. Increasing negative values of $\log_m \gamma_H$ are brought about upon subsequent addition of methanol to water. They reach a minimum at approximately 70 wt% of methanol. In terms of proton-accepting ability, this minimum displays a solvent mixture of maximum basicity.

Two explanations for this seeming increase in the basicity of the methanol-water mixtures in relation to the pure liquids have been presented. One interpretation, popular in the publications of Feakins and his associates [45], attributed it to the inductive effect of the methyl group. This group makes the methanol molecules increasingly "basic" and less "acidic" than the water molecules in that the negative charge on the oxygen atom is greater and the positive charge on the hydroxylic hydrogen atom is less. Cooperative hydrogen bonding imparts these characteristics to the water molecules in the mixtures as well. An alternative theory, presented by Braude and Stern [46], discussed a similar variation in the Hammett acidity function, $-H_o$, in aqueous mixtures of methanol in the light of a breakdown of the three-dimensional water structure caused by the methanol. Water depolymerized in this way probably has a greater number of free basic oxygen atoms available for bonding with acidic solutes.

Consider the solvation of an alkali-metal cation. Here, the solvent molecules which are around the ion in a first sheath are probably directed with their oxygen atoms pointing towards the ion,

possibly with the oxygen lone-pair orbitals overlapping the acceptor orbitals of the ion. The strength of the interaction between the ion and the solvent molecule will depend to a first approximation on the electron density on the oxygen atom of the solvent molecules.

A halide ion will be surrounded by solvent molecules so orientated that a hydroxyl-hydrogen atom is immediately adjacent to the ion and the ionic hydrogen and oxygen nuclei are co-linear, as in a hydrogen bond of maximum stability. The coulombic force between the charge on the ion and the charges on the hydroxyl-hydrogen atoms determine the strength of the attraction between the ion and the solvent molecules. As far as the primary solvation is concerned, an anion will be in a lower free-energy state in water than in the mixed solvents. The primary solvation energy of ions of both signs is inversely proportional to the ionic radii or proportional to the electrostatic field at their "surfaces". This is because the centroids of charge of the relevant sign on the solvent molecule probably approach the "surface" of the ion closely.

If we assume the effects of primary solvation to be most important, the net result will be large positive transfer free energies in the case of anions, and small negative transfer free energies in the case of cations.

Calculations of Solvation Energies for the Ions.

Rosseinsky [47] reported the hydration energies of several ions. Alfenaar [48] estimated the hydration energy of the H^+ ion to be -253 Kcal/mol. That value was combined with Rosseinsky's data for other ions and converted to molar scale. The results are given in Table 2. The last column represents the molar hydration energy of each ion converted to the logarithmic scale, which is useful for calculations.

From the hydration energy of the ion i, the energy of solvation of that ion in any other solvent s can be calculated via Equation (2) if the relevant transfer free energy, ΔG_i^o is known. The results of such calculations for methanol-water solvents are shown in Table 3. These solvation energies were used only for Equation (14) to calculate $E_{j,ion}$.

TABLE 2

Energies of Hydration for H^+, Na^+, K^+, and Cl^- Ions.

(Molar Scale, 25° C) [47,48]

Ion	G_i^o (H_2O) Kcal/mol	G_i^o (H_2O) / 1.3638
H^+	-252.23	-184.97
Na^+	-90.43	-66.31
K^+	-72.88	-53.44
Cl^-	-83.06	-60.90

TABLE 3

Calculated Solvation Energy, G^{o}_{i} (s) of H^{+}, Na^{+} and Cl^{-} Ions.

(Molar Scale, 25°C)

Wt% MeOH	$G^{o}_{H^{+}}$ (s)	$G^{o}_{Na^{+}}$ (s)	$G^{o}_{Cl^{-}}$ (s)
100	-183.19	-64.75	-58.54
90	-184.44	-64.84	-59.04
80	-185.05	-64.87	-59.44
70	-185.08	-64.96	-59.75
60	-185.07	-65.15	-60.02
50	-185.03	-65.31	-60.22
40	-184.90	-65.42	-60.48
30	-184.86	-65.60	-60.64
20	-184.77	-65.72	-60.85
10	-184.89	-66.04	-60.85
0	-184.97	-66.31	-60.90

Transport Numbers.

For the fairly dilute solutions of sodium chloride and hydrogen chloride (from $1x10^{-1}$ M to $1x10^{-3}$ M), transport numbers at infinite dilution were used. In the literature [49], transport numbers for Na^+ ions in sodium chloride solutions, t_{Na^+} were known only for water, 64 wt% MeOH and 100 wt% MeOH. These were plotted as a function of the concentration of methanol, and a smooth curve was drawn (using the computer) through the three points to be used for the interpolation of t_{Na^+} at the experimental compositions of methanol-water mixtures. In order to obtain a more reliable set of transport-number values, the equivalent conductance of sodium chloride was determined experimentally over the range of 60 wt% to 100 wt% MeOH-water mixtures. The lists of the molar concentrations, C, and the equivalent conductance, Λ, of the NaCl in different compositions of methanol-water mixture are shown in Table 4 in the Appendix 6.

The molar concentrations and corresponding conductance data for sodium chloride in MeOH-water solutions were analyzed in terms of the Fuoss-Hsia conductance theory [50] in the form of equation:

$$\Lambda = \Lambda_0 - SC^{1/2} + EClnC + J_1C - J_2C^{3/2} \qquad (36)$$

where Λ_0 is the equivalent conductance at infinite dilution, S is the Onsager coefficient, J_1 and J_2 are constants with different expressions which are shown in the Appendix 6. A chi-square computer program was used to obtain the values of limiting conductance of NaCl. The transference numbers of sodium ions corresponding to these wt% methanol compositions shown in Table 5 were interpolated from a

large-scale version of the graph of transference numbers of sodium ion vs. wt% methanol. Using these data and the limiting equivalent conductances of NaCl, the limiting equivalent conductances for the chloride ion were calculated using the following equation:

$$\lambda^{o}_{Cl^-} = \Lambda^{o}_{NaCl}(1 - t^{o}_{Na^+}) \qquad (37)$$

TABLE 5

Λ^{o}_{NaCl} (experimental), t_{Na^+} (interpolated) and $\lambda^{o}_{Cl^-}$ (calculated) for MeOH-Water Solvents.

Wt% MeOH	Λ^{o}_{NaCl}	t_{Na^+}	$\lambda^{o}_{Cl^-}$
65.2	66.30	.4448	36.81
72.2	70.73	.4487	38.99
82.5	75.24	.4542	41.06
95.4	88.15	.4608	47.53

Shedlovsky and Kay [51] and De Lisi and Goffredi [52] determined the limiting conductance of HCl throughout the range of MeOH-water solvents. A large-scale version of the graph of limiting equivalent conductance of chloride ion vs. wt% methanol was used to obtain $\lambda^{o}_{Cl^-}$ values in methanol-water solvents for which Λ^{o}_{HCl} were known [51,52]. The t_{H}^{o} values were obtained using Equation (38),

$$t^{o}_{H^+} = 1 - [\lambda^{o}_{Cl^-} / \Lambda^{o}_{HCl}] \quad (38)$$

and plotted as a function of solvent composition to allow for interpolation to experimental MeOH-water composition. The results are shown in Table 6 and Figure 4. As can be seen, the transport numbers of H^+ ions go through a very pronounced minimum at ~95 wt% MeOH.

TABLE 6

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

Wt% MeOH	Λ^o_{HCl}[a]	λ^o_{Cl}[b]	$t^o_{H^+}$[c]
0	426.16	76.34	.8200
10	343.21	63.71	.8158
20	278.32	52.82	.8102
40	190.10	41.10	.7838
60	138.71	37.20	.7412
80	108.01	38.00	.6262
90	103.22	41.30	.5698
94.3	106.87	46.83	.5618
96.2	110.88	48.23	.5650
98.0	119.81	49.90	.5835
99	132.43	51.00	.6149
99.5	149.01	51.65	.6534
99.8	166.88	52.00	.6884
100	198.51	52.38	.7360

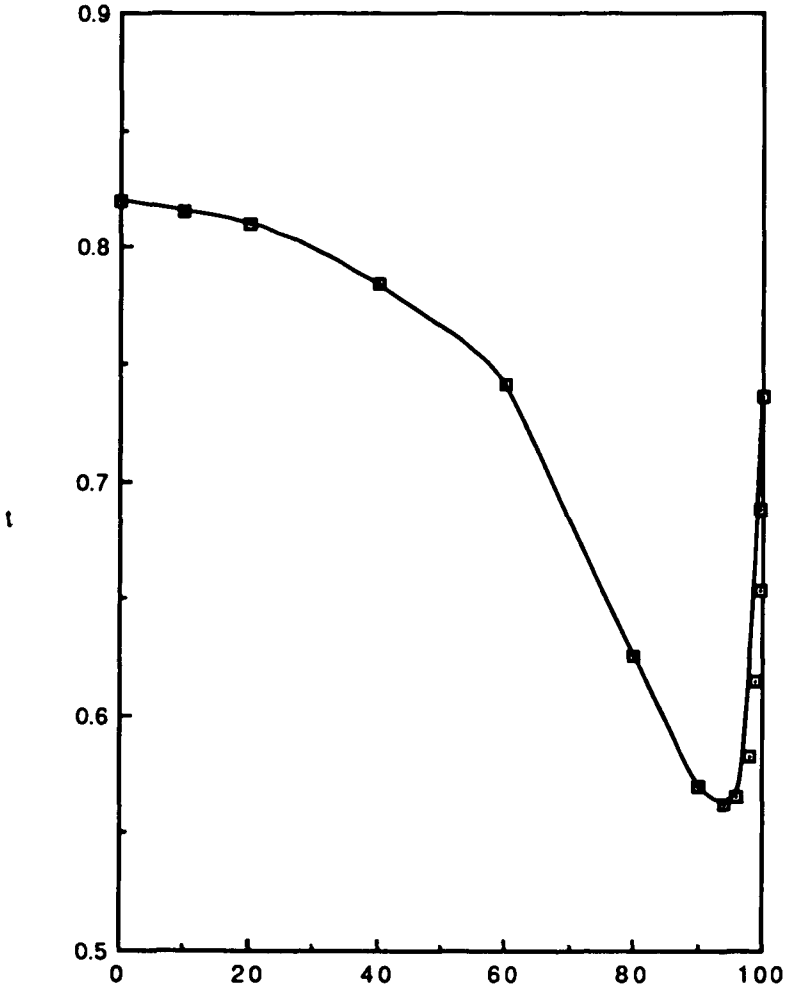
(a) reference [51] and [52]

(b) interpolated value, except for water and methanol

(c) calculated using Equation (38)

FIGURE 4

Limiting Transport Numbers of the H^+ Ion in HCl Solutions in Methanol-Water Solvents.



NaCl|NaCl and HCl|HCl Junctions in the Methanol-Water Mixtures.

The $E_{j,ion}$ values calculated from the new Equations (13) and (14) and the old Equation (10a) for the NaCl|NaCl junction as well as for the HCl|HCl junction are presented in Tables 7 and 8, and are plotted in Figures 5 and 6.

In order to make these calculations, large-scale graphs were made for all available data from the literature as well as our own, for the transfer activity coefficients and transport numbers as a function of wt% solvents. From these graphs, interpolated values were obtained for both transfer activity coefficients and transport numbers for compositions of 2.5 wt% solvent intervals. Initially, the data were interpolated by hand and the $E_{j,ion}$ values calculated on these basis are shown on the LHS of each table (columns 2-5).

Later, using the values available for transfer activity coefficients and transport numbers of ions as a function of solvent composition, smooth curves were drawn by computer (Macintosh SE/30) with reasonable polynomials which were fitted to the curves. From these polynomials, the values of transfer activity coefficient and transport numbers of ions were calculated at each 2.5 wt% solvent composition by computer (IBM Model 50Z). Based on these new sets of data, the $E_{j,ion}$ values shown on the RHS of each table (last 3 columns) were calculated.

The integration required in Equation (14) was performed both graphically (column B_3) as was done by Berne [4], and with the aid of a computer program [53] (column B_2) based on the Romberg integration algorithm [54]. The integration required in Equation (13) was performed only by using the computer program (column B_1).

In Equation (13) the $E_{j,ion}$ is calculated using the summation of

the terms $[t_i(s)\Delta G_i^o(s)/\Delta S]$ for each ion. In Equation (14), the first term can be calculated exactly knowing the standard solvation energies, G_i^o, which can be obtained via Equation (2) with the knowledge of hydration energies and transfer free energies of each ion from the literature, and the transference numbers, t_i, that are known in the two end solutions, S_1 and S_2. The second term can be evaluated as the summation of $[G_i^o(s)\Delta t_i(s)/\Delta S]$. The above-mentioned computer program [53] was used to evaluate these summations of $[t_i(s)\Delta G_i^o(s)/\Delta S\ ]$ and $[G_i^o(s)\Delta t_i(s)/\Delta S]$, respectively.

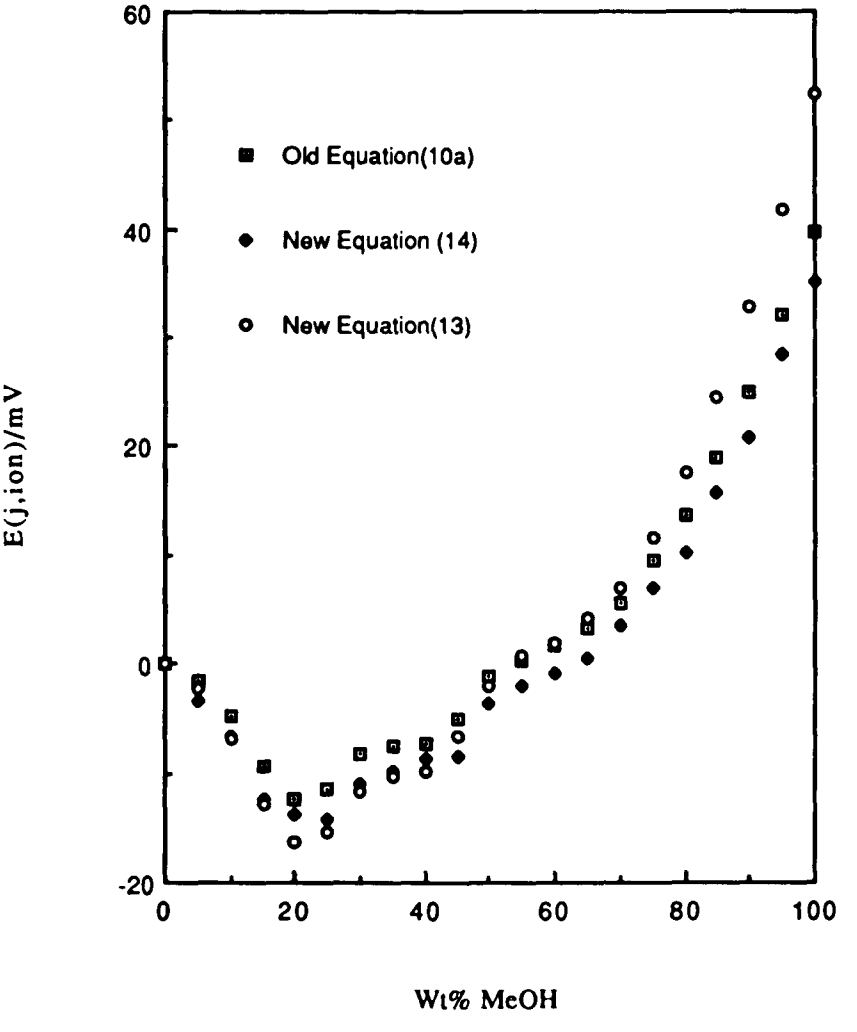
TABLE 7

$E_{j,ion}$ in NaCl | NaCl Cells, in mV at 25°C.
H_2O MeOH- H_2O

Wt% MeOH	Transport Numbers and Transfer Activity Coefficients Interpolated by hand				Interpolated by computer		
	A Eqn.10a	B_1 Eqn.13	B_2 Eqn.14	B_3 Eqn.14	A Eqn.10a	B_1 Eqn.13	B_2 Eqn.14
100	39.7	52.4	35.2	36.2	40.2	53.2	38.6
95	32.2	41.9	28.3	29.0	31.5	30.6	41.5
90	24.9	32.7	20.9	21.4	24.4	32.1	23.0
85	19.0	15.8	24.6	16.1	18.6	24.6	17.7
80	13.6	17.6	10.2	10.4	13.9	18.5	12.8
75	9.4	11.7	6.9	7.0	10.0	13.5	9.8
70	5.6	7.0	3.5	3.7	7.7	9.3	7.0
65	3.2	4.1	0.6	0.8	3.9	5.6	3.6
60	1.6	1.9	-0.9	-0.4	1.5	2.1	1.2
55	0.4	0.8	-2.0	-1.6	-0.7	-1.2	-0.9
50	-1.2	-2.0	-3.6	-3.2	-2.8	-4.0	-2.9
45	-4.9	-6.7	-8.4	-8.0	-4.6	-6.6	-5.8
40	-7.3	-9.8	-8.6	-8.1	-6.3	-8.8	-5.2
35	-7.6	-10.4	-9.9	-9.5	-7.7	-10.7	-7.8
30	-8.2	-11.6	-10.9	-10.7	-8.9	-12.0	-9.3
25	-11.4	-15.4	-14.3	-14.1	-9.5	-12.6	-10.3
20	-12.3	-16.2	-13.8	-13.6	-9.6	-12.4	-8.8
15	-9.5	-12.8	-12.5	-12.3	-8.8	-11.2	-9.6
10	-4.8	-6.8	-6.7	-6.6	-7.1	-8.7	-6.7
5	-1.5	-2.2	-3.4	-3.2	-3.8	-4.8	-3.4

FIGURE 5a

$E_{j,ion}$. Calculations from New Equation[a] and Old Equation[b] for NaCl in Methanol-Water Solvents. (Data interpolated by hand)

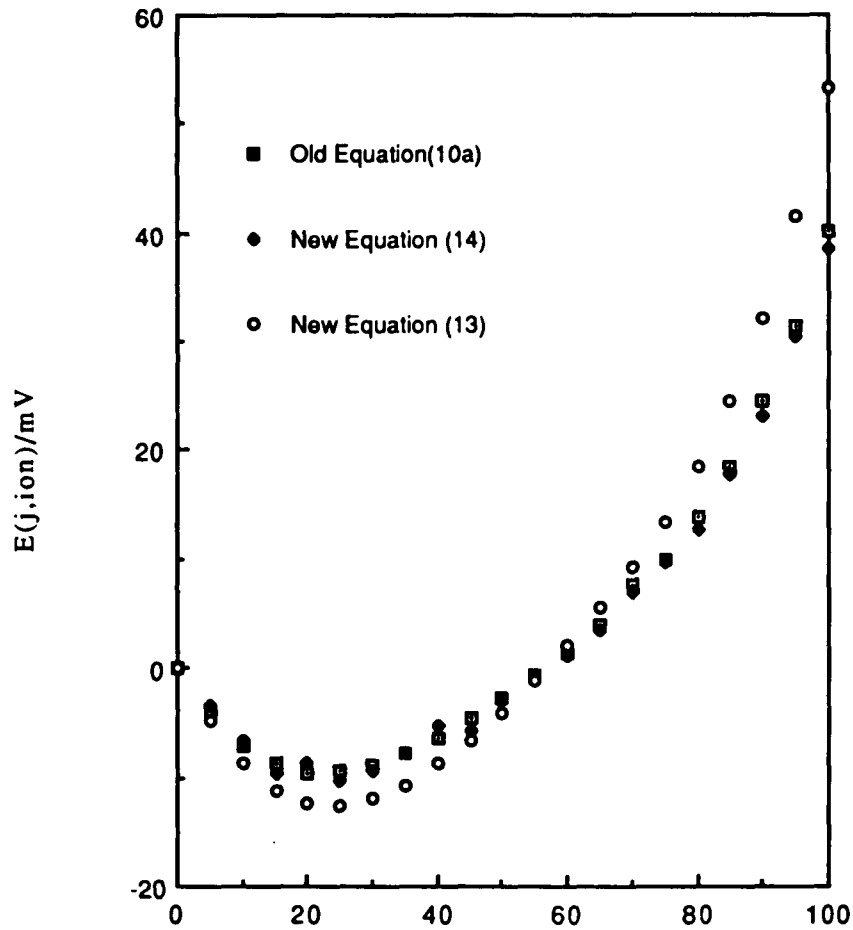


a Column B_1, Table 7, Eqn. 13
Column B_2, Table 7, Eqn. 14

b Column A, Table 7, Eqn. 10a

FIGURE 5b

$E_{j,ion}$. Calculations from New Equation[a] and Old Equation[b] for NaCl in Methanol-Water Solvents. (Data interpolated by computer)



a Column B_1 , Table 7, Eqn. 13
Column B_2 , Table 7, Eqn. 14

b Column A , Table 7, Eqn. 10a

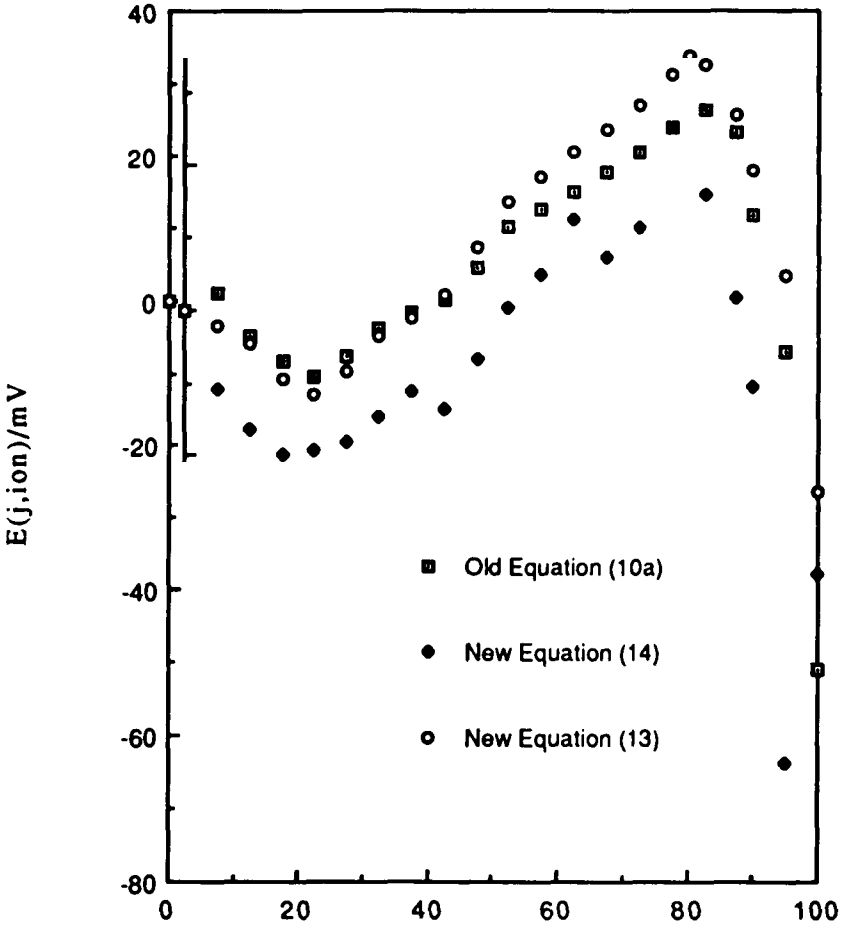
TABLE 8

$E_{j,ion}$ in HCl | HCl Cells, in mV at 25°C.
H_2O MeOH- H_2O

Wt% MeOH	Transport Numbers and Transfer Activity Coefficients Interpolated by hand				Interpolated by computer		
	A	B_1	B_2	B_3	A	B_1	B_2
	Eqn.10a	Eqn.13	Eqn.14	Eqn.14	Eqn.10a	Eqn.13	Eqn.14
100	-51.1	-26.3	-37.7	-56.9	-51.8	-25.4	-25.8
95	-7.1	3.2	-63.8	-89.4	-5.4	5.6	-64.3
90	11.6	17.9	-11.9	-53.4	14.0	-25.3	21.1
85	24.6	1.7	26.8	-8.1	23.0	29.1	-6.8
80	27.5	33.9	15.9	5.1	26.2	32.5	14.2
75	25.3	32.3	25.3	5.9	25.9	32.8	21.6
70	21.7	28.2	11.2	1.0	23.7	30.7	29.2
65	18.9	24.9	7.1	-2.9	20.3	27.0	26.5
60	16.1	21.6	12.5	1.6	16.4	22.2	17.4
55	13.7	18.3	4.6	-1.4	12.4	17.1	11.6
50	11.3	14.8	0.2	-5.1	8.6	11.8	8.9
45	5.9	8.6	-6.7	-11.4	5.1	7.0	5.3
40	1.4	1.9	-13.6	-17.8	2.1	2.6	2.1
35	-0.3	-1.1	-11.3	-15.2	-0.6	-1.2	-4.1
30	-2.4	-3.7	-14.8	-18.0	-2.8	-4.3	-6.5
25	-6.4	-8.4	-18.1	-20.8	-4.7	-6.8	-2.1
20	-9.0	-11.6	-19.1	-20.9	-6.0	-8.3	-9.7
15	-7.2	-9.6	-19.9	-20.8	-6.4	-8.8	-2.8
10	-3.6	-4.7	-16.3	-17.0	-5.9	-7.8	-1.5
5	2.3	-2.1	-10.8	-10.9	-3,6	-4.8	1.2

FIGURE 6a

$E_{j,ion}$. Calculations from New Equation[a] and Old Equation[b] for HCl in Methanol-Water Solvents. (Data interpolated by hand)

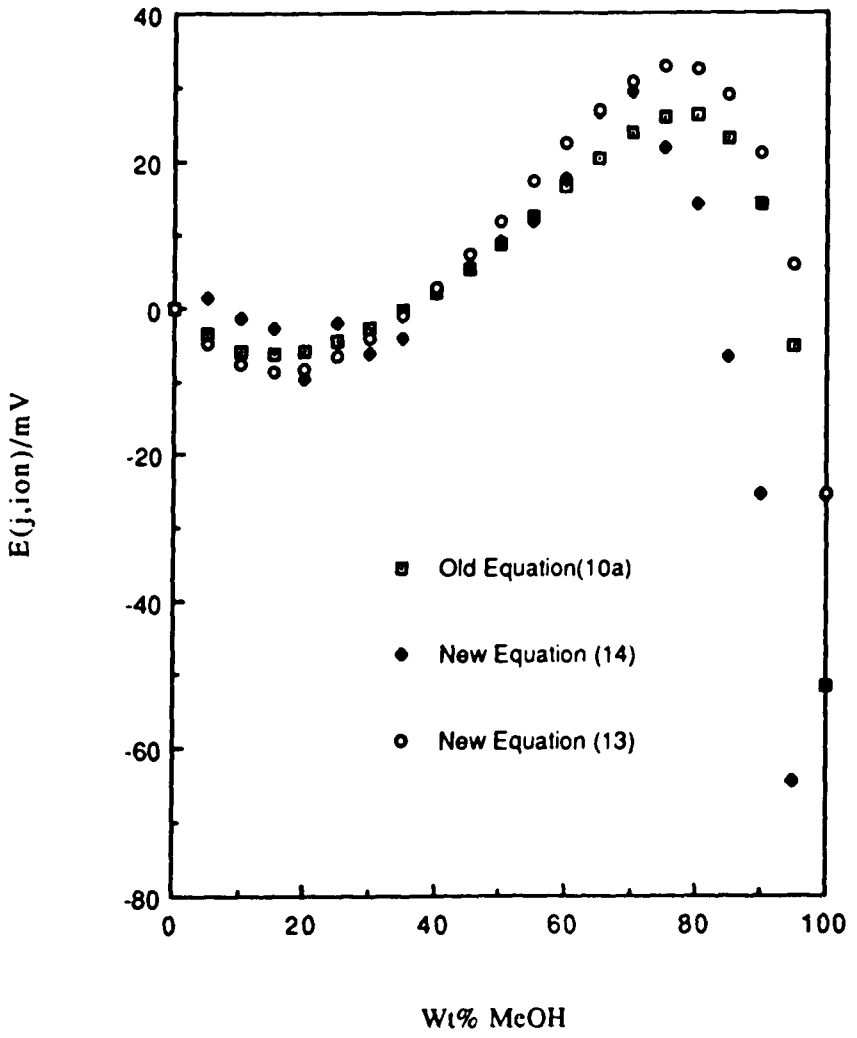


a Column B_1, Table 8, Eqn. 13
Column B_2, Table 8, Eqn. 14

b Column A, Table 8, Eqn. 10a

FIGURE 6b

$E_{j,ion}$. Calculations from New Equation[a] and Old Equation[b] for HCl in Methanol-Water Solvents. (Data interpolated by computer)



a Column B_1, Table 8, Eqn. 13
Column B_2, Table 8, Eqn. 14

b Column A, Table 8, Eqn. 10a

ETHANOL-WATER SOLVENTS.

Transfer Activity Coefficients.

Methanol-water mixtures are less basic than ethanol-water mixtures. Earlier workers [7,55] in our laboratory have estimated the transfer activity coefficients for the proton, $\log_m \gamma_H$, for the entire region of ethanol-water mixtures. From the composition of 10 wt% to 98 wt% ethanol, the transfer activity coefficient is negative and passes through a minimum at 60 wt%. The $\log_m \gamma_H$ increased steeply by approximately 1.6 log units between 98 wt% and 100 wt% ethanol. Between 10 wt% and 98 wt% ethanol the values of $\log_m \gamma_H$ are negative ($_wG_H^o > {}_sG_H^o$). This shows that in that region, ethanol-water mixtures are more basic than either pure water or ethanol. At 60 wt% ethanol, maximum basicity exists.

Braude and Stern [46] concluded that mixtures of water with other solvents are more basic than water in its pure liquid state. Here, its proton affinity is decreased by strong intermolecular hydrogen-bonding. The structure of the water is gradually destroyed by addition of the organic solvent to water, so that the number of basic sites on the water molecules for bonding with the protons is increased. The effective proton affinity of the solvent reaches its maximum when the higher aqueous solvates $H^+(H_2O)_n$ are replaced by H_3O^+ ions. The H_3O^+ ions are gradually replaced by the organic oxonium ions, such as the $C_2H_5OH_2^+$, which are more acidic than H_3O^+ (positive $\log_m \gamma_H$), after the minimum. A positive value of $\log_m \gamma$ means that the ion exists in a lower energy state in water (more favorable solvation) than in the nonaqueous medium and vice versa.

The hydrogen bonding to water molecules strengthens the hydration of the chloride ions. The transfer of chloride ions from water to ethanol and its mixtures is energetically disfavored since the relative hydrogen-bonding ability of water is superior to that of the mixed media, causing the values of $\log_m \gamma_{Cl}$ to be more positive than would be predicted on the grounds of lower dielectric constants alone.

The literature values [7,12,55] for transfer activity coefficients and transport numbers of H^+, K^+ and Cl^- ions, which were known prior to this study, are shown in Tables 9 and 10 and plotted in Figures 7-10.

TABLE 9

Transfer Activity Coefficients of K^+, H^+ and Cl^- Ions in Ethanol-Water Solvents. (Water Reference, Molar Scale) [7,55]

Wt% MeOH	$\log_m \gamma_K$	$\log_m \gamma_H$	$\log_m \gamma_{Cl}$
100	2.10	1.32	2.71
90	1.67	-0.37	2.17
80	1.16	-0.56	1.88
70	0.84	-0.74	1.71
60	0.69	-0.71	1.41
50	0.56	-0.56	1.13
40	0.56	-0.30	0.74
30	0.52	-0.06	0.41
20	0.40	0.06	0.18
10	0.22	0.08	0.05

FIGURE 7

Transfer Activity Coefficients of the H^+ Ion in Ethanol-Water Solvents [7].

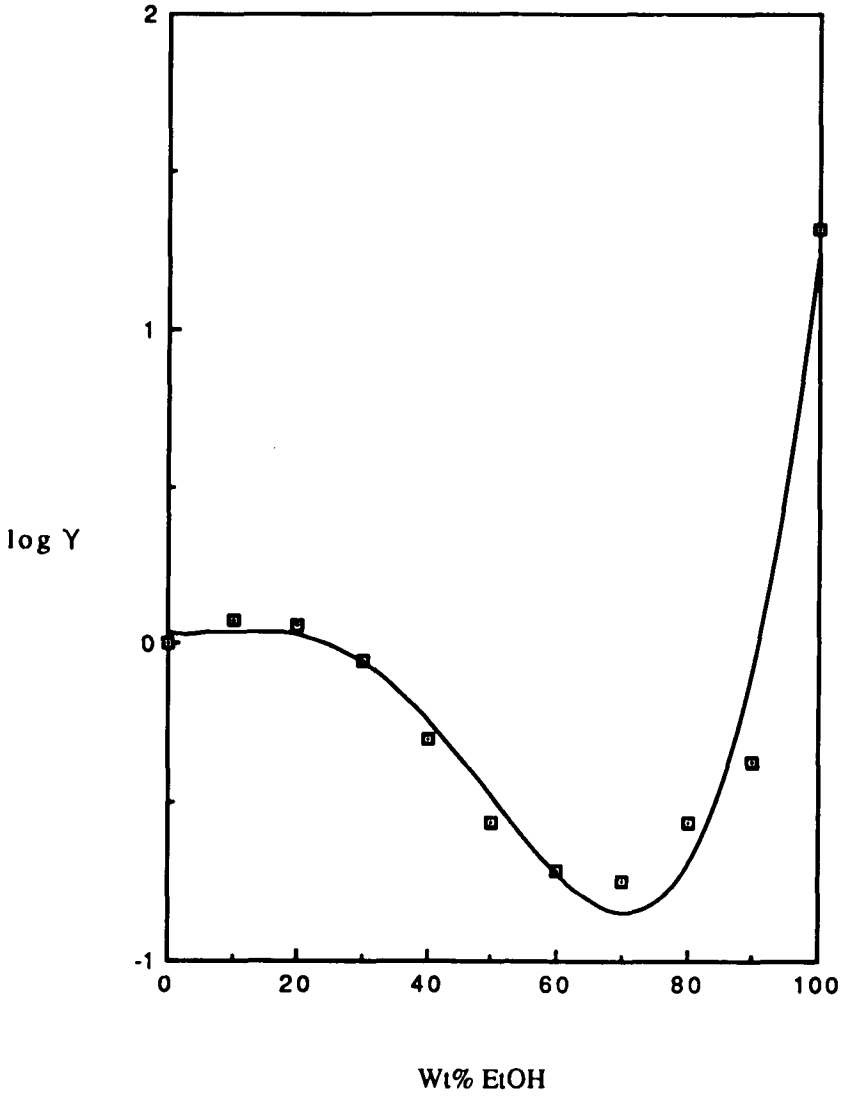


FIGURE 8

Transfer Activity Coefficients of the K^+ Ion in Ethanol-Water Solvents [55].

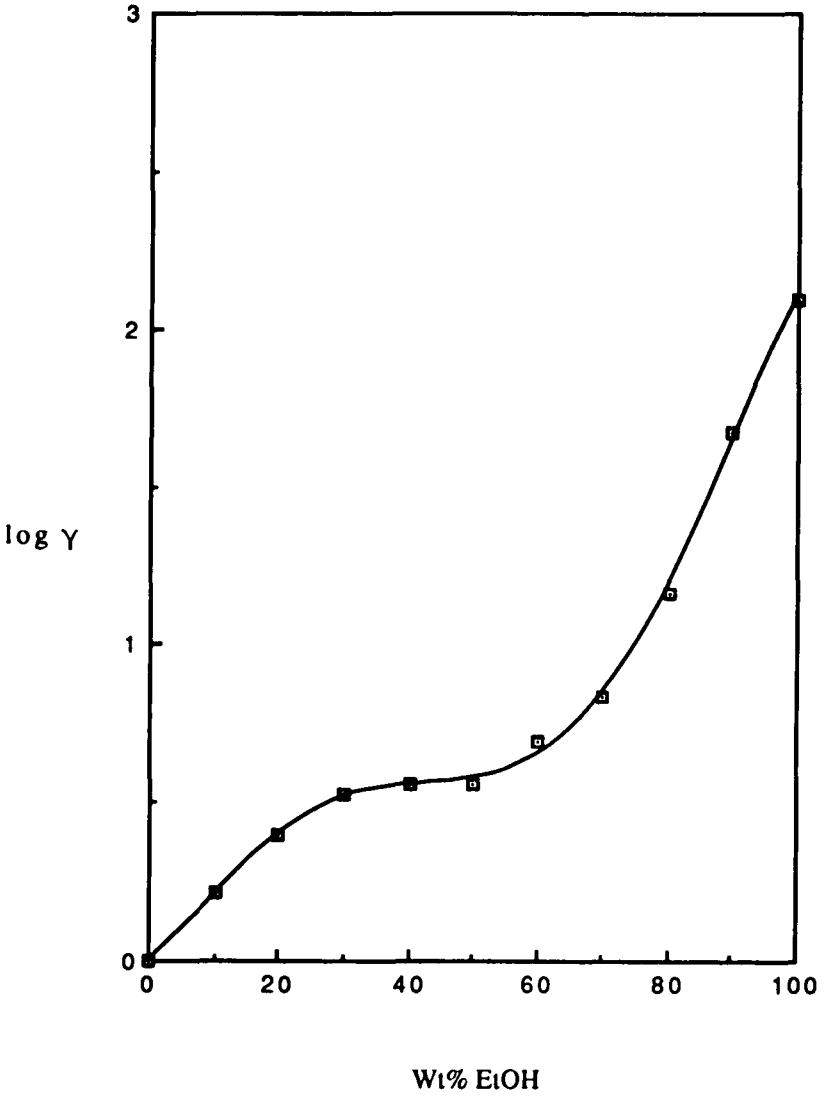


FIGURE 9

Transfer Activity Coefficients of the Cl^- Ion in Ethanol-Water Solvents [55].

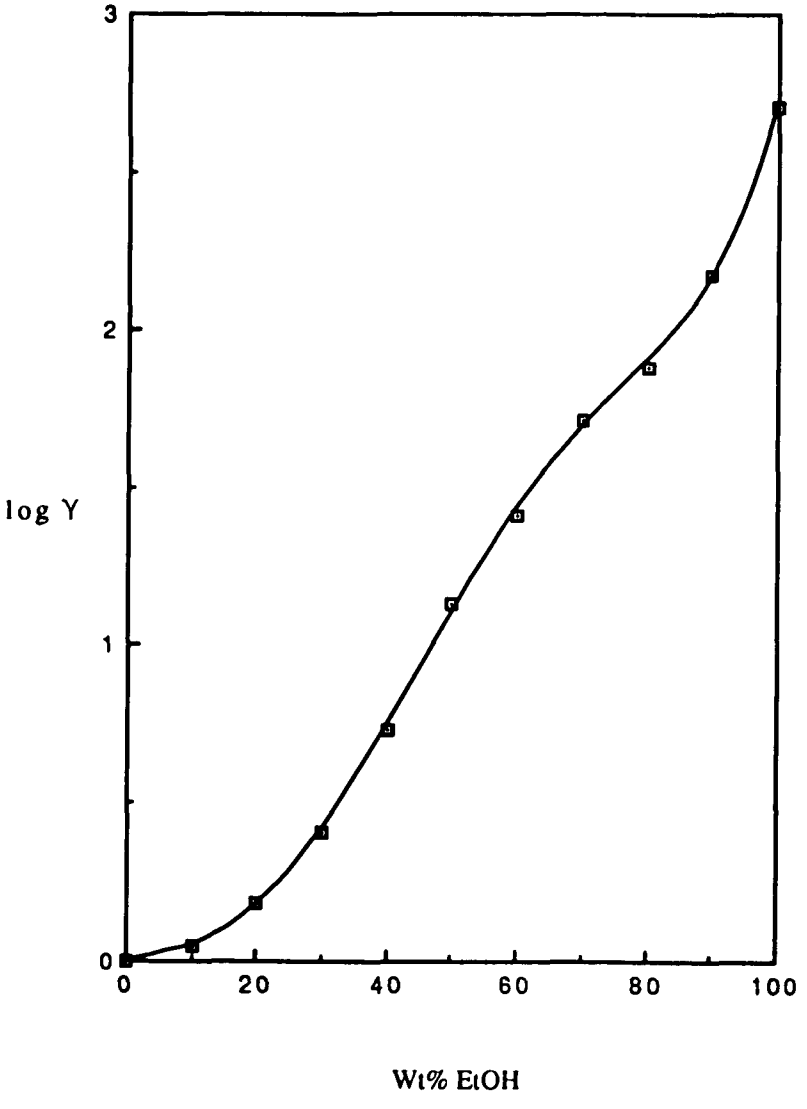


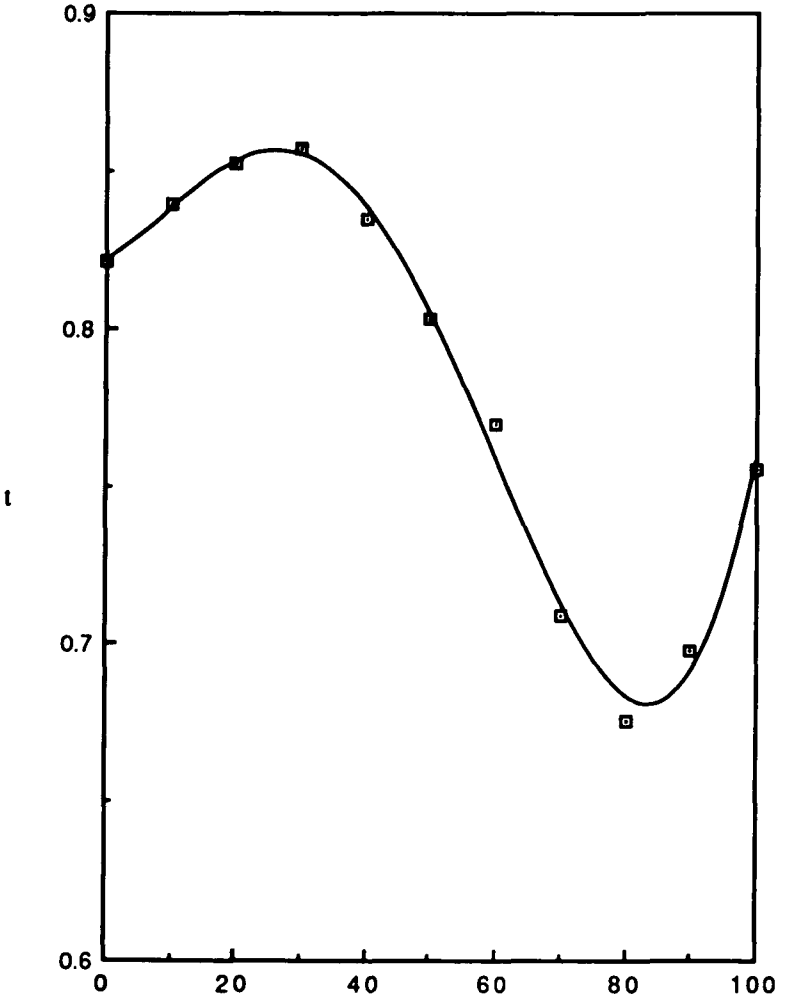
TABLE 10

Limiting Transport Numbers of the H^+ Ion in HCl in Ethanol-Water Solvents [12].

Wt% EtOH	$t^o_{H^+}$
0	.8209
10	.8405
20	.8500
30	.8570
40	.8349
50	.8027
60	.7693
70	.7089
80	.6757
90	.6980
100	.7555

FIGURE 10

Limiting Transport Numbers of the H^+ Ion in HCl Solutions in Ethanol-Water Solvents [12].



KCl|KCl and HCl|HCl Junctions in EtOH-Water Systems.

The $E_{j,ion}$ values calculated from the new Equations (13) and (14) and the old Equation (10a) for the KCl|KCl and HCl|HCl junctions are presented in Tables 11 and 12, and the plots are shown in Figures 11 and 12. Here also, the $E_{j,ion}$ values were calculated in two ways. The values from columns B_1 and B_2 were obtained with the aid of a computer program[53] and column B_3 was obtained by manual interpolation of the data from graphs.

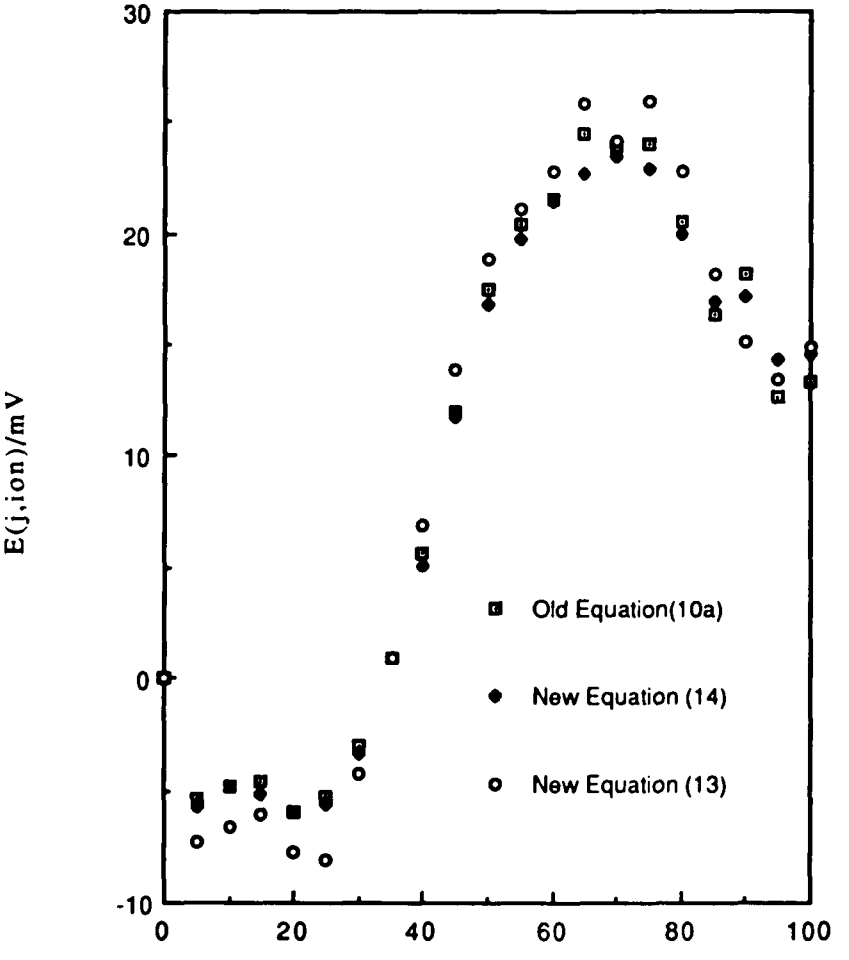
TABLE 11

$E_{j,ion}$ in KCl | KCl Cells, in mV at 25°C.
H_2O EtOH-H_2O

Wt% EtOH	Transport Numbers and Transfer Activity Coefficients Interpolated by hand				Interpolated by computer		
	A	B_1	B_2	B_3	A	B_1	B_2
	Eqn.10a	Eqn.13	Eqn.14	Eqn.14	Eqn.10a	Eqn.13	Eqn.14
100	13.3	14.9	14.6	14.6	13.2	14.6	14.5
95	12.6	13.4	14.3	14.3	12.1	13.5	12.8
90	18.2	15.1	17.2	16.4	15.4	16.2	15.7
85	16.4	18.2	16.9	17.2	16.3	17.8	16.7
80	20.5	22.8	20.0	20.7	20.2	20.1	19.6
75	24.0	25.9	22.9	24.0	23.3	23.2	22.2
70	23.9	24.1	23.5	24.5	25.1	24.5	23.7
65	24.5	25.8	22.7	23.2	25.1	23.8	24.3
60	21.6	22.8	21.4	21.7	23.5	23.9	23.3
55	20.4	21.1	19.7	19.9	20.3	19.5	19.7
50	17.5	18.9	16.8	17.0	16.1	16.7	15.5
45	12.0	13.9	11.7	11.9	11.3	11.2	10.8
40	5.7	6.9	5.1	5.2	6.0	5.4	5.4
35	0.9	0.9	0.9	0.9	1.3	1.4	1.3
30	-3.0	-4.3	-3.3	-3.3	-2.6	-2.8	-2.9
25	-5.3	-8.1	-5.6	-5.5	-5.2	-5.4	-5.6
20	-6.0	-7.8	-6.0	-6.0	-6.5	-6.7	-6.4
15	-4.6	-6.1	-5.2	-5.2	-6.2	-6.4	-6.8
10	-4.8	-6.6	-4.8	-4.8	-4.6	-4.6	-4.6
5	-5.4	-7.3	-5.7	-5.7	-2.2	-2.4	-2.6

FIGURE 11a

$E_{j,ion}$, Calculated from New Equation[a] and Old Equation[b] for KCl in Ethanol-Water Solvents. (Data interpolated by hand)

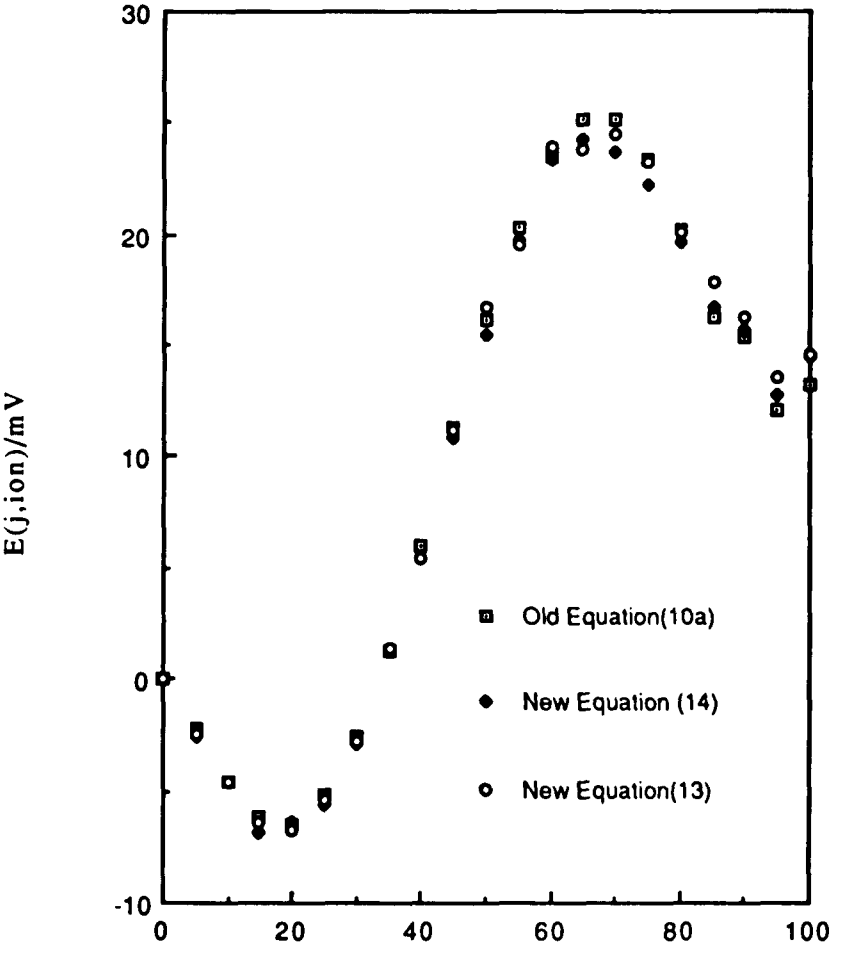


a Column B_2, Table 11, Eqn. 13
Column B_2, Table 11, Eqn. 14

b Column A, Table 11, Eqn. 10a

FIGURE 11b

$E_{j,ion}$, Calculated from New Equation[a] and Old Equation[b] for KCl in Ethanol-Water Solvents. (Data interpolated by computer)



a Column B_2, Table 11, Eqn. 13
Column B_2, Table 11, Eqn. 14

b Column A, Table 11, Eqn. 10a

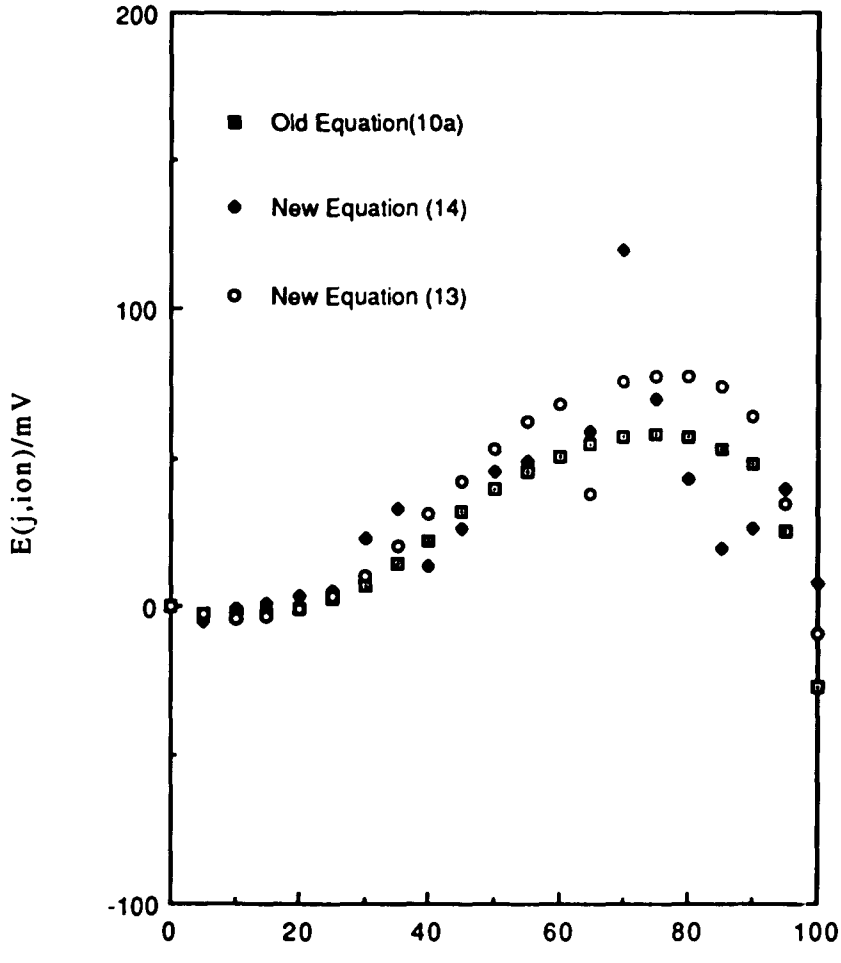
TABLE 12

$E_{j,ion}$ in HCl | HCl Cells, in mV at 25°C.
H_2O EtOH- H_2O

Wt% EtOH	Transport Numbers and Transfer Activity Coefficients Interpolated by hand				Interpolated by computer		
	A	B_1	B_2	B_3	A	B_1	B_2
	Eqn.10a	Eqn.13	Eqn.14	Eqn.14	Eqn.10a	Eqn.13	Eqn.14
100	-27.6	-9.8	7.3	25.2	-27.5	-13.1	-14.3
95	25.4	34.1	39.2	80.2	16.0	24.4	7.2
90	47.7	63.6	26.2	80.4	40.7	50.4	28.0
85	52.9	73.8	19.3	100.4	54.2	67.4	42.3
80	57.3	77.7	42.5	112.2	60.2	77.3	47.2
75	57.9	77.8	70.1	130.6	61.0	81.3	54.9
70	57.4	75.7	119.7	105.7	58.5	80.4	52.7
65	54.5	37.7	59.0	44.4	54.0	75.5	48.3
60	50.5	68.5	68.1	61.1	48.2	67.6	46.5
55	45.5	61.9	48.5	49.0	41.9	57.8	44.3
50	39.7	52.7	45.6	46.1	35.5	46.9	38.3
45	31.6	42.1	25.6	32.9	29.2	35.9	32.2
40	22.1	30.9	13.0	19.4	22.9	25.7	26.3
35	13.7	19.8	32.4	21.3	16.7	16.7	24.0
30	6.7	9.9	22.7	13.8	10.7	9.5	14.4
25	2.1	3.2	4.9	4.1	4.8	4.1	8.6
20	-1.1	-1.3	3.3	1.9	-0.5	0.7	3.2
15	-2.7	-3.8	0.3	-0.8	-4.6	-1.1	2.7
10	-3.4	-4.5	-1.1	-1.3	-6.7	-1.7	-3.1
5	-2.6	-3.2	-5.5	-4.6	-5.4	-1.7	-5.4

FIGURE 12a

$E_{j,ion}$, Calculated from New Equation[a] and Old Equation[b] for HCl in Ethanol-Water Solvents. (Data interpolated by hand)

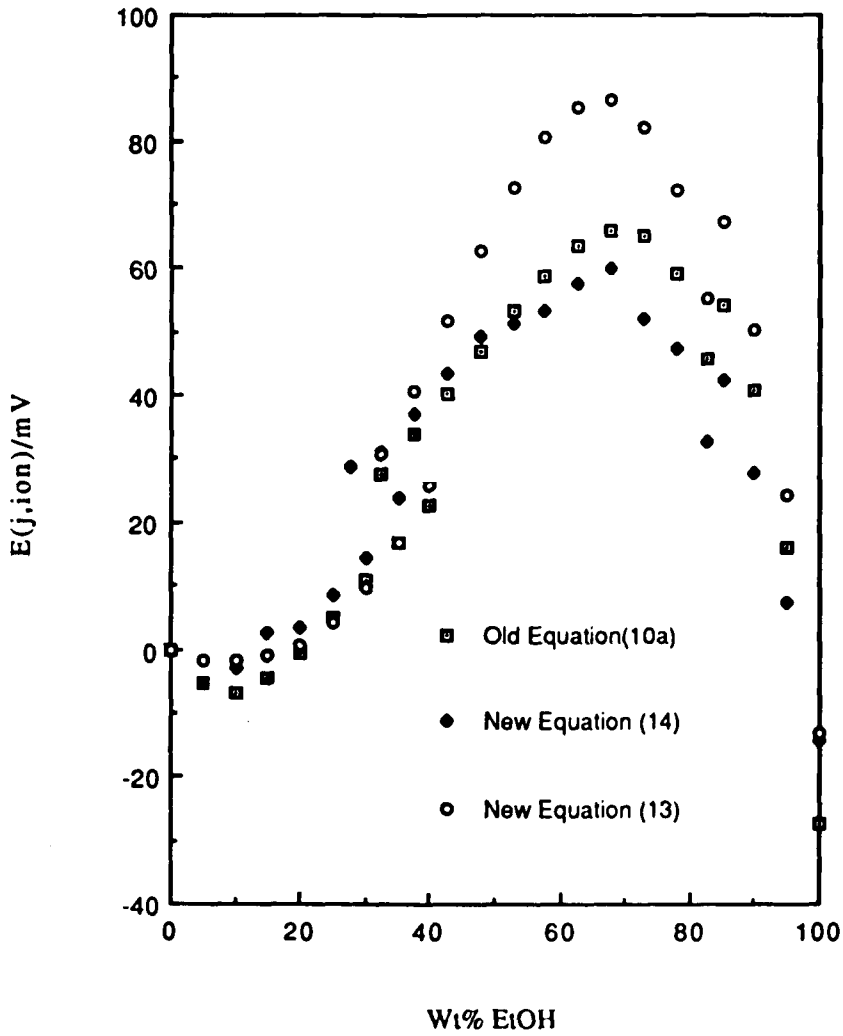


a Column B_1, Table 12, Eqn. 13
Column B_2, Table 12, Eqn. 14

b Column A, Table 12, Eqn. 10a

FIGURE 12b

$E_{j,ion}$, Calculated from New Equation[a] and Old Equation[b] for HCl in Ethanol-Water Solvents. (Data interpolated by computer)



a Column B_1, Table 12, Eqn. 13
Column B_2, Table 12, Eqn. 14

b Column A, Table 12, Eqn. 10a

A Comparison of the $E_{j,ion}$ Calculated from the Old Equation and the New Equation for the Protic Solvents.

In the old equation, we used the average transport numbers for each ion computed for the solvents S_1 and S_2. While this was an improvement over the assumption prevailing in the literature which stated that the t_i values can be taken as solvent independent, meaning that the $E_{j,ion}$ has always been evaluated by placing t_i outside the integral, averaging was still an approximation. A precise formulation was derived by Berne [4] for the $E_{j,ion}$, which accounts for the dependence of t_i and G_i^o on solvent composition in an analytical way. This formulation requires knowledge of the functional dependence of the transport numbers and the transfer activity coefficients of each ion on the mixed-solvent composition in the diffusion layer.

Consider the methanol-water solvent system first. The $E_{j,ion}$ values calculated by the old Equation (10a) and the new Equations (13) and (14) are very similar for the NaCl|NaCl junction through the entire composition of methanol (Figure 3). We can explain these results by considering the curves of transport numbers and transfer activity coefficients of sodium and chloride ions with wt% MeOH. The transport numbers and transfer activity coefficients of sodium and chloride ions vary smoothly over the entire range of MeOH. Because of these smooth variations of the above properties with wt% MeOH we did not obtain any significant difference in $E_{j,ion}$ values between the old equation and the new equation. The differences in $E_{j,ion}$ from both the old and the new equations varied from 0 to 13 mV, with the greatest difference corresponding to pure methanol.

However, the same is not the case for the HCl|HCl junction in

methanol-water solvents. The variation of transfer activity coefficients and transport numbers of hydrogen ion with wt% methanol were discussed earlier. Here, with increasing composition of methanol, the transfer activity coefficients and transport numbers of hydrogen ion decrease smoothly up to 60 wt% MeOH. Up to this region, the differences in $E_{j,ion}$ between the old and the new equations are negligible. But in the composition of methanol between 60 to 100 wt%, the variation of the above properties is not smooth, but showing minima at ~70 wt% and ~ 90 wt% MeOH for the behavior of transfer activity coefficients and transport numbers of hydrogen ions, respectively. As the results in Table 8 show for the $E_{j,ion}$ calculation from both the old and the new equations, the significant differences are observed for the solvent compositions between 70 to 100 wt% MeOH, because in this region the t_H passes through a pronounced minimum. It is also noteworthy that in this region the differences in $E_{j,ion}$ values between old equation (10a) and new equation (14) are greater than that between the old (10a) and the new (13) equation (Figure 6). As was discussed earlier, to calculate $E_{j,ion}$ using Equation (14) we have to evaluate the drastically changing slope $\Delta t/\Delta s$ and also we need the values for hydration energies for each ion from the literature. Because of these reasons, Equation (14) gives more erratic results in $E_{j,ion}$ calculations than Equation (13). The differences in $E_{j,ion}$ values range from 0-60 mV between Equation (10a) and (14), so that the changes are much higher than those between Equation (10a) and (13), which range from 0-25 mV. The highest $E_{j,ion}$ difference between Equation (10a) and (14) corresponds to 95 wt% MeOH, and that between Equation (10a) and (13) corresponds to 100 wt% MeOH.

Similar results were obtained for EtOH-water mixtures. The

difference of $E_{j,ion}$ between both Equation (13) and (14) on the one hand and the old equation (10a) on the other hand varied from 0 - 4 mV for the entire range of ethanol-water solvents for KCl|KCl junctions. We can explain these results when considering the variation of transport numbers and transfer activity coefficients of K^+ and Cl^- ions. The above properties of K^+ and Cl^- ions vary smoothly with increasing ethanol composition. Because of the smooth variation of transfer activity coefficients and transport numbers of ions, the differences in $E_{j,ion}$ between the old equation and the new equations were not significant. Smooth curves were obtained for the plots of $E_{j,ion}$ vs. wt% EtOH, from both new equations and the old equation.

However, this is not the case for HCl|HCl junction in EtOH-water solvents. The plots of transfer activity coefficients (Figure 7) and transport numbers (Figure 10) of hydrogen ion vs. wt % EtOH show a smooth variation with composition of ethanol up to 50 wt%, and then minima at ~ 70 wt% and ~80 wt% EtOH, respectively. Because of this smooth behavior of the above properties, the difference in $E_{j,ion}$ values from both new and the old equations are negligible for the composition of ethanol up to 50 wt%. But differences in $E_{j,ion}$ values between the old equation and the new equations were observed for the solvent compositions between 50 to 100 wt% EtOH. The differences of $E_{j,ion}$ between Equations (13) and (10a) (which vary from 0 - 22 mV) are greater than between Equations (14) and (10a) (which vary from 0 - 13 mV) for the entire range of EtOH. The difference in $E_{j,ion}$ between Equation (10a) and (13) increases with the concentration of ethanol up to 70 wt% EtOH, and then decreases from 70 - 100 wt% EtOH.

Here, we must consider the changing slopes $\Delta t/\Delta s$ and $\Delta G^p/\Delta s$

when calculating $E_{j,ion}$ from Equations (14) and (13), respectively. Although both slopes $\Delta t/\Delta s$ and $\Delta G^{o}/\Delta s$ change appreciably, it seems that Equation (13) gives more erratic results than Equation (14). This is so because the transfer activity coefficients of the hydrogen ion pass through a pronounced minimum at ~70 wt% EtOH. In the calculations of $E_{j,ion}$ from Equation (13) we have to consider the drastically changing slope $\Delta G^{o}/\Delta s$. Because of this, the difference in $E_{j,ion}$ between the Equation (13) and the old equation is significant in the region where $\log_m \gamma_H$ passes through a pronounced minimum.

Studies in Aqueous Mixtures of Dipolar Aprotic Solvents.

The dipolar aprotic solvents with high dielectric constants and large dipole moments have been of special interest in this study. They are high-boiling liquids with a large liquid range and a variety of viscosities and refractive indices, and are poor conductors of electricity. Positive charge density is usually centered at a crowded site in such a molecule, and these solvents are not donors of hydrogen bonds. However, the center of negative charge density is usually on a highly basic oxygen or nitrogen atom which is very much exposed for intermolecular interaction with positive or acidic centers.

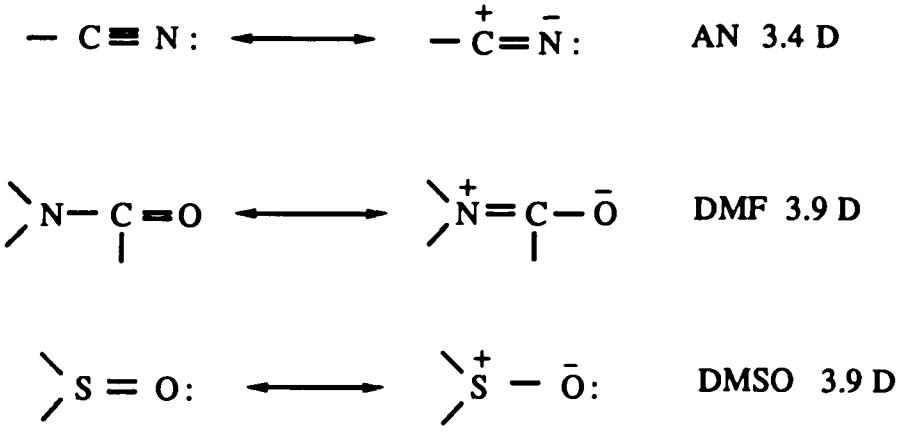


Figure 13

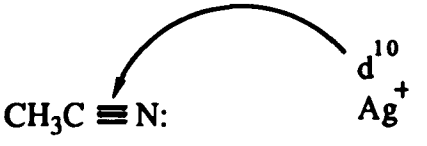
Together with the dipole moments, the typical structures of dipolar aprotic solvents are shown in Figure 13. The resonance structures help to interpret ionic solvation.

Aqueous AN mixtures were observed [56] to discriminate between cations and anions to a lesser extent than aqueous DMSO and DMF mixtures, the anion-destabilization and cation-solvation being more or less similar in magnitude in aqueous mixtures of both DMF and DMSO. The decreasing polarizabilities and dipole moments of DMSO>DMF>AN [56] are in agreement with the increasingly negative values of ΔG_t^o of ions in aqueous mixtures of DMSO>DMF>AN.

ACETONITRILE-WATER SOLVENTS.

Because of the contrasting behavior of alkali-metal cations, which are more strongly solvated by water on the one hand and silver (and cuprous) cations, which interact more strongly with acetonitrile [12] on the other hand, acetonitrile-water mixtures are particularly interesting in relation to studies of ion-solvent interactions.

Being rather weak bases, nitriles interact with most cations much less strongly than water, but they interact strongly with a limited number of cations which are capable of back donation, i.e., cations like Ag^+, Cu^+ and Au^+, which donate d electrons into π^* antibonding orbitals of the nitrile group. A synergistic effect between back bonding and the normal weak acid-base interaction between acidic cation and basic nitrile provides a strong interaction, e.g.,



Thus, acetonitrile solvates silver and cuprous cations more strongly than water, whereas most cations, e.g., Na^+ ion and especially the H^+ ion are less solvated by acetonitrile than by water. Transfer from water to acetonitrile and even to 0.1 mole fraction AN-water produces a very significant stabilization of the Ag^+ ion. In dilute AN-water mixtures, most cations are solvated much as though they were in a purely aqueous medium, but the AN is not an "inert" diluent when Ag^+ ion is present. The values of transfer free energies

for the Ag^+ ion rapidly become quite exoenergetic for transfer to solutions containing only a small amount of AN.

There were some transfer activity coefficients and transport numbers for the aqueous mixtures of the acetonitrile available in the literature [57-59], but additional data had to be determined experimentally in the course of this study. For example, there were no transfer activity coefficients for the nitrate ion, $^{\log_m \gamma_{NO_3}}$, available for the AN-water system, and they were needed for the calculation of $E_{j,ion}$ at the junction of silver nitrate solutions. The literature values for transfer activity coefficient and transference numbers of Ag^+ and NO_3^- ions in AN-water mixtures that were available prior to this study are shown in Tables 13 and 14, and plotted in Figures 14 and 15.

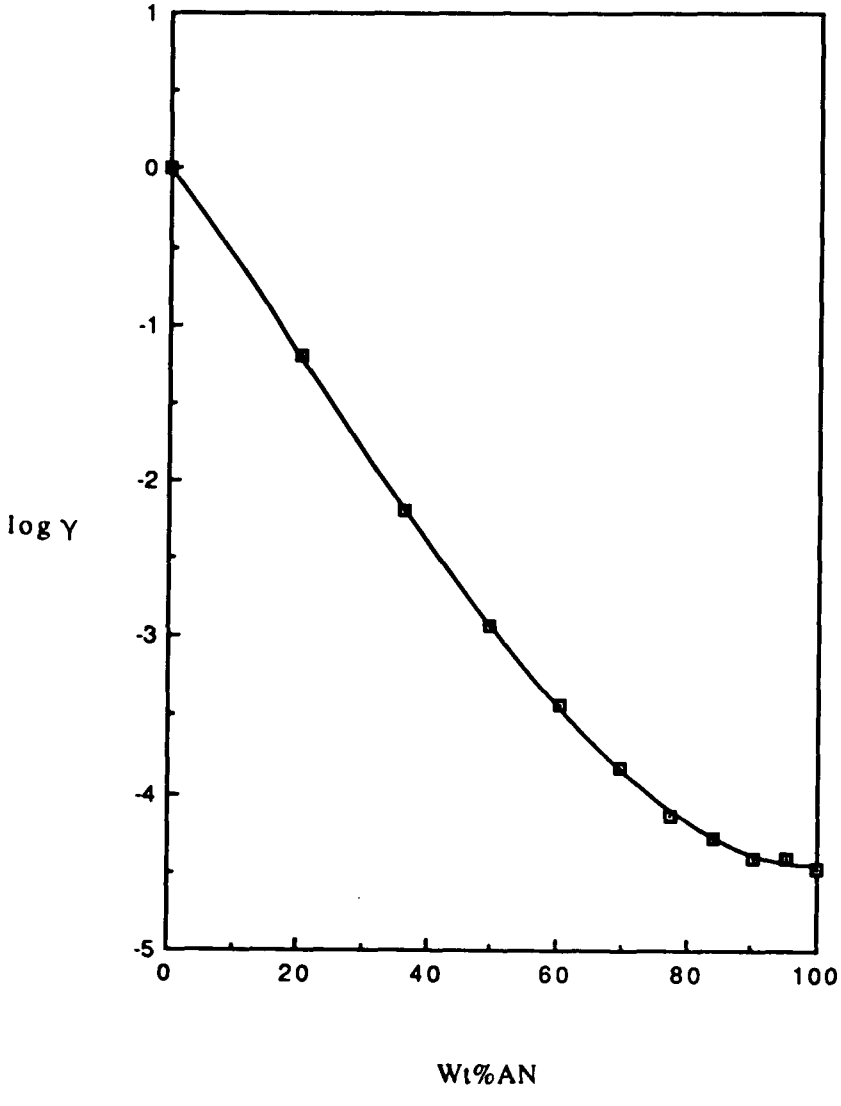
TABLE 13

Transfer Activity Coefficients of the Ag^+ and Ph_4P^+ Ions in Acetonitrile-Water Solvents. (Molar Scale at 25°C) [59].

Wt% AN	$\log {}_m\gamma_{Ag}$	$\log {}_m\gamma_{Ph_4P}$
20.2	-1.20	-1.53
36.3	-2.20	-2.91
49.4	-2.93	-3.77
60.3	-3.42	-4.36
69.5	-3.83	-4.73
77.4	-4.13	-5.17
84.2	-4.28	-5.16
90.1	-4.40	-5.30
95.4	-4.41	-5.44
100	-4.47	-5.56

FIGURE 14

Transfer Activity Coefficients of the the Ag^+ Ion in AN-Water Solvents [59].



Transport Numbers

Strehlow and Koepp [58] determined the conductivity, the transference numbers and the viscosity of $AgNO_3$ solutions in AN-water mixtures in order to obtain the Walden product of the single ions by using the following relationship:

$$\lambda_o\eta = FeZ/6pr_s \qquad (39)$$

where F is the Faraday constant, e the electronic charge, Z the absolute ionic valence and r_s the radius of the solvated ion. The Walden product ($\lambda_o\eta$) is inversely proportional to the radius of the solvated ion. With the addition of acetonitrile to the pure aqueous solution, the Walden product decreases very steeply with the increase of the radius of the solvated silver ion. The ions solvated by nitrile are bulkier than those solvated by water, because of the larger acetonitrile molar volumes. Therefore, the silver ions are preferentially solvated by the larger acetonitrile molecules at low mole fractions. On the other hand, the solvation radius of the nitrate ion increases up to the mole fraction 0.7 on the addition of water to a solution of silver nitrate in pure acetonitrile. This is due to a preferential hydration of the nitrate ion.

The transport numbers of the nitrate ion were found to be almost independent of $AgNO_3$ concentration, but they varied significantly with the mixed-solvent composition [57]. Figure 15 shows the variation of the limiting transference numbers of the nitrate ion with wt% of aqueous AN. A strong structural effect appears in AN-water mixtures at ~26 wt% AN and at ~80 wt% AN, where a maximum and a minimum in the curve were observed, respectively.

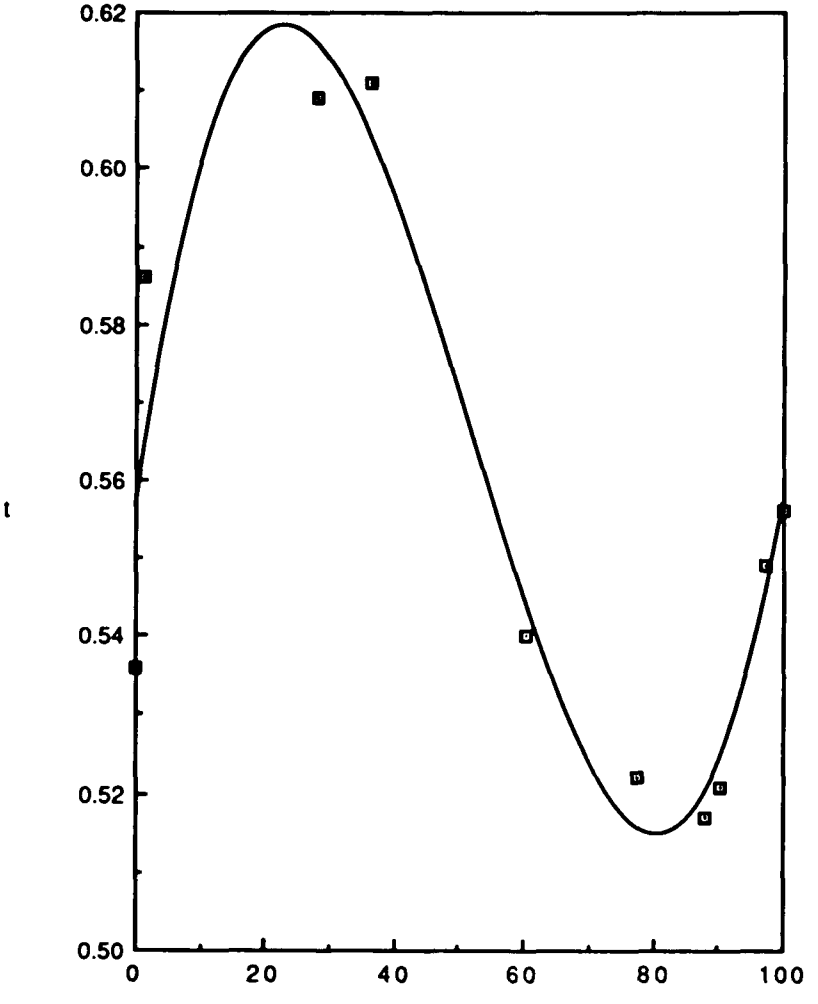
TABLE 14

Limiting Transport Numbers of NO_3^- and Ag^+ Ions in Acetonitrile-Water Solvents [57,58].

Wt% AN	$t_{NO_3^-}$	t_{Ag^+}
0	.536	.464
1.3	.586	.414
27.9	.609	.391
36.3	.611	.389
60.3	.540	.460
77.4	.522	.478
87.8	.517	.483
90.1	.521	.479
97.4	.549	.451
100	.556	.444

FIGURE 15

Limiting Transport Numbers of the NO_3^- in Acetonitrile-Water Solvents [57,58].



Determination of Transfer Activity Coefficients of the Nitrate Ion in Acetonitrile-Water Solvents.

1. The Solubility Method of Determining Transfer Activity Coefficients

As previously discussed, transfer activity coefficients of the nitrate ion, $^{log}{}_{m}\gamma_{NO_3}$ are required to calculate the $E_{j,ion}$ at the junction of $AgNO_3$ solutions. Transfer activity coefficients of tetraphenylphosphonium nitrate were calculated from solubility measurements, using Equation (40):

$$\log {}_{m}\gamma_i = p({}_{s}K_{sp}) - p({}_{w}K_{sp}) \qquad (40)$$

where s and w refer to the solvent of interest and water, respectively. The values of $^{log}{}_{m}\gamma_{NO_3}$ were calculated from available data [59] for the transfer activity coefficients of the $^{log}{}_{m}\gamma_{Ph_4P^+}$ ion by using the following relationship:

$$\log {}_{m}\gamma_{NO_3} = \log {}_{m}\gamma_{Ph_4PNO_3} - \log_{m}\gamma_{Ph_4P} \qquad (27e)$$

The solubility of Ph_4PNO_3 in acetonitrile-water mixtures was found spectrophotometrically. The experimentally determined values of the molar absorptivity were obtained using solutions of known concentration of Ph_4PNO_3. The results are shown in Table 15.

TABLE 15

Peak Molar Absorptivity of the Tetraphenylphosphonium Ion in Acetonitrile-Water Solvents at 25° C.

Wt% AN	$10^{-3}\ \varepsilon_{max}$ 265nm	272nm
0	3.83	3.12
18.8	3.85	3.13
33.3	3.82	3.15
47.4	3.90	3.24
57	3.80	3.20
64.4	3.84	3.23
70.5	3.82	3.22
85.5	3.94	3.36
100	4.08	3.51

The mean activity coefficients (molar scale) for this electrolyte were calculated by means of the Davies equation:

$$\log f_{\pm} = -A[c^{1/2}/(1+c^{1/2}) - 1/3\ c] \qquad (41)$$

where f is the activity coefficients, A is the Debye-Huckel constant, and c is the molar solubility. The solubility products for Ph_4PNO_3 were calculated as:

$$K_{sp} = (cf_{\pm})^2 \qquad (42)$$

Table 16 summarizes the solubility, activity coefficients, solubility products and transfer activity coefficients of Ph_4PNO_3, and the nitrate ion.

TABLE 16

Solubilities, Activity Coefficients, Solubility Products and Transfer Activity Coefficients of Tetraphenylphosphonium Nitrate and of the Nitrate Ion in Acetonitrile-Water Solvents at 25° C (Molar Scale).

Wt% AN	Solubility moles/L c	Activity Coefficients $f_{\pm}$	Solubility Products $c^2 f_{\pm}^2$	$\log {}_m\gamma_{Ph_4P\,NO_3}$	$\log {}_m\gamma_{NO_3}$
0.00	.082	.099	6.72×10^{-5}	0.0	0.0
9.40	.284	.728	4.27×10^{-2}	-2.50	-1.77
19.30	.934	.770	5.17×10^{-1}	-4.12	-2.68
26.5	1.25	.847	1.12	-5.91	-3.83
36.0	1.48	.911	1.81	-6.88	-3.98
47.2	1.61	.960	2.40	-7.91	-4.27
58.8	1.524	.907	1.91	-8.50	-4.21
77.0	1.290	.752	9.41×10^{-1}	-8.79	-3.85
86.7	1.075	.621	4.45×10^{-1}	-8.43	-3.22
100	0.553	.089	2.35×10^{-3}	-8.61	-3.05

2. The Determination of Transfer Activity Coefficients of the Nitrate Ion from the E.M.F. of Cells with Liquid Junction.

Goldberg [25], and Goldberg and Popovych [26] suggested a new method to determine transfer activity coefficients of ions by using e.m.f. cells with salt bridges between the reference solvent and the solvent of interest. In this method, the transfer activity coefficients of one of the salt-bridge ions can be estimated when the transfer activity coefficient of the other salt-bridge ion and of the electroactive ion are known. Later, this method was successfully applied by Berne and Popovych [27] using several salt-bridge electrolytes in various dipolar aprotic solvent pairs. In this study the above method was used to determine transfer activity coefficients of the nitrate ion with the aid of the following cell:

$$\begin{array}{c} Ag \mid AgNO_3 \mid Ph_4PNO_3 \mid AgNO_3 \mid Ag \\ H_2O \quad H_2O \quad AN\text{-}H_2O \end{array} \qquad \text{(XXI)}$$

The $AgNO_3$ concentrations were kept approximately equal in both half-cells. E.m.f. measurements were made with $1x10^{-1}$, $1x10^{-2}$ and $1x10^{-3}$M solutions of $AgNO_3$. Tetraphenylphosphonium nitrate was used as the salt-bridge electrolyte.

The formulation for the e.m.f. of cell (XXI) consists of three terms, E_1, $E_{j,G}$ and $E_{j,H}$. For this study, $E_{j,S}$, the solvent contribution to liquid-junction potential E_j, is assumed to be negligible.

E_1 is a term representing the difference between the electrode potentials:

$$E_1 = 59.16 \log_m \gamma_{Ag} + 59.16 \log ({}_{AN}a_{Ag} / {}_{w}a_{Ag}) \qquad (43)$$

where the transfer activity coefficients of the silver ion, $\log_m \gamma_{Ag}$, pertains to the transfer from water to the AN-water, and ${}_{AN}a_{Ag}$ and ${}_{w}a_{Ag}$ are the conventional activities of Ag^+ ion in acetonitrile and water respectively.

The $E_{j,G}$ term accounts for the contributions of transfer activity coefficients and transport numbers of all the ions present in the diffusion layer (Equation 10b). As applied to cell (XXI), it is given by:

$$E_{j,G} = -59.16\ [t_{Ag} \log_m \gamma_{Ag} + t_{Ph_4P} \log_m \gamma_{Ph_4P} - t_{NO_3} \log_m \gamma_{NO_3}] \quad (44)$$

The last term in the formulation of the e.m.f. of cell (XXI) is the term $E_{j,H}$, which is the result of applying the Henderson equation to a junction with a salt-bridge, in this case a Ph_4NO_3 bridge:

$$E_{j,H} = -59.16\ (t_{Ph_4P} - t_{NO_3}) \log ({}_{AN}a_{AgNO_3} / {}_{w}a_{AgNO_3}) \quad (45)$$

where t_{Ph_4P} and t_{NO_3} are the average transport numbers of the tetraphenylphosphonium and nitrate ions, respectively and the a_{AgNO_3} is the conventional mean ionic activity of $AgNO_3$ in either solvent.

When the measured e.m.f. of cell (XXI) is combined with the equations for E_1, $E_{j,G}$ and $E_{j,H}$, the resulting expression can be rearranged in terms of all the known quantities and solved for $\log_m \gamma_{NO_3}$, which is the unknown quantity.

$$\log\gamma_{NO_3} = \frac{E_{Cell}}{59.16\, t_{NO_3}} \left[\frac{1 - t_{Ag}}{t_{NO_3}}\right] \log\gamma_{Ag} + \frac{t_{Ph_4P}}{t_{NO_3}} \log\gamma_{Ph_4P} + \left[\frac{t_{Ph_4P} - t_{NO_3}}{t_{NO_3}}\right] \log\frac{^2a_{Ag}}{^1a_{Ag}} \quad (46)$$

In order to use Equation (46) to calculate $^{\log_m}\gamma_{NO_3}$, the following sets of data had to be available:

a). Transfer activity coefficients of Ag^+ and Ph_4P^+ ions between water and all the AN/water solvents.

b). Transport numbers of the Ag^+, NO_3^- and Ph_4P^+ ions in all the solvents.

c). Activities of the Ag^+ ion in all the solvents.

The calculated transfer activity coefficients of NO_3^- ion from the solubility method (Equation 40) and the E_j method (Equation 46) are shown in Table 17 and are plotted in Figure 16.

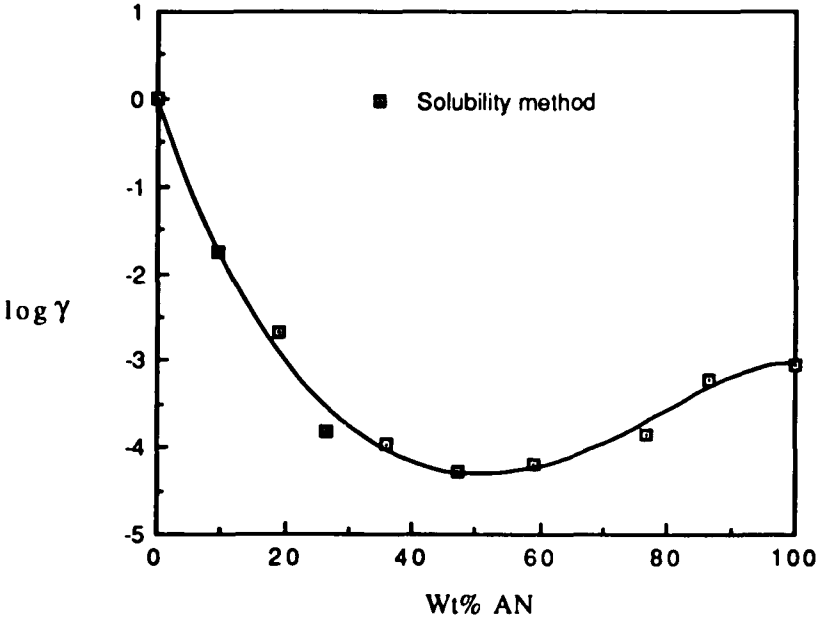
TABLE 17

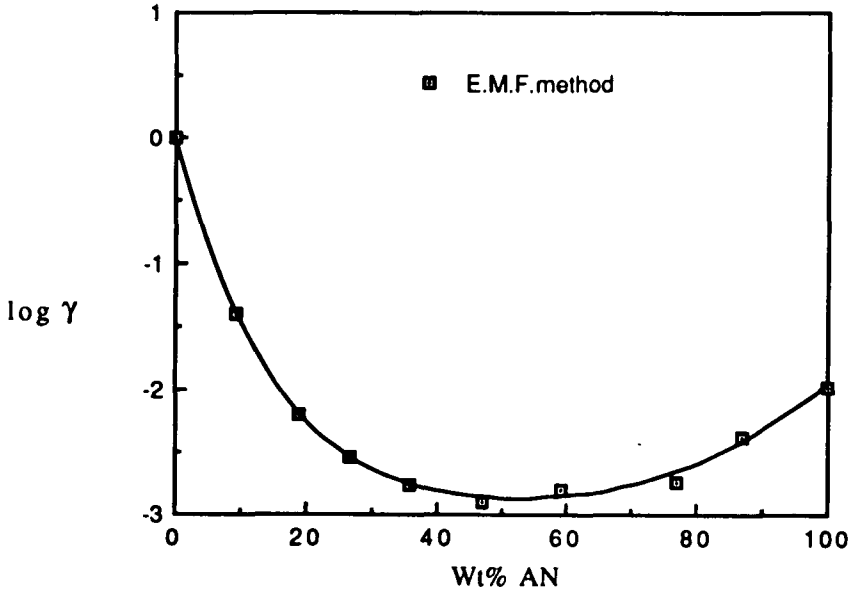
Transfer Activity Coefficients of the NO_3^- Ion in Acetonitrile-Water Mixtures. (Molar Scale, 25°C)

Wt% AN	$\log_m \gamma_{NO_3}$ (From E_j in cell XXI) (Eqn 46)	$\log_m \gamma_{NO_3}$ (From solubility) (Eqn 40)
9.4	-1.39	-1.77
19.1	-2.20	-2.68
26.5	-2.54	-3.83
36.1	-2.76	-3.98
47.1	-2.89	-4.27
58.9	-2.80	-4.21
76.7	-2.74	-3.85
86.7	-2.38	-3.22
100	-1.98	-3.05

FIGURE 16

Transfer Activity Coefficients of the NO_3^- Ion in Acetonitrile-Water Mixtures.





$AgNO_3|AgNO_3$ Junction in the Acetonitrile-Water Systems.

Using these transfer activity coefficients and transport numbers for Ag^+ and NO_3^- ions, the values of $E_{j,ion}$ from the new Equations (13) and (14) and the old equation were calculated and compared. The values of transfer activity coefficients of the nitrate ion from the e.m.f. method were used for the calculations. The results are shown in Table 18 and plotted in Figure 17. The columns A and B_1 represent the $E_{j,ion}$ values from the old equation and the new equation (13), respectively. As mentioned earlier, the $E_{j,ion}$ values in columns B_2 and B_3 were obtained by Equation 14 (two terms). The second term of this equation was solved both by computer and by graphic integration.

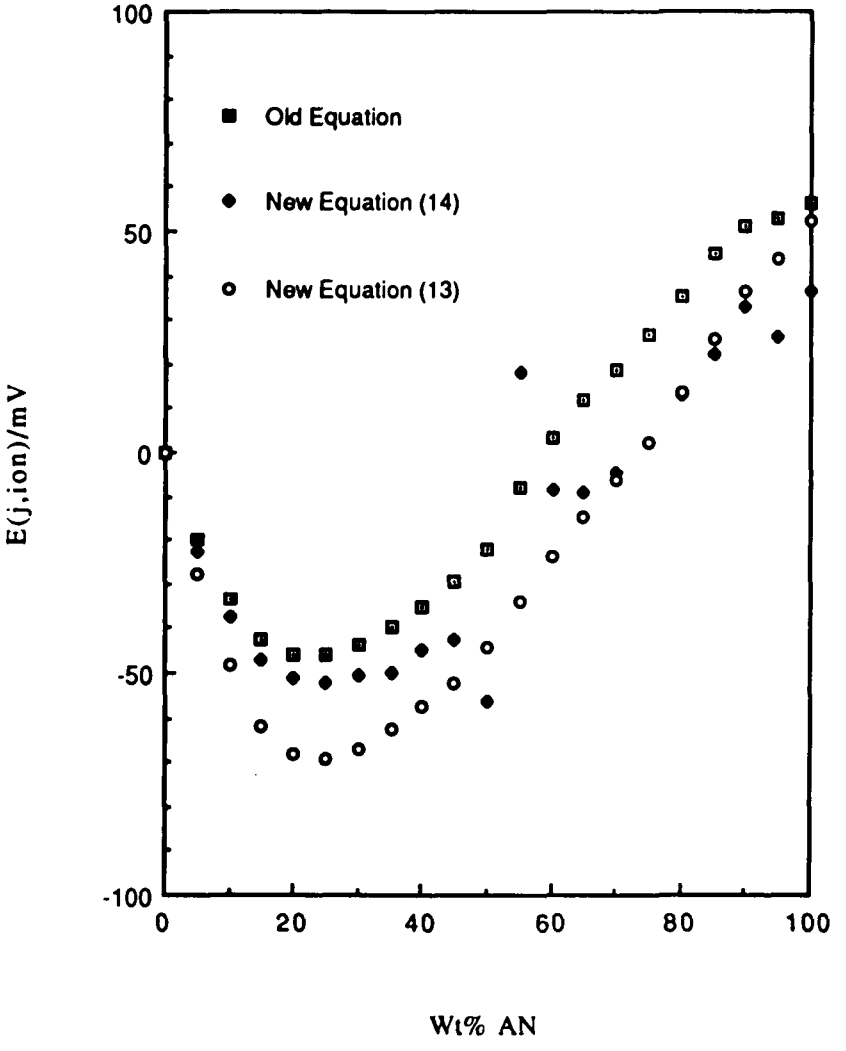
TABLE 18

$E_{j,ion}$ in $AgNO_3$ (H_2O) | $AgNO_3$ (AN-H_2O) Cells, in mV at 25°C.

	Transport Numbers and Transfer Activity Coefficients						
	Interpolated by hand				Interpolated by computer		
Wt% AN	A Eqn.10a	B_1 Eqn.13	B_2 Eqn.14	B_3 Eqn.14	A Eqn.10a	B_1 Eqn.13	B_2 Eqn.14
100	56.1	52.2	36.4	46.7	56.4	45.6	35.2
95	52.9	43.7	26.1	23.7	52.8	36.9	35.1
90	51.3	36.1	33.2	38.4	48.1	27.6	22.5
85	44.7	25.7	22.3	22.3	42.3	17.6	14.8
80	35.2	13.5	13.2	13.7	35.8	7.7	8.5
75	26.5	2.5	2.3	5.1	28.5	-2.1	1.5
70	18.9	-6.4	-4.5	-2.0	20.5	-12.0	-8.4
65	11.8	-14.5	-9.2	-6.2	12.3	-21.7	-14.0
60	3.4	-23.9	-8.6	-5.5	3.6	-31.1	-18.8
55	-7.9	-34.2	18.0	41.1	-5.5	-39.5	-27.5
50	-21.9	-44.5	-56.1	-39.9	-14.6	-48.2	-32.9
45	-29.8	-52.1	-42.8	-40.2	-23.6	-56.5	-37.0
40	-35.0	-57.5	-45.1	-44.2	-32.1	-64.0	-46.0
35	-39.6	-62.4	-49.8	-47.4	-39.7	-70.3	-53.2
30	-43.6	-66.9	-50.8	-50.9	-45.5	-74.6	-58.2
25	-46.0	-69.3	-52.4	-52.4	-48.7	-76.0	-58.7
20	-46.0	-68.2	-51.4	-51.9	-48.6	-73.4	-57.9
15	-42.4	-61.8	-47.2	-47.2	-44.1	-65.4	-53.3
10	-33.8	-48.2	-37.4	-37.7	-34.6	-50.9	-42.1
5	-19.7	-27.7	-22.5	-22.5	-19.8	-28.7	-32.3

FIGURE 17a

$E_{j,ion}$ Calculated from New Equation[a] and Old Equation[b] for $AgNO_3$ in Acetonitrile-Water Solvents. (Data interpolated by hand)

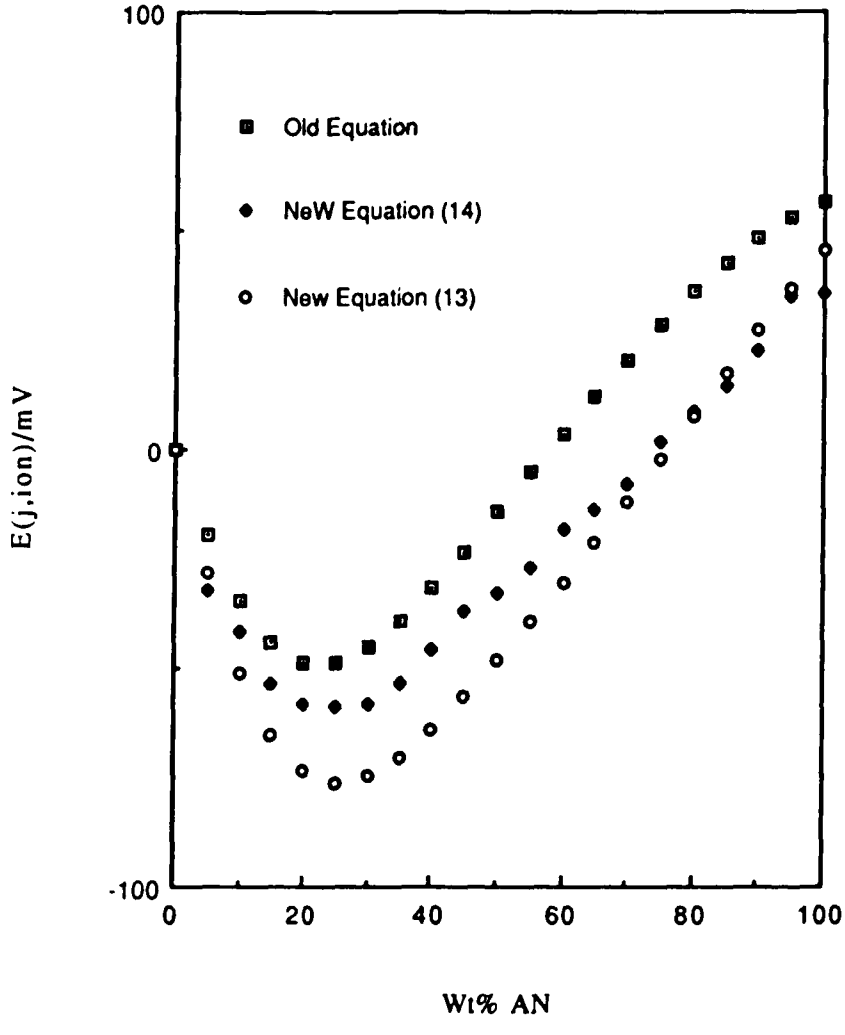


a Column B_1, Table 18, Eqn. 13
Column B_2, Table 18, Eqn. 14

b Column A, Table 18, Eqn. 10a

FIGURE 17b

$E_{j,ion}$ Calculated from New Equation[a] and Old Equation[b] for $AgNO_3$ in Acetonitrile-Water Solvents. (Data interpolated by computer)



a Column B_1, Table 18, Eqn. 13
Column B_2, Table 18, Eqn. 14

b Column A, Table 18, Eqn. 10a

A Comparison of the $E_{j,ion}$, Calculated from the Old Equation and the New Formulation for the Acetonitrile-Water Solvents.

The calculated results for $AgNO_3$ in AN-water solvents are noteworthy. In the curve of transport numbers of nitrate ion vs. wt% AN, a maximum and a minimum were observed at ~25 wt% and ~80 wt% AN, respectively. Also, a minimum is observed at ~ 55 wt% AN for the curve of transfer activity coefficients of nitrate ion vs. wt% AN. The difference between the results of $E_{j,ion}$ calculated from the old equation (10a) and the new equations (13) and (14) are significant for the entire solvent composition, because $^{t}NO_3$ passes through a pronounced maximum and minimum and $\log_m \gamma$ passes through a minimum. The difference between the $E_{j,ion}$ from Equation (10a) (old equation) and Equation (13) (one term) is greater than that between Equation (10a) and Equation (14) (two-term equation) for the range of 0 - 75 wt% AN. The difference in $E_{j,ion}$ values between Equations (10a) and (13) is nearly constant (which is ~20 mV) throughout the range from 15 wt% AN to 95 wt% AN, but the difference between Equations (10a) and (14) increases with the increasing concentration of AN from 0 - 20 mV for the entire range of AN. In this system, if we use Equation (14) to calculate the $E_{j,ion}$, we have to consider the drastically changing slope $\Delta t/\Delta s$ and the hydration-energy values from the literature for each ion. On the other hand, if we use Equation (13) to evaluate the $E_{j,ion}$, we have to consider the slope of $\Delta G^{o}/\Delta s$. In AN-water solvents the calculated $E_{j,ion}$ values from Equations (12), (13) and (14) vary smoothly with the increasing composition of AN.

DIMETHYLFORMAMIDE-WATER SOLVENTS.

Transfer Activity Coefficients.

The transfer activity coefficients of cations decrease with increasing composition of DMF over an entire range of DMF-water solvents. Different authors postulated that the protophilic, i.e., hydrogen-bond accepting, character of DMF enables it to form stable hydrates in aqueous mixtures. The basicity of hydrated DMF is expected to lie between that of pure water and unhydrated DMF, the order being $H_2O<DMF.xH_2O<DMF$.

With respect to the reference solvent, water [60], it is well recognized that $\Delta G_t^o(H^+)$ can be considered as a measure of the solvent basicity. At compositions of $X_{DMF}>0.4$, it is found that the basicity of the mixed solvent in aqueous DMF is constant. Around this composition in DMF-water mixtures [61], many other properties also show extrema or inflection points. Beyond that composition, it may be assumed that the environment of the solution loses its "water-like" character, preventing any further appreciable change in the activity of hydrogen ions.

The thermodynamic evidence for the well-known destabilization of anions by dipolar aprotic solvents, owing to lack of hydrogen-bond donating abilities [62,63], is provided by the large positive ΔG_t^o values for the chloride ions.

The available literature values [41,56,64,65] of transfer activity coefficients and transport numbers of H^+, K^+, Cs^+ and Cl^- ions in DMF-water solvents needed to calculate $E_{j,ion}$ are listed in Tables 19, 20 and plotted in Figures 18-24.

TABLE 19

Transfer Activity Coefficients of K^+, Cs^+, H^+ and Cl^- Ions in Dimethylformamide-Water Solvents. (Molar Scale, 25°C) [56].

Wt% DMF	$\log_m \gamma_K$	$\log_m \gamma_{Cs}$	$\log_m \gamma_H$	$\log_m \gamma_{Cl}$
20	0.03	-0.01	-0.31	0.31
40	-0.43	-0.45	-1.12	1.19
60	-0.90	-0.94	-2.01	2.35
80	-1.88	-1.80	-2.01	3.24
100	-3.03	-2.51	-2.49	8.07

FIGURE 18

Transfer Activity Coefficients of the H^+ Ion in Dimethylformamide-Water Solvents [56,65].

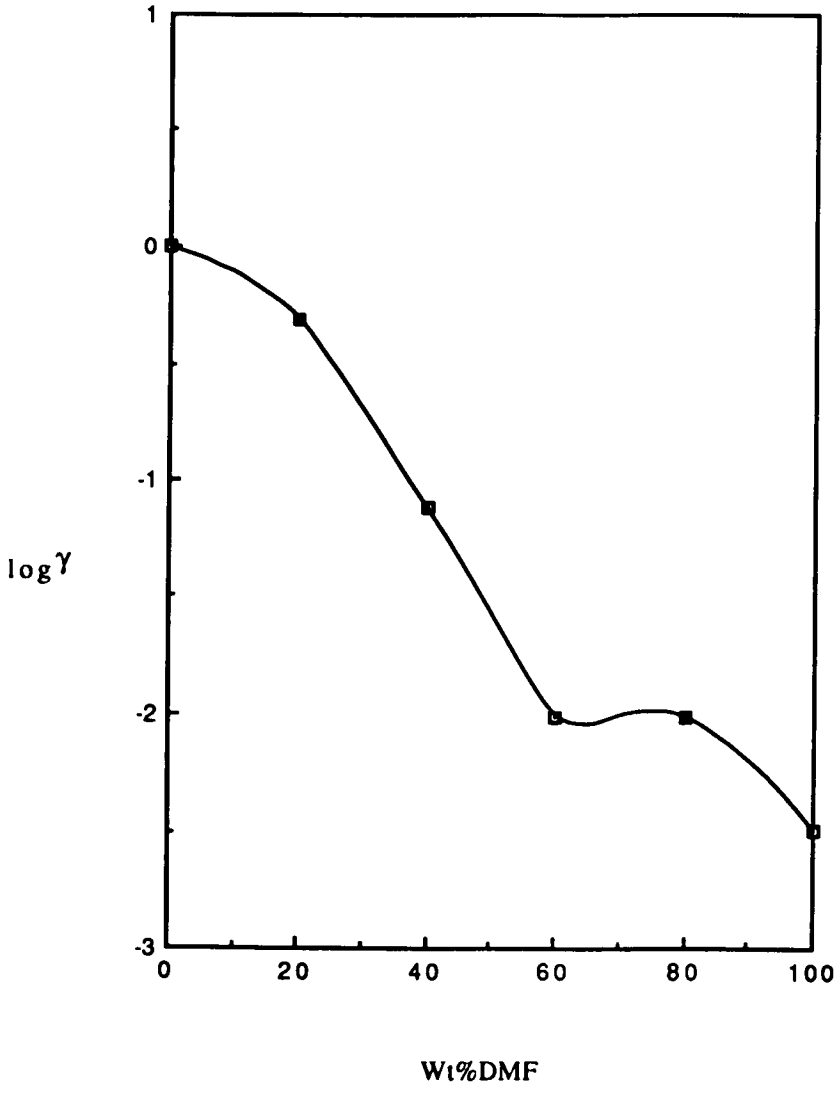


FIGURE 19

Transfer Activity Coefficients of the K^+ Ion in Dimethylformamide-Water Solvents [56].

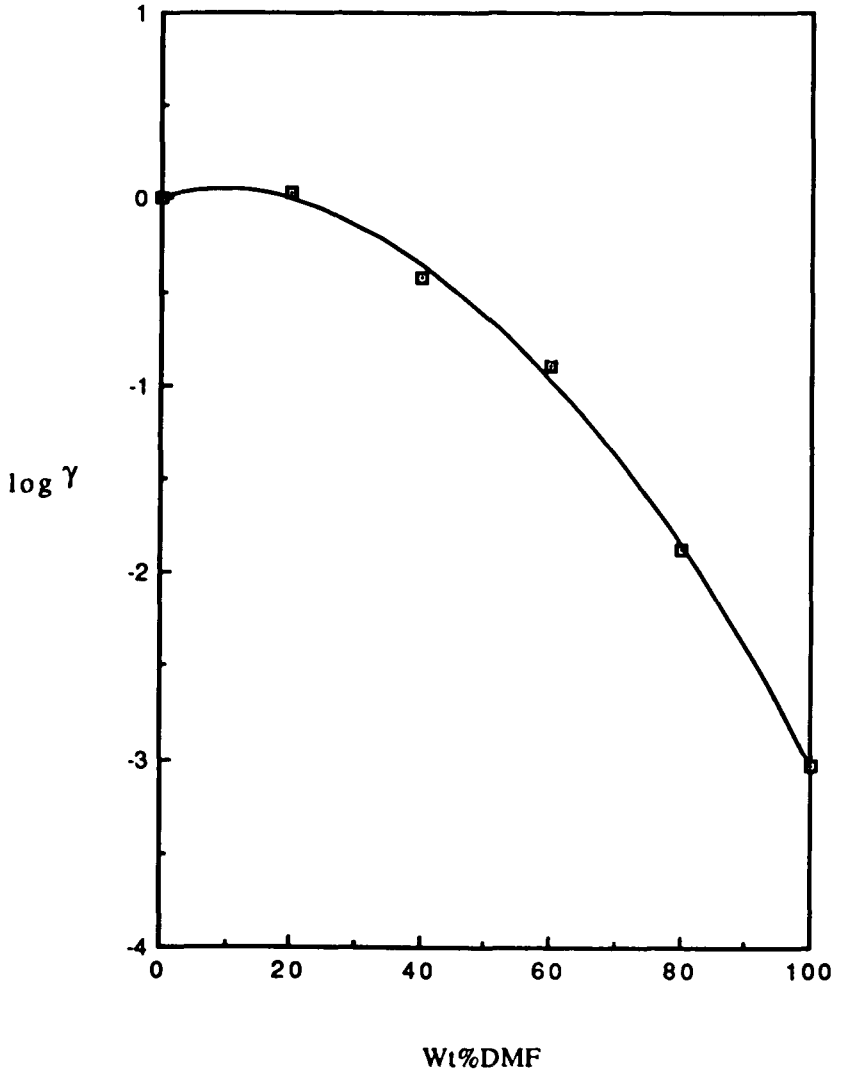


FIGURE 20

Transfer Activity Coefficients of the Cs^+ Ion in Dimethylformamide-Water Solvents [56].

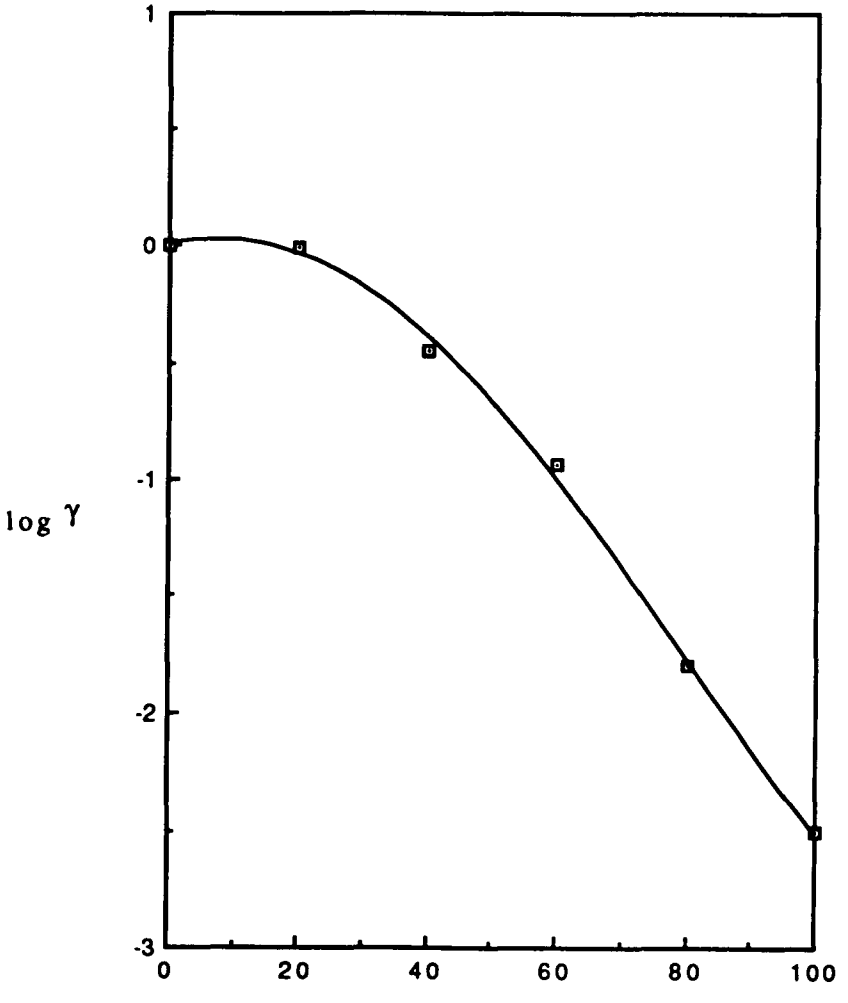
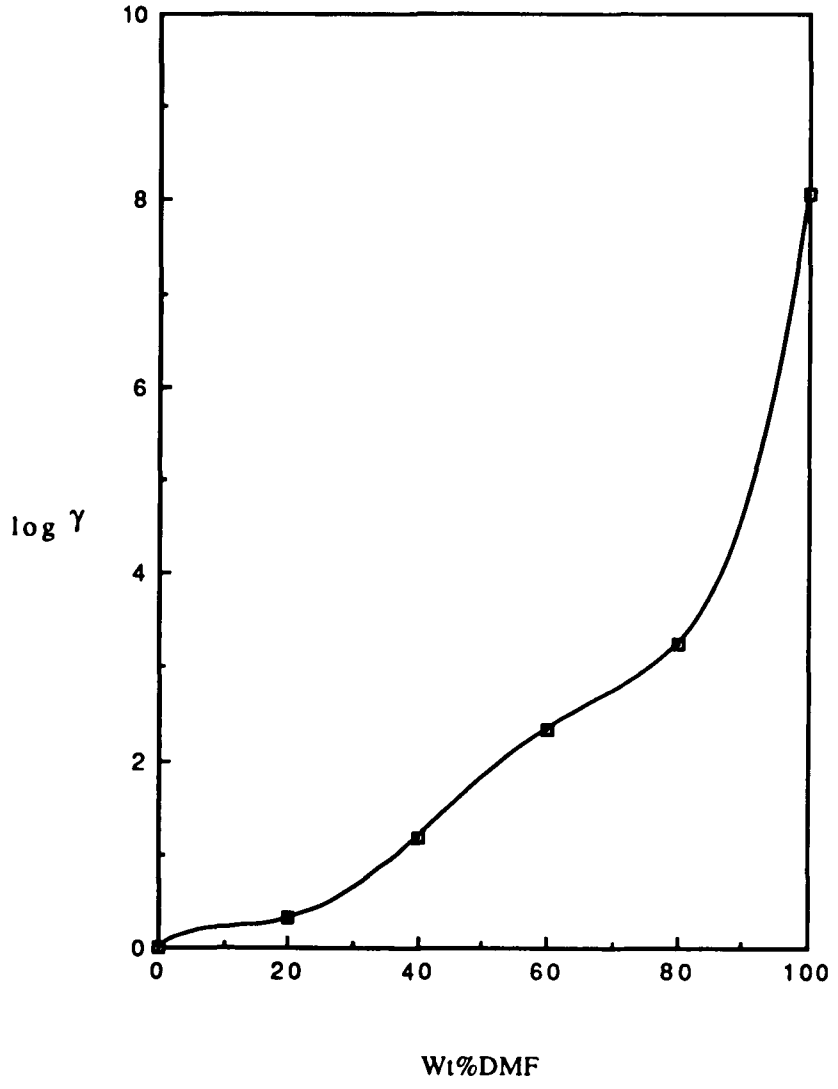


FIGURE 21

Transfer Activity Coefficients of the Cl^- Ion in Dimethylformamide-Water Solvents [56].



Transport Numbers.

It is well known that caused by the abnormal proton transfer mechanism between the associated water molecules, there is large $\lambda^{o}_{H^+}$ in water. The addition of DMF to water results in a rapid decrease of the anomalous proton conductivity caused by a break up of the hydrogen-bonded water network and hence the breakdown of the abnormal proton-transfer mechanism. The increase in the solvation radius of H^+ with the addition of DMF, is another reason for the decrease of $\lambda^{o}_{H^+}$. In general, DMF is likely to solvate smaller cations, H^+ in particular [66], which results in a decrease of the ionic mobility. Between 40 to 60 wt% DMF, the formation of the bulky DMF.nH_2O type complexes and the solvation of hydrogen ions by these complexes increases this effect further, resulting in a decrease of the mobility of hydrogen ion.

TABLE 20

Limiting Transport Numbers of H^+, K^+ and Cs^+ Ions in Dimethylformamide -Water Solvents [41,64].

Wt% DMF	$t^o_{H^+}$	$t^o_{K^+}$	$t^o_{Cs^+}$
0	0.820	0.491	0.503
10	0.812		
20	0.778	0.511	
28.7			0.520
38.8		0.523	
40	0.764		
60	0.922		
60.1		0.524	
63.5			0.520
80	0.711	0.489	
80.3		0.471	0.515
92.4		0.397	0.492
100	0.386	0.331	0.385

FIGURE 22

Limiting Transport Numbers of the H^+ Ion in Dimethylformamide-Water Solvents [41,64].

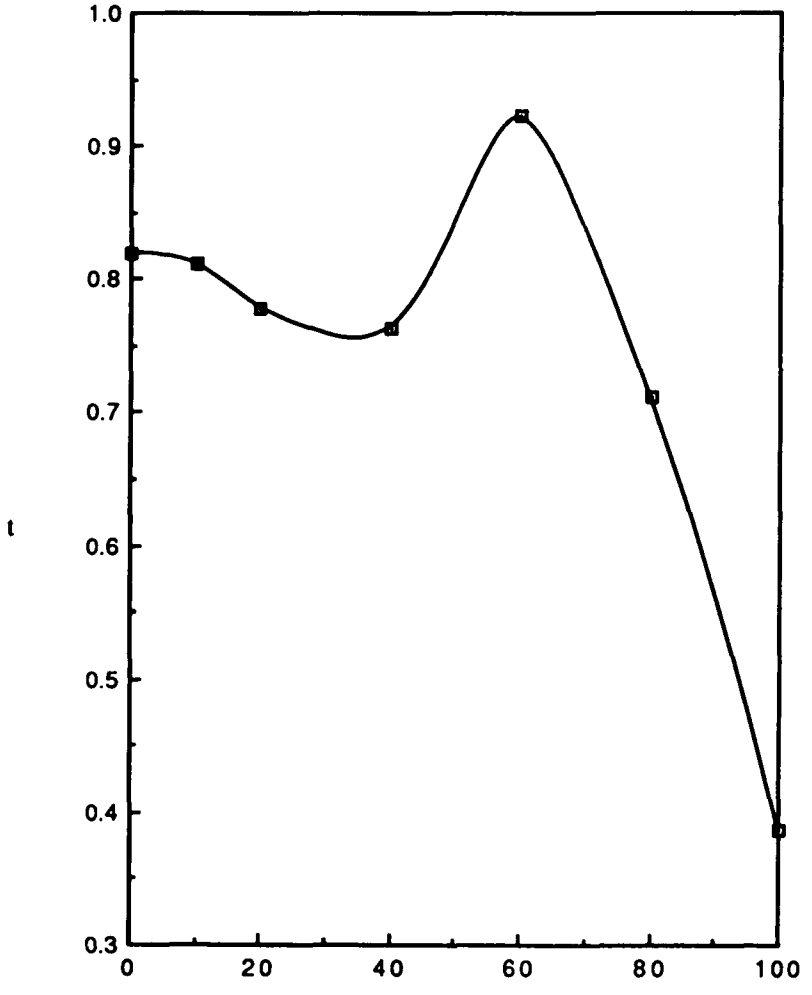


FIGURE 23

Limiting Transport Numbers of the K^+ Ion in Dimethylformamide-Water Solvents [41].

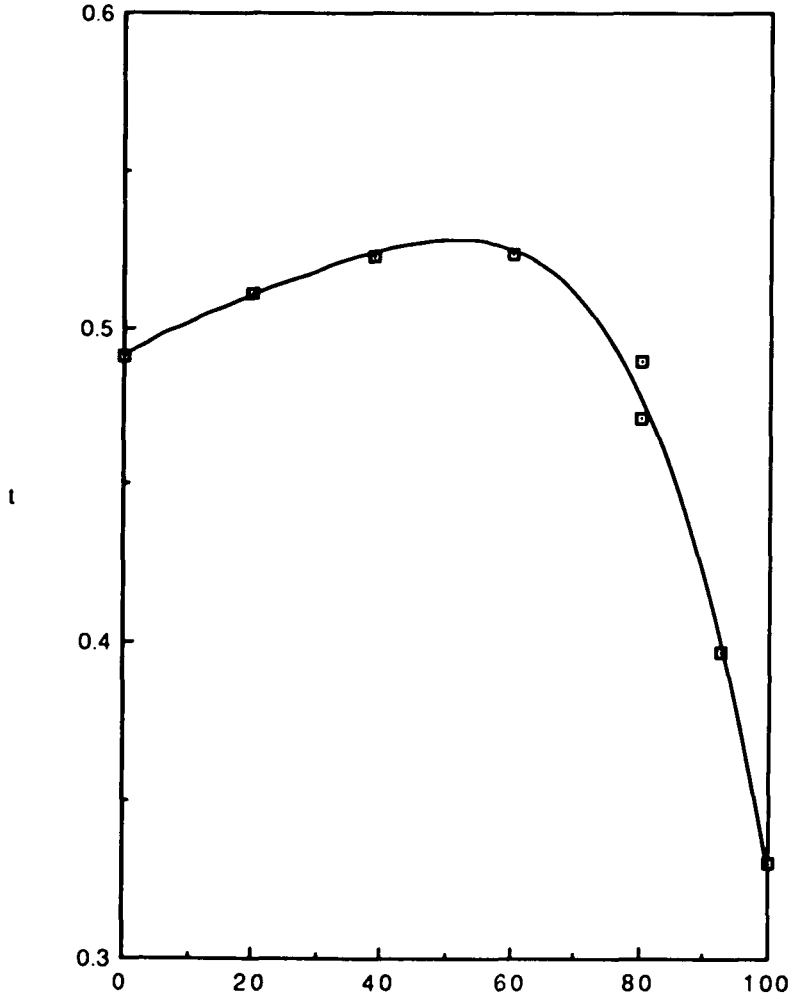
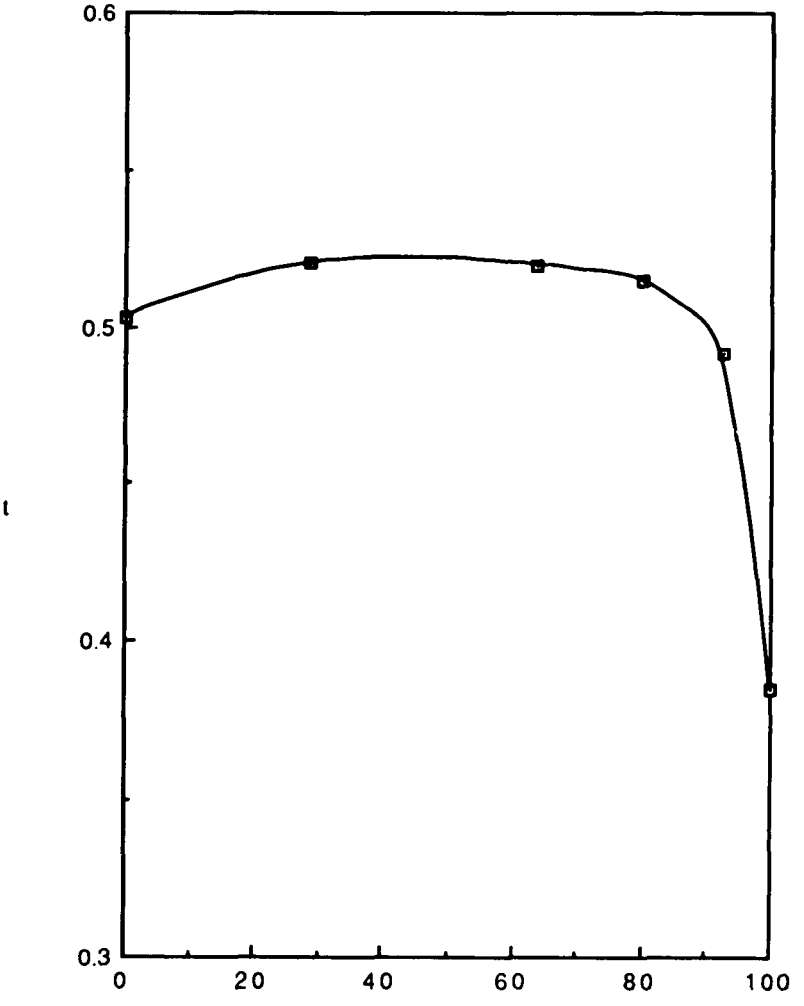


FIGURE 24

Limiting Transport Numbers of the Cs^+ Ion in Dimethylformamide-Water Solvents [41].



KCl|KCl, CsCl|CsCl and HCl|HCl Junctions in the Dimethylformamide-Water Systems.

Using the above transfer activity coefficients and transport numbers for the K^+, H^+, Cs^+ and Cl^- ions, the $E_{j,ion}$ values were calculated by using the old equation (10a) and the new equations(13) and (14) and compared. The results are shown in Tables 21-23 and are plotted in Figures 25-27.

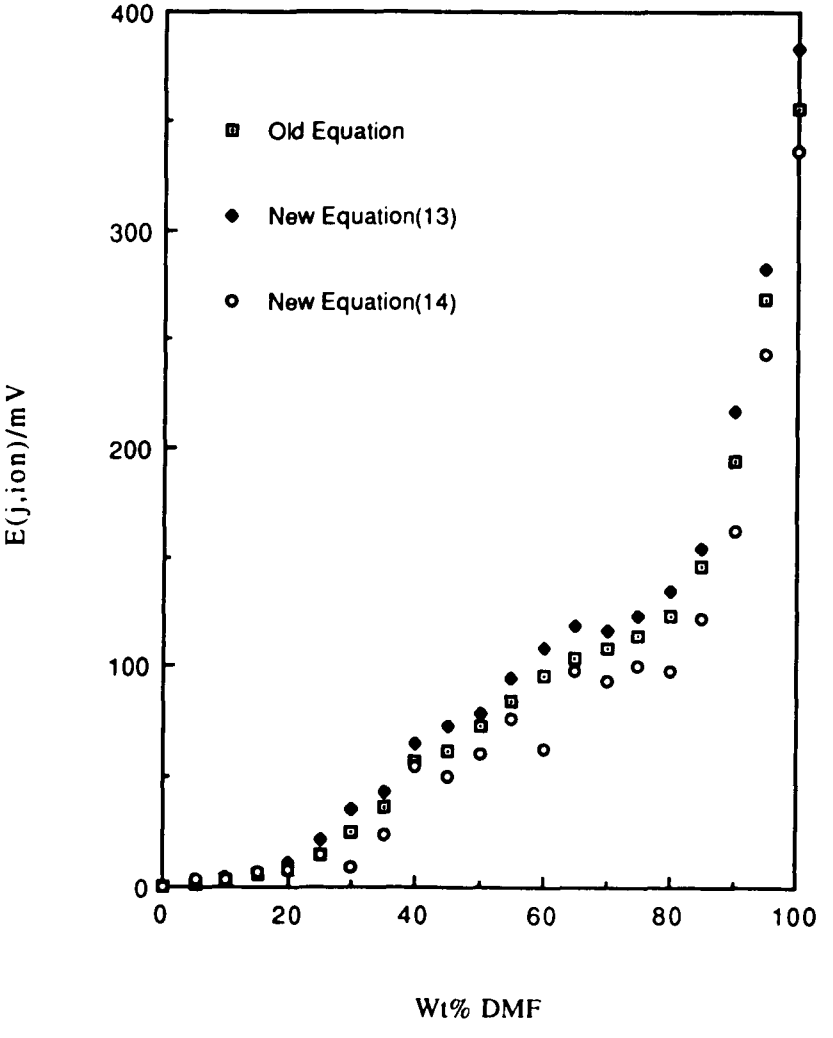
TABLE 21

$E_{j,ion}$ in KCl | KCl Cells, in mV at 25°C.
H_2O DMF-H_2O

	Transport Numbers and Transfer Activity Coefficients					
	Interpolated by hand			Interpolated by computer		
Wt%	A	B_1	B_2	A	B_1	B_2
DMF	Eqn.10a	Eqn.13	Eqn.14	Eqn.10a	Eqn.13	Eqn.14
100	355.0	335.5	383.4	355.0	376.3	369.5
95	268.4	243.2	281.8	248.4	225.6	268.8
90	194.7	162.7	216.8	182.6	162.0	190.8
85	146.2	122.8	154.7	144.5	129.7	160.7
80	123.3	98.4	134.9	123.9	107.4	134.6
75	113.8	100.8	123.6	113.3	101.4	121.4
70	108.5	94.0	116.1	107.2	94.3	114.1
65	103.6	97.8	118.7	101.9	117.1	127.7
60	95.5	63.0	108.8	95.4	108.2	109.1
55	84.4	76.1	94.4	86.4	99.8	97.2
50	72.8	60.7	78.8	75.0	94.8	91.8
45	62.2	49.9	73.4	61.7	81.7	83.8
40	57.2	55.4	65.1	47.7	64.4	64.8
35	36.2	24.1	43.5	34.1	50.9	46.5
30	25.0	9.7	35.8	22.5	39.4	30.8
25	15.3	15.2	21.2	13.7	33.9	18.8
20	8.3	8.5	11.8	8.3	25.2	11.5
15	5.3	7.0	7.2	6.0	29.7	8.4
10	3.0	2.9	4.1	5.8	32.8	7.9
5	1.3	3.0	1.9	5.1	28.8	6.6

FIGURE 25a

$E_{j,ion}$ Calculated from New Equation[a] and Old Equation[b] for KCl in Dimethylformamide-Water Solvents. (Data interpolated by hand)

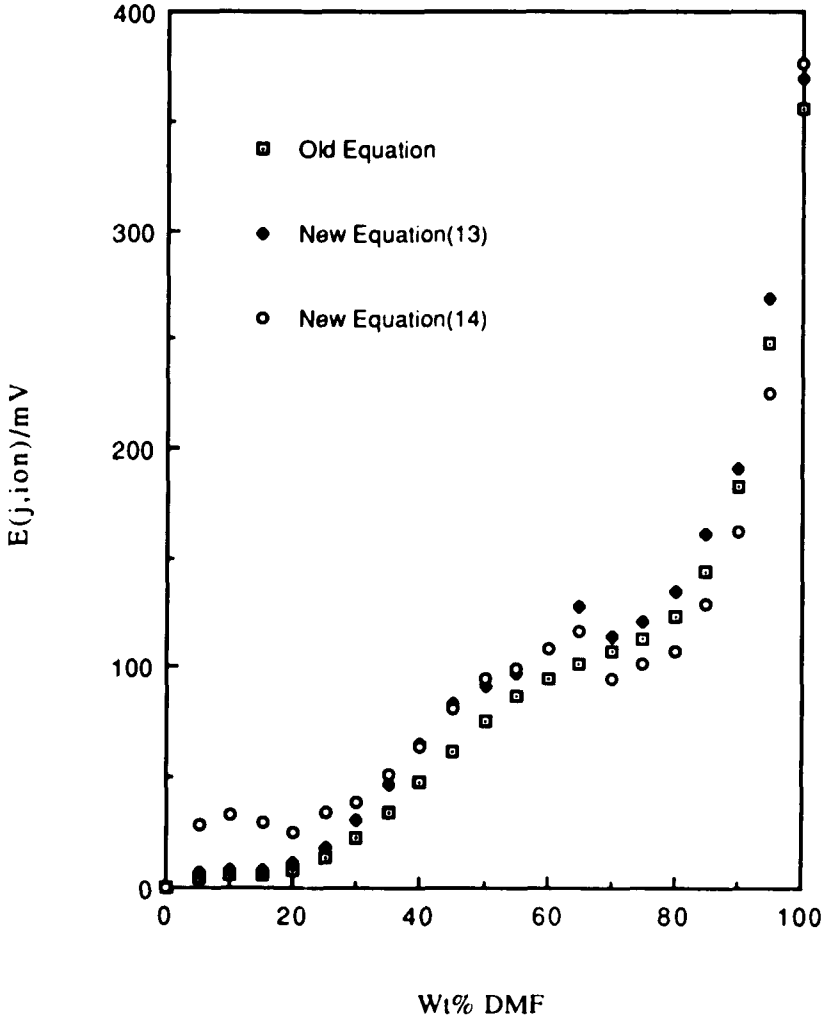


a Column B_1, Table 21, Eqn. 13
Column B_2, Table 21, Eqn. 14

b Column A, Table 21, Eqn. 10a

FIGURE 25b

$E_{j,ion}$ Calculated from New Equation[a] and Old Equation[b] for KCl in Dimethylformamide-Water Solvents. (Data interpolated by computer)



a Column B_1, Table 21, Eqn. 13
Column B_2, Table 21, Eqn. 14

b Column A, Table 21, Eqn. 10a

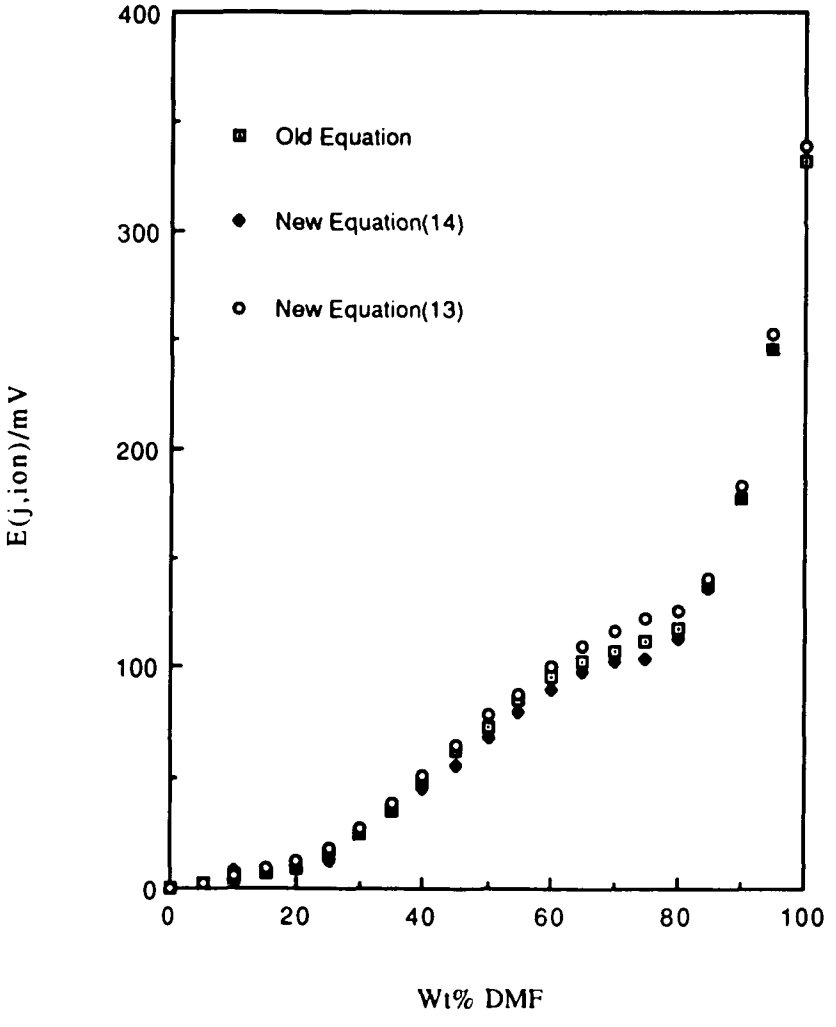
TABLE 22

$E_{j,ion}$ in CsCl | CsCl Cells, in mV at 25°C.
H_2O DMF- H_2O

	Transport Numbers and Transfer Activity Coefficients					
	Interpolated by hand			Interpolated by computer		
Wt%	A	B_1	B_2	A	B_1	B_2
DMF	Eqn.10a	Eqn.13	Eqn.14	Eqn.10a	Eqn.13	Eqn.14
100	331.2	337.8	338.2	327.1	333.6	335.8
95	245.6	252.2	246.2	228.3	233.6	238.3
90	177.7	182.7	178.6	168.6	173.8	179.2
85	136.8	140.7	136.1	135.0	148.0	151.5
80	118.1	125.9	113.2	118.0	128.0	122.9
75	111.9	121.9	103.8	109.5	117.9	122.3
70	107.4	116.6	102.9	105.5	112.6	113.1
65	102.7	109.3	98.1	101.5	114.6	116.3
60	96.3	100.5	90.8	95.3	102.4	105.3
55	85.6	88.0	80.3	86.6	97.5	99.0
50	73.7	78.3	68.1	75.2	82.0	90.4
45	62.8	64.7	56.3	62.3	73.9	77.8
40	48.0	51.9	45.7	47.8	54.7	56.9
35	35.9	38.6	35.9	34.4	42.4	45.9
30	24.6	27.5	25.8	22.9	30.8	27.3
25	15.7	18.7	12.4	14.5	19.3	20.8
20	9.4	12.1	10.3	9.4	12.4	13.0
15	7.0	9.4	8.4	7.5	10.2	7.5
10	4.4	6.0	8.1	7.3	10.2	4.2
5	2.0	2.8	2.0	6.2	8.3	0.2

FIGURE 26a

$E_{j,ion}$ Calculated from New Equation[a] and Old Equation[b] for CsCl in Dimethylformamide-Water Solvents. (Data interpolated by hand)

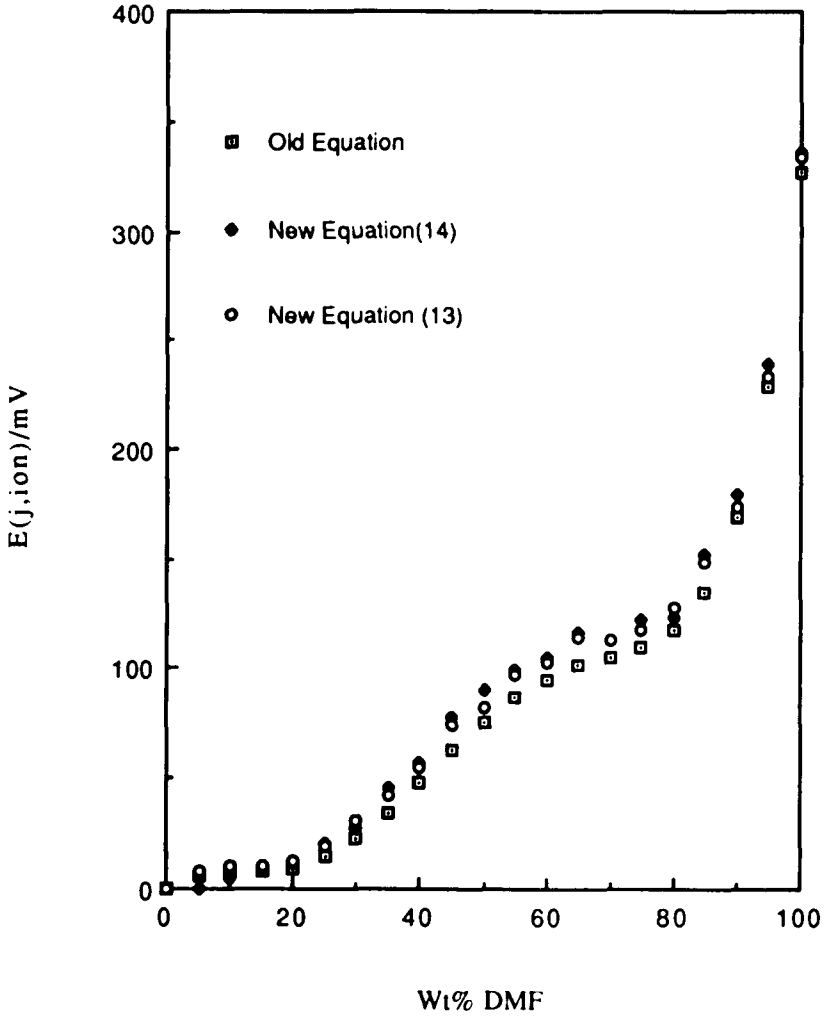


a Column B_1, Table 22, Eqn. 13
Column B_2, Table 22, Eqn. 14

b Column A, Table 22, Eqn. 10a

FIGURE 26b

$E_{j,ion}$ Calculated from New Equation[a] and Old Equation[b] for CsCl in Dimethylformamide-Water Solvents. (Data interpolated by computer)



a Column B_1, Table 22, Eqn. 13
Column B_2, Table 22, Eqn. 14

b Column A, Table 22, Eqn. 10a

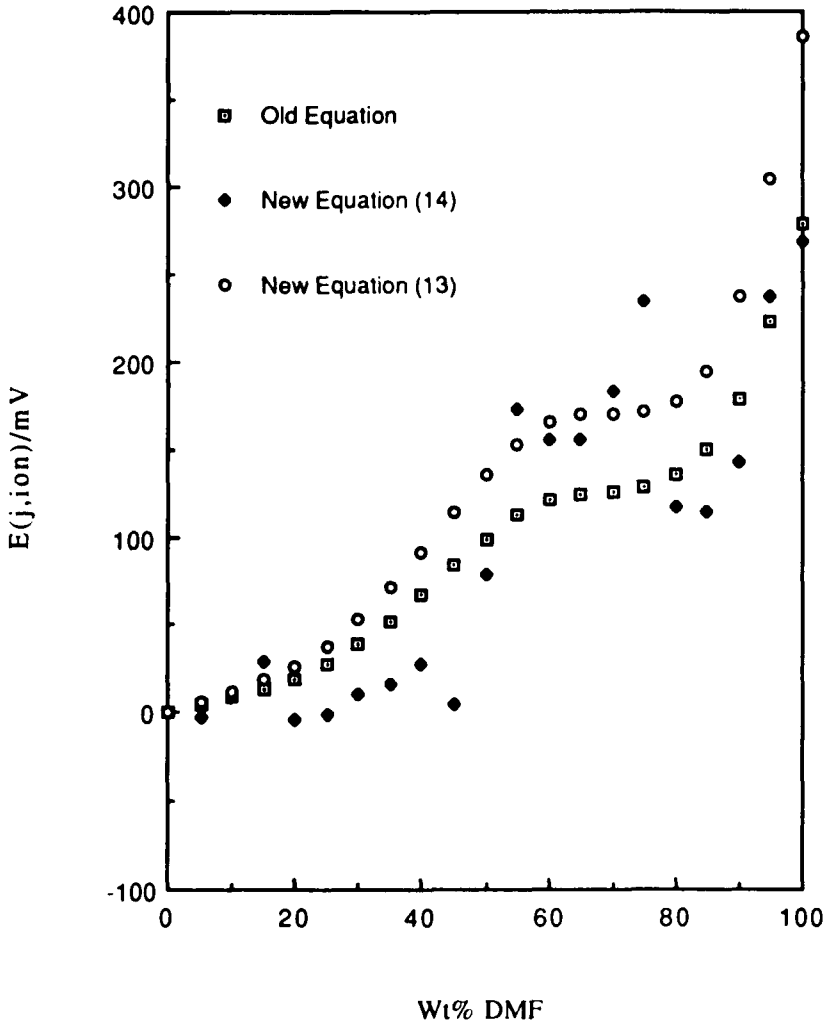
TABLE 23

$E_{j,ion}$ in HCl | HCl Cells, in mV at 25°C.
H_2O DMF- H_2O

Wt% DMF	Transport Numbers and Transfer Activity Coefficients Interpolated by hand A Eqn.10a	B_1 Eqn.13	B_2 Eqn.14	Interpolated by computer A Eqn.10a	B_1 Eqn.13	B_2 Eqn.14
100	278.3	385.6	267.9	278.4	385.0	280.3
95	222.9	304.5	237.1	208.2	282.3	227.0
90	178.6	236.7	142.5	168.9	226.7	183.3
85	149.8	194.7	115.0	148.1	198.7	163.7
80	136.0	176.9	117.4	137.3	184.9	153.5
75	129.1	172.1	233.7	131.2	177.8	148.0
70	126.3	170.7	182.5	127.4	172.7	142.5
65	124.6	169.6	155.1	122.3	167.0	137.0
60	121.5	165.6	156.2	116.5	159.2	133.0
55	112.5	153.4	172.6	108.7	148.7	121.6
50	98.9	135.4	78.6	98.7	135.1	115.6
45	83.6	114.3	4.8	86.5	118.6	89.8
40	67.0	91.7	26.7	72.6	99.6	76.8
35	51.5	71.0	15.9	57.6	79.3	54.0
30	38.5	52.9	10.1	42.4	58.9	39.1
25	26.9	36.9	-1.7	28.1	39.7	21.0
20	18.3	25.4	-4.7	15.7	22.9	12.6
15	13.1	18.0	27.9	5.9	9.9	-1.8
10	8.3	11.4	8.7	-0.4	1.7	-7.9
5	4.1	5.7	-3.1	-2.5	-0.8	-9.8

FIGURE 27a

$E_{j,ion}$ Calculated from New Equation[a] and Old Equation[b] for HCl in Dimethylformamide-Water Solvents. (Data interpolated by hand)

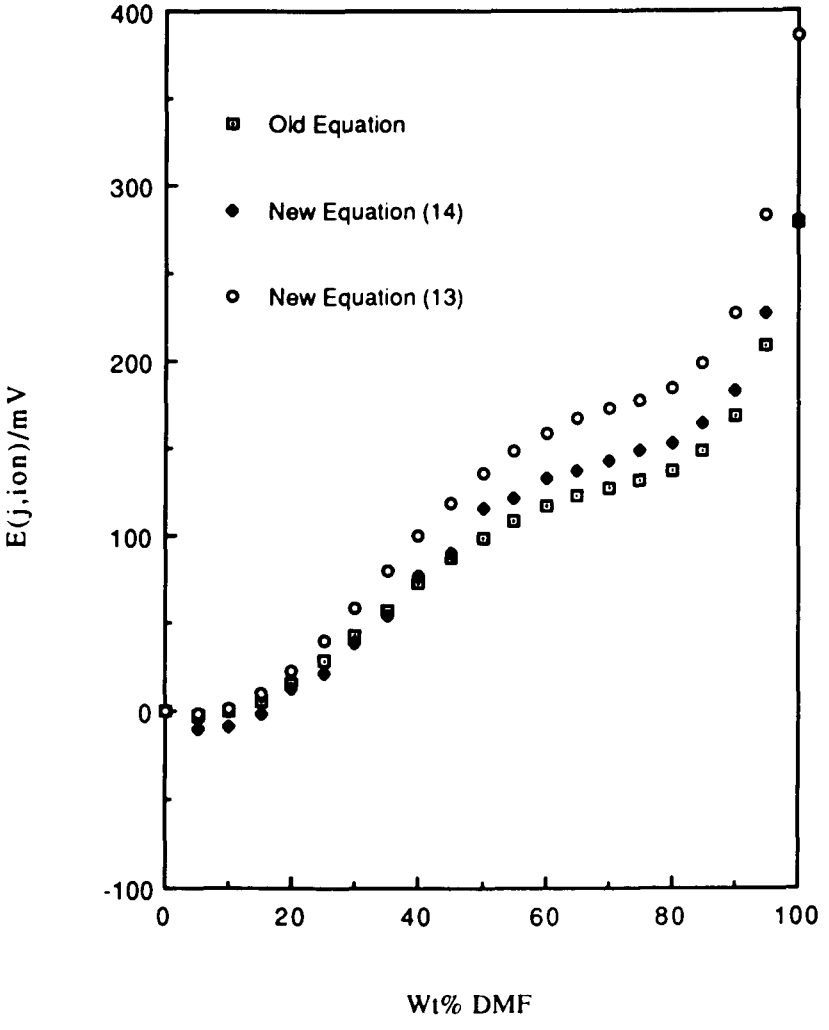


a Column B_1, Table 27, Eqn. 13
Column B_2, Table 27, Eqn. 14

b Column A, Table 27, Eqn. 10a

FIGURE 27b

$E_{j,ion}$ Calculated from New Equation[a] and Old Equation[b] for HCl in Dimethylformamide-Water Solvents. (Data interpolated by computer)



a Column B_1, Table 27, Eqn. 13
Column B_2, Table 27, Eqn. 14

b Column A, Table 27, Eqn. 10a

A Comparison of the $E_{j,ion}$, Calculated from the Old Equation and the New Formulation in DMF-Water Solvents.

In DMF-water mixtures, $E_{j,ion}$ values for KCl|KCl, CsCl|CsCl and HCl|HCl junctions are calculated using the old equation and the new equations and compared. The results from both methods are very similar, e.g., there are ~8 mV differences in $E_{j,ion}$ values, between the old equation and the new equations for both KCl|KCl and CsCl|CsCl junctions through the entire range of DMF-water compositions. This result agrees with the smooth variation of both transfer activity coefficients and transport numbers of each ion with the composition of the DMF-water solvents.

The results from the HCl|HCl junction in DMF-water mixtures are different from the results of the KCl|KCl and CsCl|CsCl junctions. With increasing concentration of DMF, the transfer activity coefficients and transport numbers of the hydrogen ion show a minimum and a maximum at ~ 60 wt% DMF, respectively. Here, we also observe that the difference in $E_{j,ion}$ between Equation (10a) and (13) is greater than that between Equation (10a) and (14). The difference of $E_{j,ion}$ between Equations (10a) and (13) increases from 0 to 110 mV with the increasing concentration of DMF. We observed ~20 mV difference in $E_{j,ion}$ between equations (10a) and (14), in the range of 50 to 95 wt% DMF. In this region both transfer activity coefficients and transport numbers of hydrogen ion go through a minimum and a maximum, respectively.

If we use Equation (13) to calculate $E_{j,ion}$ we have to evaluate the sharply changing slope $\Delta G^{o}/\Delta s$. In the region of 40-80 wt% DMF, $\log_m \gamma$ of the hydrogen ion passes through a minimum. It is interesting that in the above region the differences in $E_{j,ion}$ values

between Equations (10a) and (13) are significant. On the other hand, if we use Equation (14) to calculate $E_{j,ion}$ we have to evaluate the changing slope $\Delta t/\Delta s$. In the region of 40 - 80 wt% DMF the transport number of hydrogen ion passes through a pronounced maximum. Because of this variation in above region, the differences in $E_{j,ion}$ values between Equations (10a) and (14) are significant as well.

DIMETHYLSULFOXIDE-WATER SOLVENTS.

Transfer Activity Coefficients.

In DMSO-water mixtures, most studies indicate that the strongest interactions between water and DMSO, occur at about 0.35 mole fraction DMSO, suggesting the existence of a thermally labile DMSO-$2H_2O$ association complex. In this mixture, the transfer free energies of electrolytes from water to DMSO become more favorable (ΔG_t^o less positive) in the order LiX>NaX, which is expected if the cations interact more strongly with DMSO than with water. One expects preferential solvation of cations by DMSO to be favored by their stronger interactions with DMSO than with water.

The transfer activity coefficients of cations in this study decrease with the increasing composition of DMSO for the entire range of DMSO-water solvents.The literature values [65,67-71] of transfer activity coefficients and transport numbers of K^+, H^+, Rb^+ and Cl^-, which were known prior to this study, are shown in Tables 24 and 25 and plotted in Figures 28-34.

TABLE 24

Transfer Activity Coefficients of K^+, Rb^+, H^+ and Cl^- Ions in Dimethylsulfoxide-Water Solvents. (Molar Scale, 25°C) [65,67]

Wt% DMSO	$\log_m \gamma_K$	$\log_m \gamma_{Rb}$	$\log_m \gamma_H$	$\log_m \gamma_{Cl}$
5			-0.25	
10			-0.49	
10.9	-0.03	-0.03	-0.53	0.18
15			-0.71	
20			-0.93	
21.6	-0.04	-0.03	-0.98	0.41
25			-1.12	
30			-1.31	
32.1	-0.18	-0.18	-1.38	0.77
35			-1.49	
40			-1.67	
42.4	-0.22	-0.22	-1.74	1.17
45			-1.82	
50			-1.98	
52.5	-0.04	-0.11	-2.05	1.43
55			-2.12	
60			-2.29	
62.3	-0.62	-0.70	-2.40	2.53
65			-2.42	
70			-2.56	
72.0	-0.92	-0.85	-2.61	3.34

74.3			-2.66	
81.5	-1.28	-1.20		4.21
90.6	-1.72	-1.58		5.39
100	-2.13	-1.91	-3.30	6.75

FIGURE 28

Transfer Activity Coefficients of the K^+ Ion in Dimethylsulfoxide-Water Solvents. (Water Reference. Molar Scale) [67].

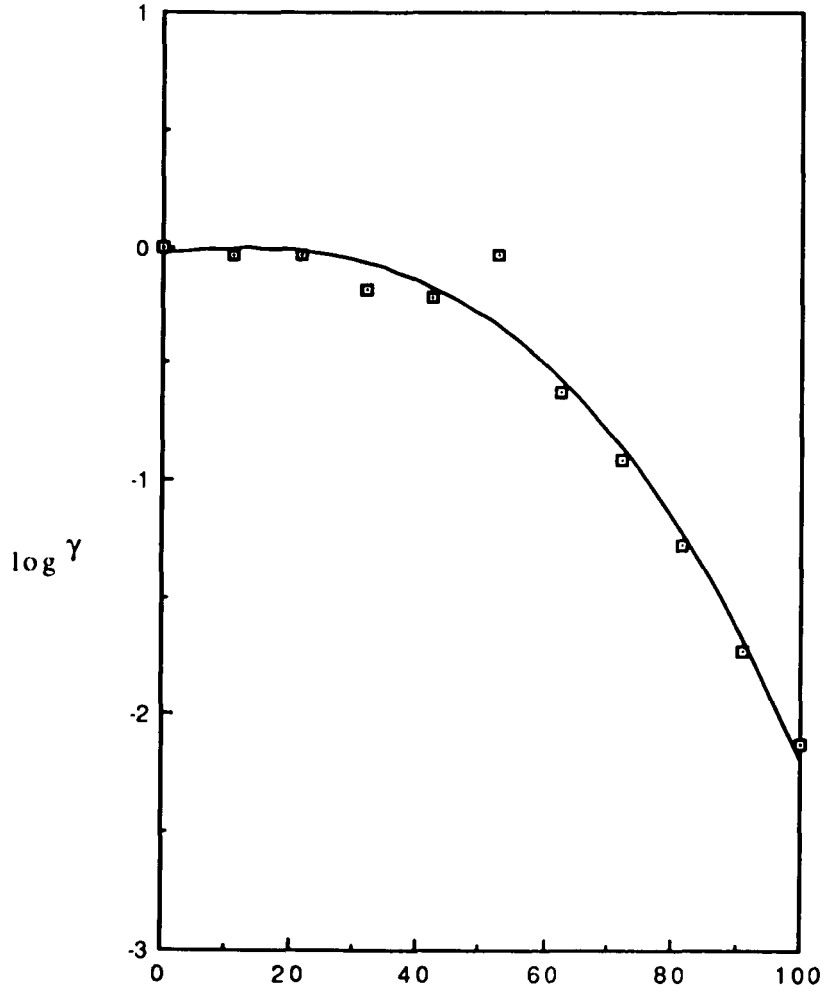


FIGURE 29

Transfer Activity Coefficients of the Rb^+ Ion in Dimethylsulfoxide-Water Solvents, (Water Reference, Molar Scale) [67].

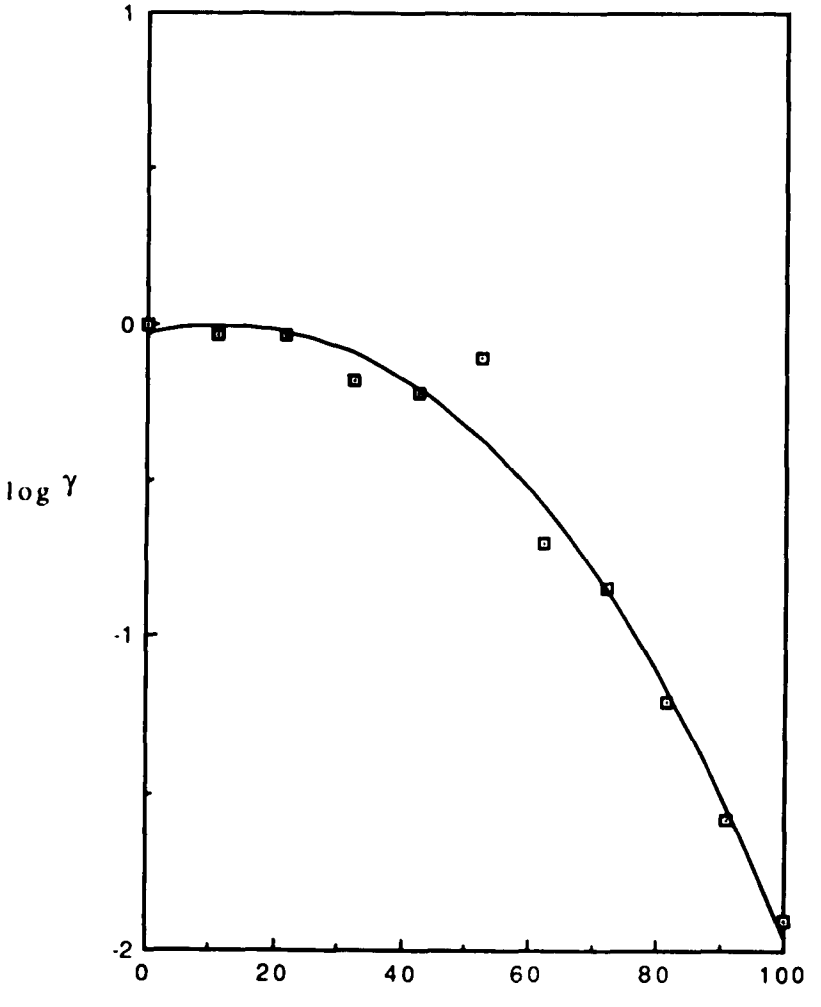


FIGURE 30

Transfer Activity Coefficients of the H^+ Ion in Dimethylsulfoxide-Water Solvents. (Water Reference, Molar Scale) [65].

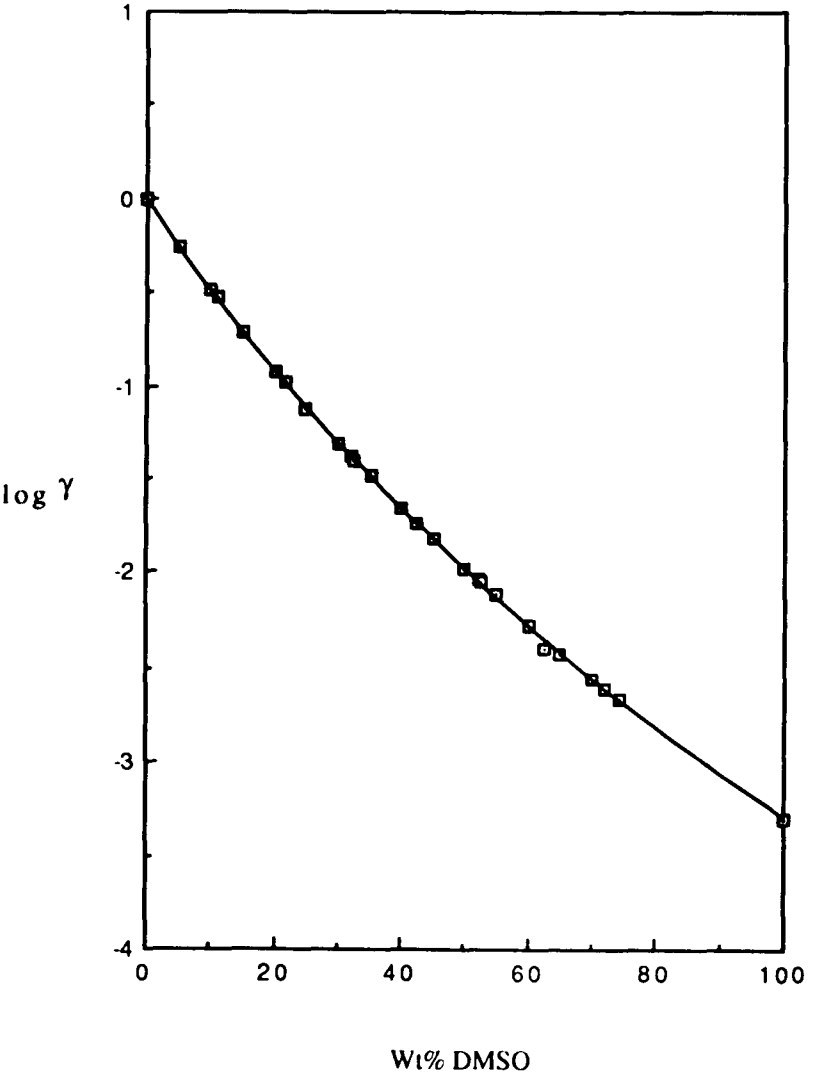


FIGURE 31

Transfer Activity Coefficients of the Cl^- Ion in Dimethylsulfoxide-Water Solvents, (Water Reference, Molar Scale) [67].

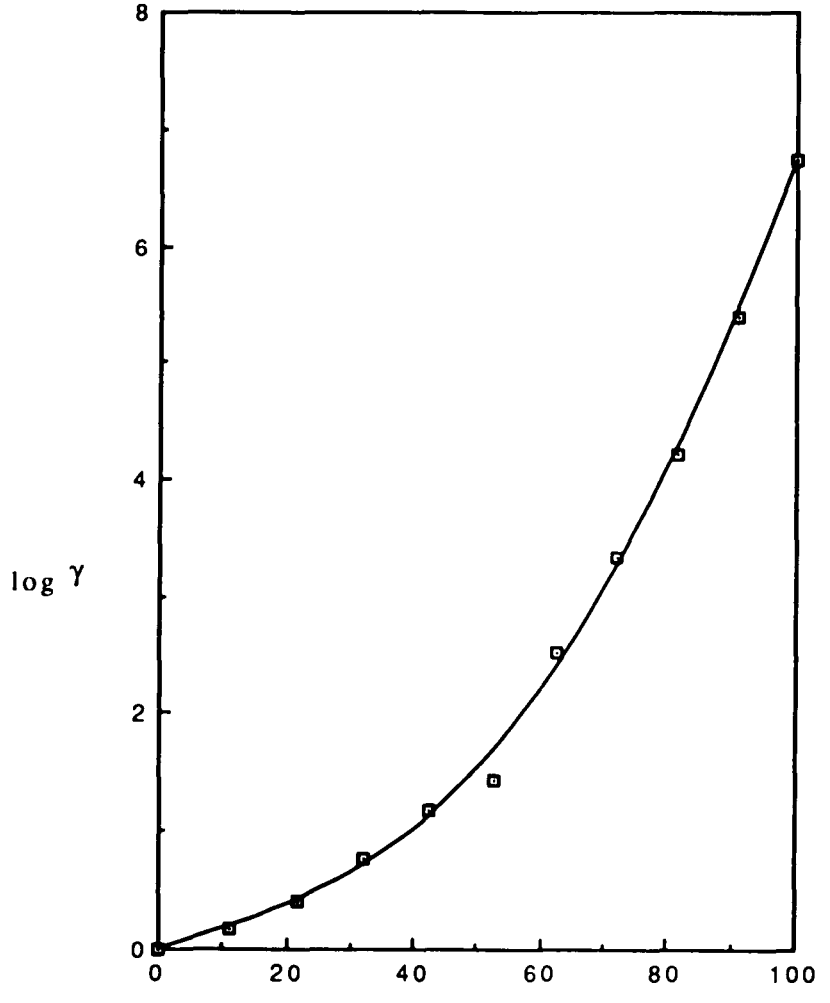


TABLE 25

Limiting Transport Numbers of H^+, K^+ and Rb^+ Ions in Dimethylsulfoxide-Water Solvents [68-71].

Wt% DMSO	$t^o_{H^+}$	$t^o_{K^+}$	$t^o_{Cs^+}$
0	0.821	0.490	0.503
10	0.823		0.503
20	0.829	0.498	0.513
30	0.830		0.516
40	0.831	0.516	0.527
50	0.824		0.526
60	0.803	0.514	0.516
70	0.675	0.489	
80			0.441
85	0.501		
90	0.443		
95	0.413		
100	0.404	0.385	0.304

FIGURE 32

Limiting Transport Numbers of the K^+ Ion in Dimethylsulfoxide-Water Solvents [68-71].

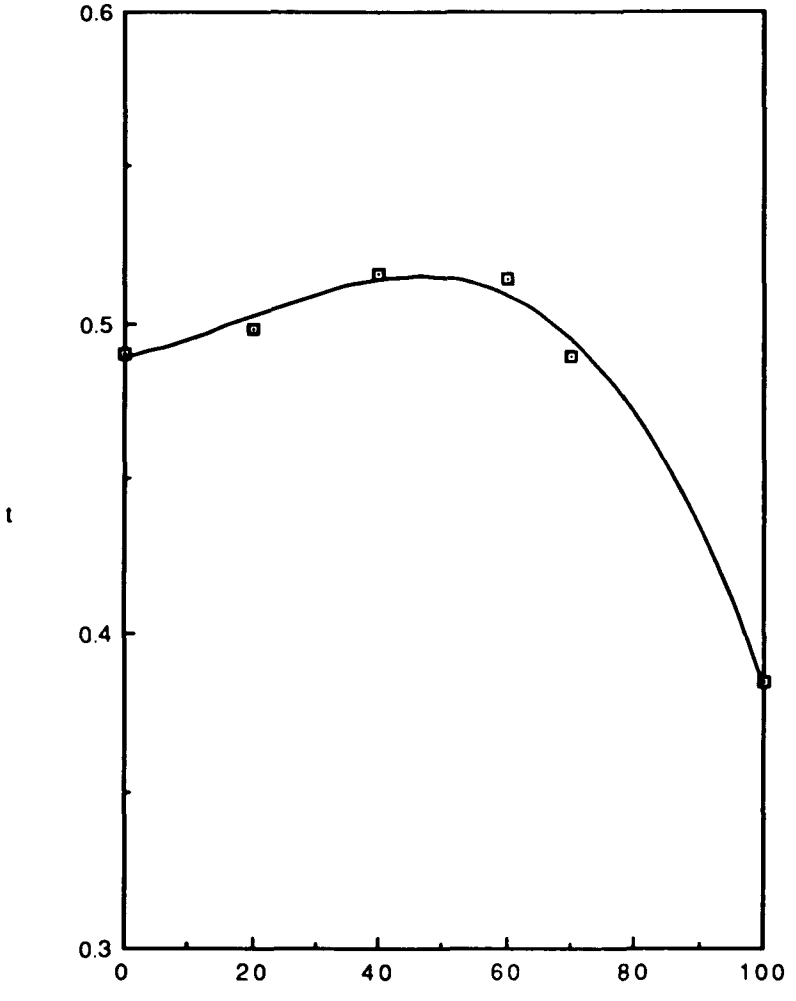


FIGURE 33

Limiting Transport Numbers of the Rb^+ Ion in Dimethylsulfoxide-Water Solvents [68-71].

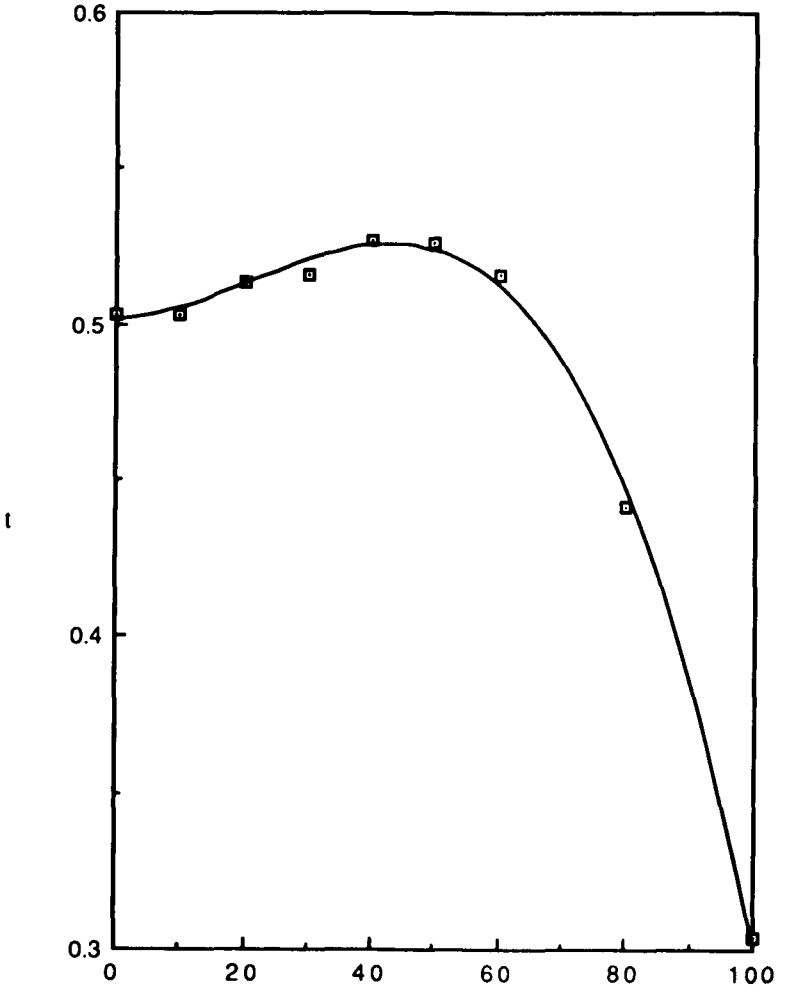
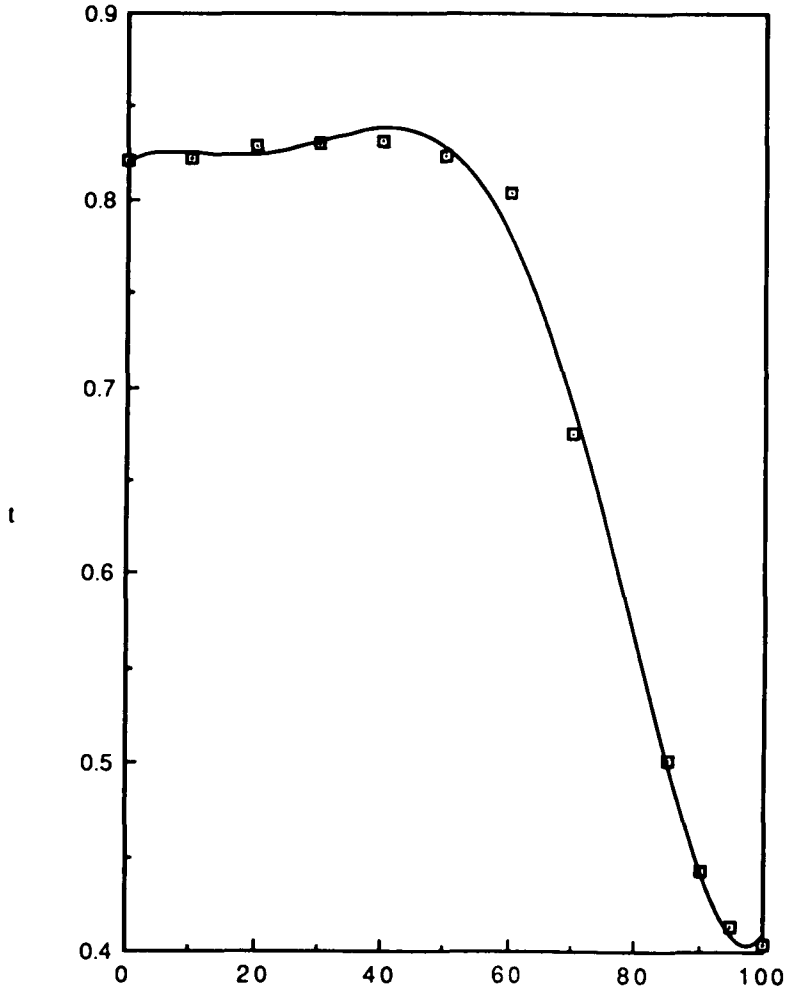


FIGURE 34

Limiting Transport Numbers of the H^+ Ion in Dimethylsulfoxide-Water Solvents [68-71].



KCl|KCl, RbCl|RbCl and HCl|HCl Junctions in the DMSO-Water Systems.

Using the above transfer activity coefficients and transport numbers of the K^+, H^+, Rb^+ and Cl^- ions, $E_{j,ion}$ values were calculated from the old equation (10a) and the new equations (13) and (14). Similar $E_{j,ion}$ values are observed for both the KCl|KCl and RbCl|RbCl junctions in the DMSO-water solvents from the above equations. But the results of $E_{j,ion}$ for HCl|HCl junction are different from the above junctions. Tables 26-28 show the calculated $E_{j,ion}$ values and plots are shown in Figures 35-37.

TABLE 26

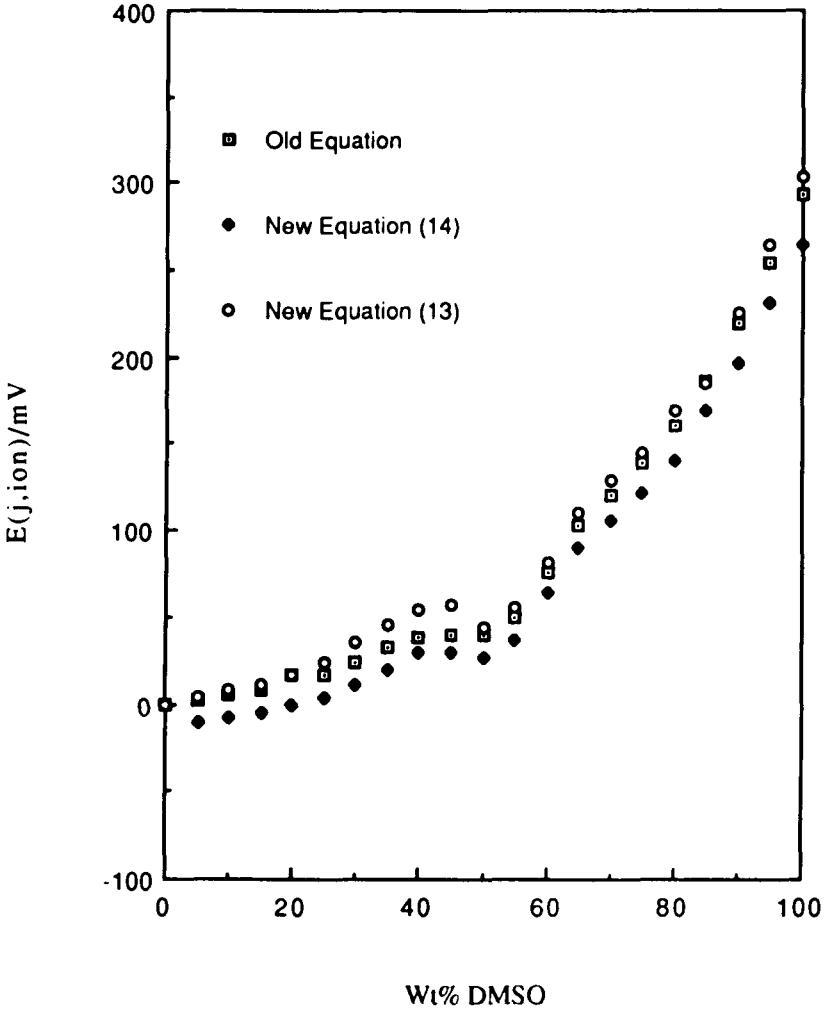
$E_{j,ion}$ in KCl | KCl Cells, in mV at 25°C.

H_2O DMSO-H_2O

	Transport Numbers and Transfer Activity Coefficients						
	Interpolated by hand				Interpolated by computer		
Wt%	A	B_1	B_2	B_3	A	B_1	B_2
DMSO	Eqn.10a	Eqn.13	Eqn.14	Eqn.14	Eqn.10a	Eqn.13	Eqn.14
100	293.0	303.0	265.2	259.2	278.6	297.7	259.1
95	254.3	264.0	230.9	228.5	246.9	268.5	221.6
90	219.2	226.0	196.5	194.6	216.8	230.0	200.3
85	187.1	184.6	168.9	166.3	188.2	202.9	162.3
80	160.9	168.9	140.2	138.3	161.6	187.8	140.0
75	138.9	145.2	122.5	120.5	137.2	155.3	116.7
70	120.5	128.4	105.9	103.5	115.2	125.7	98.0
65	102.8	109.8	90.9	88.0	95.7	119.3	78.1
60	76.3	81.2	64.9	62.1	78.6	106.3	58.3
55	49.3	55.2	37.1	34.3	63.9	86.6	48.2
50	39.4	44.5	26.3	24.1	51.7	70.1	37.7
45	40.1	56.5	29.8	28.2	41.5	56.5	30.7
40	38.7	54.5	29.3	27.4	35.3	45.4	12.8
35	32.4	45.7	19.7	19.3	28.3	36.6	8.9
30	24.5	34.9	10.3	10.3	21.4	27.6	3.5
25	16.6	24.3	3.1	3.1	17.1	33.9	2.4
20	17.4	16.1	-0.7	-1.0	13.6	19.1	-6.9
15	8.2	11.5	-4.6	-4.6	10.5	14.7	-0.1
10	5.6	7.9	-8.5	-8.1	7.3	10.1	-6.7
5	2.9	4.1	-10.5	-10.5	3.7	5.0	-8.5

FIGURE 35a

$E_{j,ion}$ Calculated from New Equation[a] and Old Equation[b] for KCl in Dimethylsulfoxide-Water Solvents. (Data interpolated by hand)

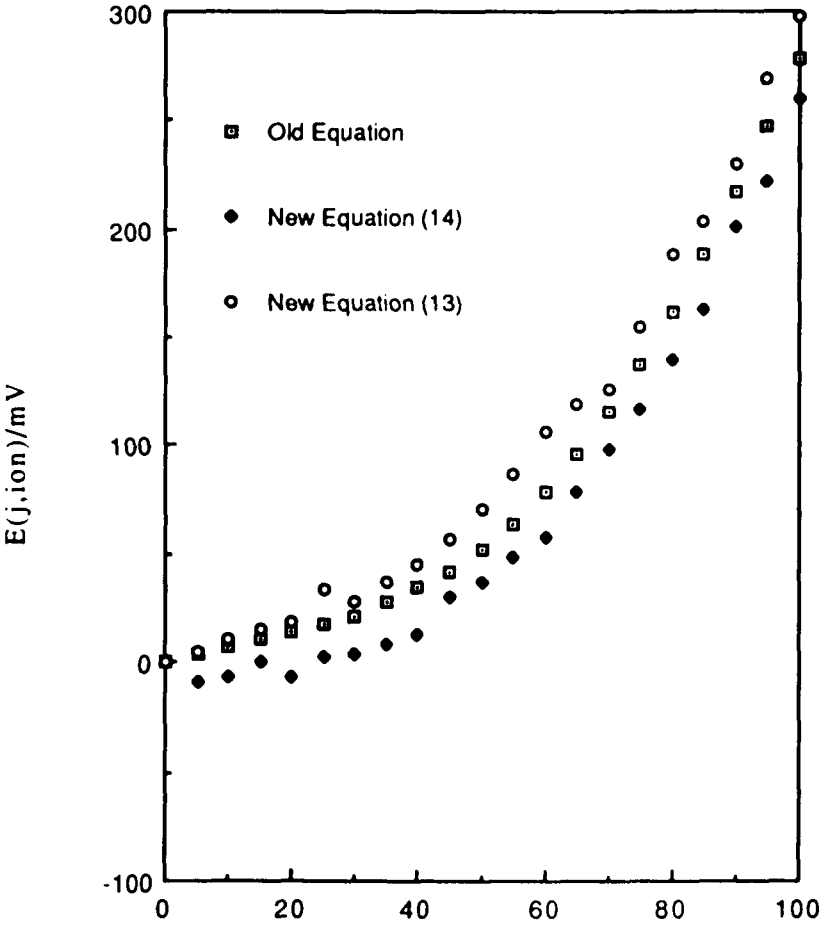


a Column B_2, Table 26, Eqn. 13
Column B_2, Table 26, Eqn. 14

b Column A, Table 26, Eqn. 10a

FIGURE 35b

$E_{j,ion}$ Calculated from New Equation[a] and Old Equation[b] for KCl in Dimethylsulfoxide-Water Solvents, (Data interpolated by computer)



a Column B_2, Table 26, Eqn. 13
Column B_2, Table 26, Eqn. 14

b Column A, Table 26, Eqn. 10a

TABLE 27

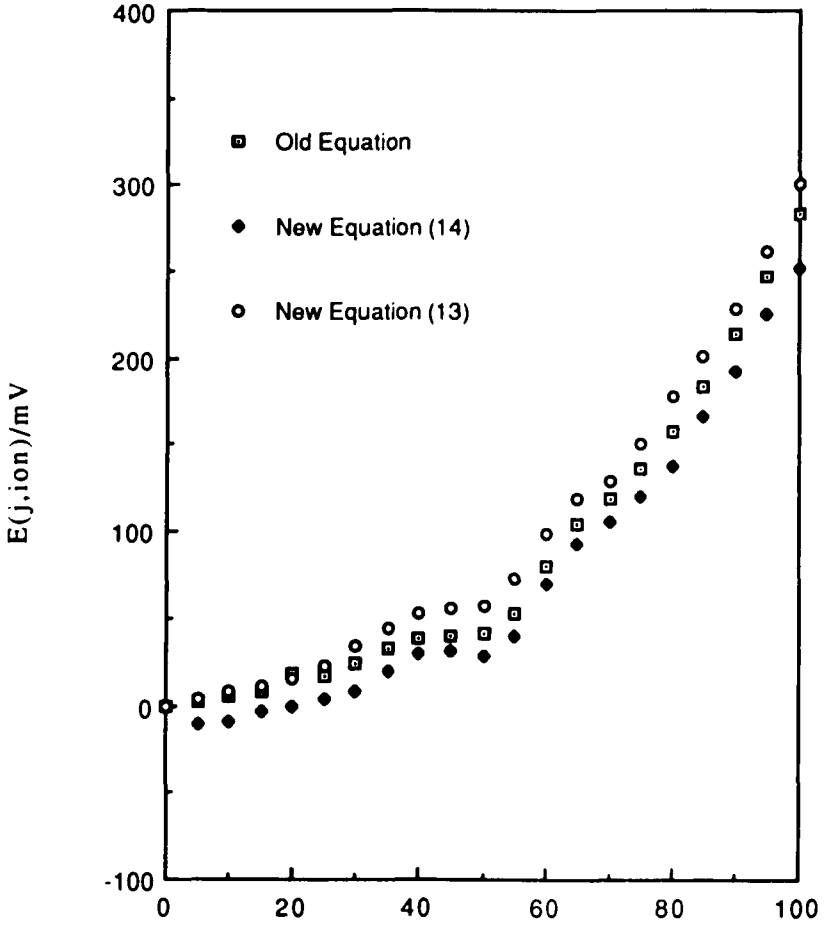
$E_{j,ion}$ in RbCl | RbCl Cells, in mV at 25°C.

H_2O DMSO-H_2O

	Transport Numbers and Transfer Activity Coefficients						
	Interpolated by hand				Interpolated by computer		
Wt%	A	B_1	B_2	B_3	A	B_1	B_2
DMSO	Eqn.10a	Eqn.13	Eqn.14	Eqn.14	Eqn.10a	Eqn.13	Eqn.14
100	283.5	300.2	251.1	243.1	282.9	296.9	269.4
95	247.1	261.1	225.9	219.0	248.2	259.9	233.1
90	214.2	229.2	191.8	186.2	214.6	225.4	209.7
85	183.9	200.9	166.8	160.5	186.9	198.5	179.6
80	158.3	178.0	137.2	132.3	160.2	171.2	154.7
75	136.2	150.2	119.9	114.8	136.2	150.8	135.3
70	119.4	129.1	105.4	100.1	114.7	124.4	118.4
65	103.9	119.0	92.5	86.7	95.6	108.9	105.0
60	80.8	98.2	70.2	64.3	79.0	86.6	84.3
55	52.7	72.6	40.1	34.5	64.6	76.2	67.7
50	41.0	56.5	27.9	22.6	52.3	63.3	58.5
45	40.4	55.1	30.6	27.7	42.0	53.9	41.5
40	38.9	52.8	30.0	27.6	33.4	42.5	36.0
35	32.6	44.4	19.9	19.4	26.6	36.3	29.1
30	24.5	33.7	8.7	9.4	21.1	28.9	17.2
25	16.7	23.0	3.8	3.9	16.7	23.0	16.0
20	17.5	15.8	-0.5	-0.9	13.1	18.2	12.5
15	8.3	11.4	-4.0	-4.1	10.0	13.8	9.4
10	5.7	7.8	-9.4	-8.8	7.1	10.0	6.4
5	3.0	4.1	-10.6	-10.6	3.7	4.9	0.4

FIGURE 36a

$E_{j,ion}$ Calculated from New Equation and Old Equation for RbCl in Dimethylsulfoxide-Water Solvents. (Data interpolated by hand)

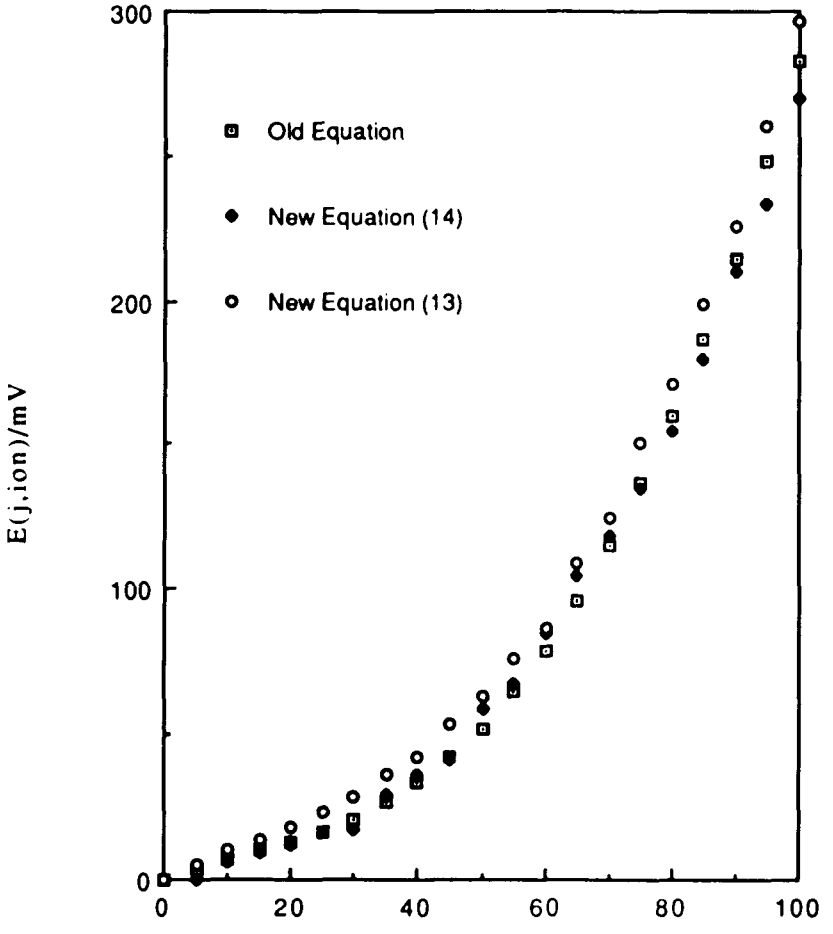


a Column B_2, Table 27, Eqn. 13
Column B_2, Table 27, Eqn. 14

b Column A, Table 27, Eqn. 10a

FIGURE 36b

$E_{j,ion}$ Calculated from New Equation and Old Equation for RbCl in Dimethylsulfoxide-Water Solvents. (Data interpolated by computer)



a Column B_2, Table 27, Eqn. 13
Column B_2, Table 27, Eqn. 14
b Column A, Table 27, Eqn. 10a

TABLE 28

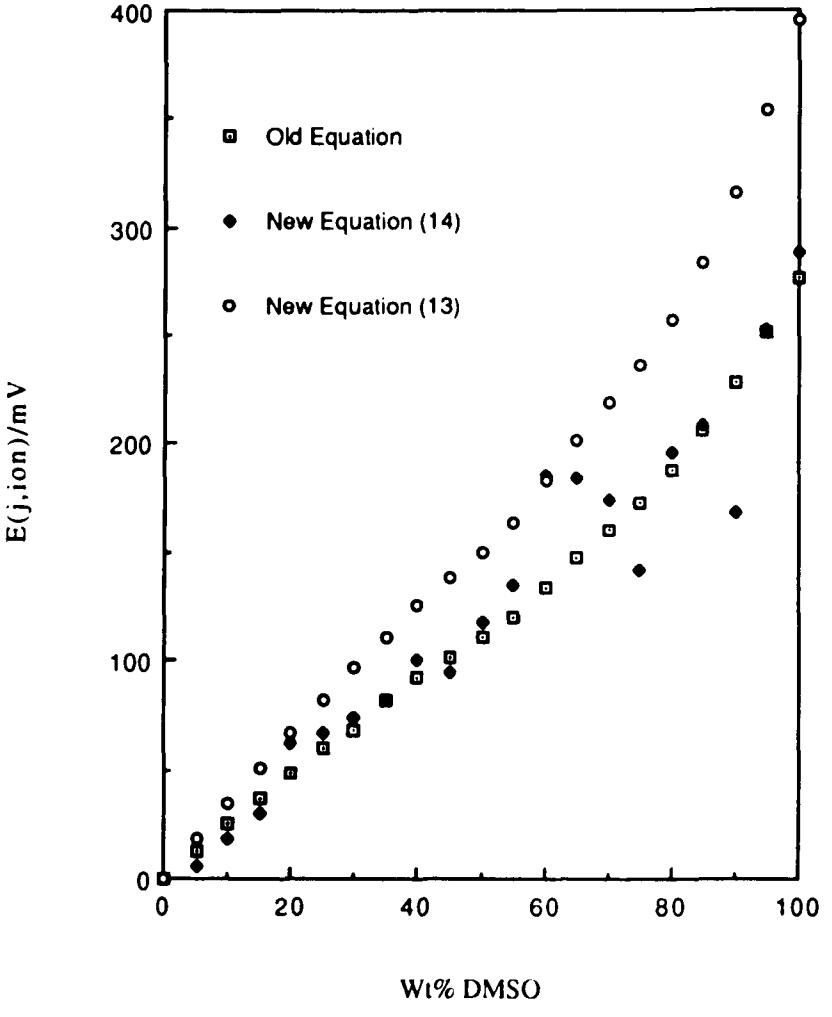
$E_{j,ion}$ in HCl | HCl Cells, in mV at 25°C.

H_2O DMSO-H_2O

Wt% DMSO	Transport Numbers and Transfer Activity Coefficients Interpolated by hand A Eqn.10a	B_1 Eqn.13	B_2 Eqn.14	Interpolated by computer A Eqn.10a	B_1 Eqn.13	B_2 Eqn.14
100	276.1	394.9	288.1	274.4	394.7	373.0
95	251.3	353.8	252.1	252.2	357.1	348.6
90	228.2	315.9	168.3	229.8	322.1	311.4
85	206.1	283.0	208.1	208.7	290.8	296.5
80	187.8	256.8	195.9	189.9	263.4	282.7
75	173.1	236.2	141.9	173.2	239.6	272.4
70	160.2	218.6	174.4	158.7	218.9	258.0
65	147.1	201.3	183.9	145.9	200.6	244.7
60	134.0	182.9	185.2	134.3	183.9	232.5
55	120.2	164.1	134.8	123.3	168.3	145.1
50	110.2	149.9	117.5	112.7	153.5	130.6
45	101.6	138.4	94.3	102.2	138.9	123.8
40	92.7	125.8	99.9	91.7	124.6	106.0
35	82.0	111.2	81.7	81.1	110.2	91.8
30	67.9	96.5	74.2	70.4	95.9	84.8
25	59.9	81.3	67.2	59.6	81.5	66.7
20	48.6	66.6	62.7	48.7	66.7	55.9
15	37.3	50.8	30.0	37.4	51.6	48.7
10	25.3	34.5	18.0	25.9	35.5	36.6
5	13.2	18.0	5.9	13.4	18.3	31.5

FIGURE 37a

$E_{j,ion}$ Calculated from New Equation[a] and Old Equation[b] for HCl in Dimethylsulfoxide-Water Solvents. (Data interpolated by hand)

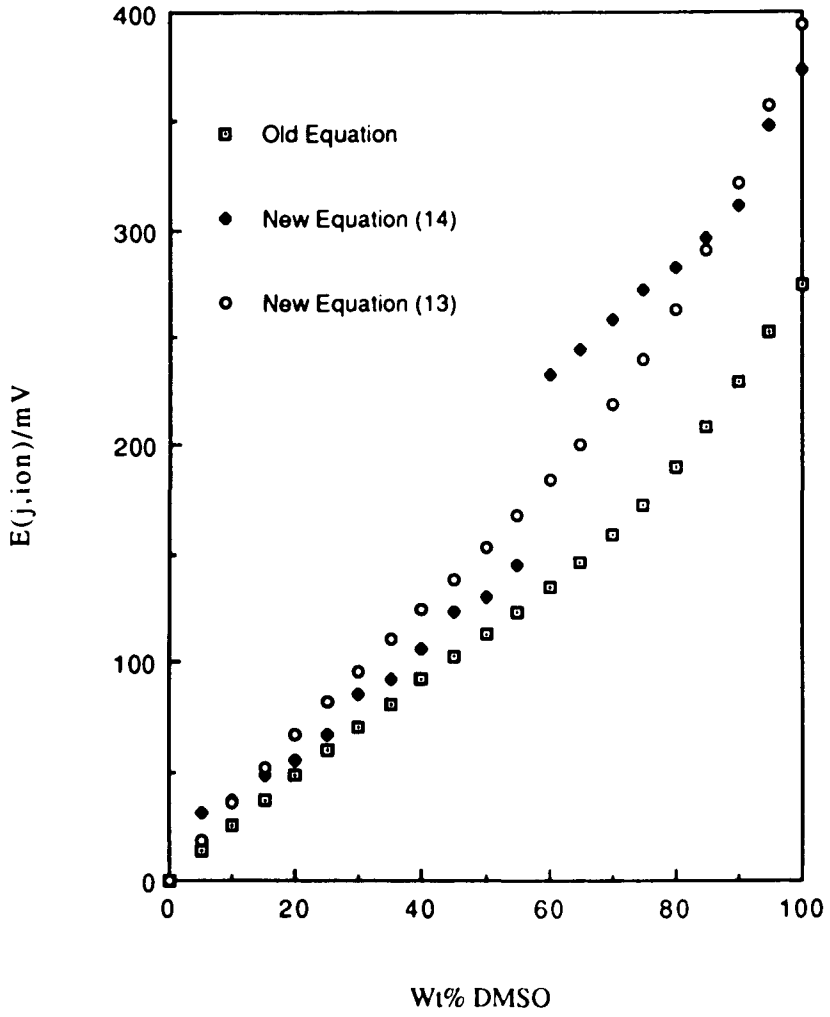


a Column B_1, Table 28, Eqn. 13
Column B_2, Table 28, Eqn. 14

b Column A, Table 28, Eqn. 10a

FIGURE 37b

$E_{j,ion}$ Calculated from New Equation[a] and Old Equation[b] for HCl in Dimethylsulfoxide-Water Solvents. (Data interpolated by computer)



a Column B_1, Table 28, Eqn. 13
Column B_2, Table 28, Eqn. 14

b Column A, Table 28, Eqn. 10a

A Comparison of the $E_{j,ion}$ Calculated from the Old Equation and the New Formulation in DMSO-Water Solvents.

For the DMSO-water mixtures, we observed similar values for the calculated $E_{j,ion}$ from the old and the new equations for KCl|KCl and RbCl|RbCl junctions, because of the transport numbers and transfer activity coefficients of those ions changing smoothly over the entire DMSO-water composition. The differences in $E_{j,ion}$ between either Equations (10a) and (13) or Equations (10a) and (14) show the maximum value of ~15 mV.

The differences in $E_{j,ion}$ between Equations (10a) and (14) are more significant than those between Equations (10a) and (13) for the HCl junction in the region 60 - 100 wt% DMSO. In this region, the transport numbers of the hydrogen ion experience a steep drop. It is important that for the HCl junction in this region, Equation (14) gives more erratic results than Equation (13), because in Equation (14) we have to evaluate the sharply changing slope $\Delta t/\Delta s$, which causes greater errors in the calculation of $E_{j,ion}$. The differences in $E_{j,ion}$ between Equations (10a) and (14) range from 0 to 22 mV up to 55 wt% DMSO and from 100 to 120 mV for 60 - 100 wt% DMSO. We can expect this sudden change in $E_{j,ion}$ (22 - 100 mV) from 55 - 60 wt % DMSO due to the steep slope of the t_H vs. solvent composition of DMSO at 60 wt%. In this case, Equation (14) gives more erratic results than Equation (13).

From all of the solvent systems mentioned, the HCl junction in the DMSO-water system is the most reasonable system in which to demonstrate the difference between Equations (13) and (14) for the calculation of $E_{j,ion}$. Here, if we consider Equation (14) to obtain $E_{j,ion}$, we have to deal with the $\Delta t/\Delta s$ term, which introduces errors

in to the calculation because of the sudden change in the transport numbers of the hydrogen ion at 60 wt% DMSO. On the other hand, the $E_{j,ion}$ calculation from Equation (13) (using the $\Delta G/\Delta s$ term) gave a smooth variation in values through the entire range of DMSO, because the transfer activity coefficients (or transfer free energy) of hydrogen ions varies smoothly and uniformly with the DMSO-water composition.

In conclusion, for systems which do not show a smooth behavior of the transfer activity coefficients of an ion with the solvent composition, we prefer Equation (14), based on the $\Delta t/\Delta s$ term to calculate the $E_{j,ion}$. On the other hand, for systems which do not show a smooth behavior of the transport numbers of ions with solvent composition, we prefer Equation (13), which involves the $\Delta G^o/\Delta s$ term to calculate the $E_{j,ion}$. The latter is true for the system of HCl|HCl junctions in DMSO-water solvents.

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

Calculations of the Solvent Component of the Liquid-Junction Potential, $E_{j,s}$, for the Solvent Systems in This Study.

The term $E_{j,s}$ depends on the two solvents forming the junction, but there is no general formula from which it can be calculated. Although the existence of $E_{j,s}$ was predicted theoretically by Staverman (28) in 1952 and was subsequently confirmed experimentally by many workers, its nature is not yet fully understood. On the basis of our knowledge so far, it is likely that the $E_{j,s}$ is a composite of at least two effects: 1. Solvent-solvent interactions, as reflected by the free energies of transfer of the solvents across the junction and 2. The transport of solvent molecules in the solvation shells of ions crossing the junction.

A comparison of the $E_{j,ion}$ values calculated according to the new and the old equation does not in itself involve the e.m.f. of the cell in which the junction occurs. However, the e.m.f. must be known if we want to evaluate the $E_{j,s}$, the solvent contribution to the overall E_j. If we consider cell (XXII):

$$\begin{array}{c} \text{M (s), MX (s)} \mid \text{NX } (a_1) \mid \text{NX } (a_2) \mid \text{MX (s), M(s)} \\ \qquad\qquad\quad H_2O \qquad\quad S \end{array} \qquad \text{(XXII)}$$

The e.m.f. of the cell (XXII) can be viewed as a sum of three terms:

$$E_{Cell} = E_1 + E_{j,ion} + E_{j,s} \qquad (47)$$

E_1 is the difference between the Nernst equations for the M electrode in the two solvents,

$$E_1 = -59.16 \log_m \gamma_X - 59.16 \log ({}_w a_{X^-} / {}_S a_{X^-}) \quad (48)$$

where $\log_m \gamma_X$ is the transfer activity coefficient of the X^- ion from water to solvent S.

Combining Equations (47) and (48) we obtain:

$$E_{j,s} = E_{Cell} - [-59.16 \log_m \gamma_X - 59.16 \log({}_w a_{X^-} / {}_S a_{X^-})] - E_{j,ion} \quad (49)$$

Thus, the "solvent contribution" , $E_{j,s}$, can be evaluated by using Equation (49), where the value of the $E_{j,ion}$ is calculated either from the old Equation (10a) or from the new formulations, Equation (13) or (14).

In order to use Equation (49) to calculate $E_{j,s}$, the following sets of data had to be available or calculated:

a) Transfer activity coefficients of X^- ion between all the solvents.

b) The e.m.f. of cell C.

c) The activities of X^- in the solvents.

d) The values of the $E_{j,ion}$, the component of E_j due to the passage of ions.

The results of the e.m.f. measurements of cell (XXII) and the calculations of E_1 , $E_{j,ion}$ and $E_{j,s}$ are listed in the Tables that follow.

The $E_{j,s}$ Values Obtained in this Study

In this investigation, the $E_{j,s}$ values for HCl|HCl and NaCl|NaCl junctions between water and methanol-water solvents, for HCl|HCl and KCl|KCl junctions between water and ethanol-water, dimethylformamide-water and dimethylsulfoxide-water solvents and for $AgNO_3|AgNO_3$ junctions between water and acetonitrile-water solvents were calculated. Generally, the concentrations of the electrolytes ranged from $1x10^{-1}$M to $1x10^{-3}$M for the each solvent system. The $E_{j,s}$ values calculated for the various junctions varied from -405 mV to 107 mV. In this study, in dipolar aprotic solvents the $E_{j,s}$ values were found to be more significant than in the protic solvents. There are two different $E_{j,s}$ values reported here by using Equation (49): one calculated using the $E_{j,ion}$ values from the new Equations (13) or (14) and one from the old Equation (10a). For further discussion, the $E_{j,s}$ calculated using the $E_{j,ion}$ from the new equation is referred to $E_{j,s}$(new) and those calculated by using the old equation as $E_{j,s}$(old). The last two columns in each Table show these $E_{j,s}$ values.

One of our objectives was to check whether the new formulations for $E_{j,ion}$ would reduce the contribution of $E_{j,s}$. In fact for most of the junctions, we observed greater values for $E_{j,s}$(new) than for $E_{j,s}$(old).

A Comparison of $E_{j,s}$ values Obtained in This Study with the Literature Values in Methanol-Water Solvents.

NaCl|NaCl Junction

The $E_{j,s}$ calculations for the NaCl|NaCl junction were carried out by using Equation (49) and the $E_{j,ion}$ values calculated from both the new and the old equations, as well as E_1 and E_{cell} values from the literature [4]. The results are shown in Table 29. For this junction, $E_{j,s}$(new) and $E_{j,s}$(old) values vary from 14 to 34 mV and 11 to 30 mV, respectively when increasing the composition of methanol from 50 to 90 wt%. These results are plotted in Figure 38. As can be seen from these results, the $E_{j,s}$ tends to increase with increasing wt% methanol. We also can see that as the concentration of NaCl decreases, $E_{j,s}$ generally increases positively. The values of $E_{j,s}$ for the most concentrated NaCl solution ($1X10^{-1}M$) is appreciably lower than the values determined at the other concentrations ($3X10^{-2}M$, $3X10^{-3}M$) studied. For example, for a junction between water and 90 wt% methanol, $E_{j,s}$ for $1X10^{-1}M$ NaCl solution is 27.5 mV, compared to 33 mV for a solution of $3X10^{-3}M$ NaCl. Similarly, the $E_{j,s}$ values of 57.8 mV for a junction between $2.0X10^{-5}$ mole fraction NaCl solution in water and 87.68 wt% methanol was calculated from experimental measurements of Alfenaar, De Ligny and Remijnse [2], using a values of $\log_m \gamma_{NaCl}$ from reference [72]. Although this measurement was made at 87.68 wt% methanol rather than at 90 wt% methanol, it seems to indicate a trend toward larger values of $E_{j,s}$ with decreasing concentration of NaCl.

Murray and Aikens [1] reported a value of $E_{j,s}$ equal to 18 mV

for a junction between saturated solutions of KCl in water and methanol. Alfenaar, De Ligny and Remijnse [2] calculated a value of 53 mV for the same junction between very dilute solution ($2.0X10^{-5}$ mole fraction). Goldberg [25] obtained values of $E_{j,s}$ ranging from 2 mV to 14 mV for junctions between saturated solution of NaCl in water and series of methanol-water solvents. Those values were considerably lower (by 15-25 mV) than the values of $E_{j,s}$ obtained by him for the given junction using dilute ($3X10^{-2}M$ and $3X10^{-3}M$) solutions of NaCl. Berne [4] obtained values of $E_{j,s}$ ranging from 12 mV to 29 mV for NaCl solutions (concentration ranging from $1X10^{-3}M$ to $1X10^{-1}M$) in water and a series of methanol-water solvents. From these results there is enough evidence to say that the magnitude of $E_{j,s}$ is inversely related to the concentration of the electrolyte forming the interface between the two solvents.

In conclusion, although there was hope that the values of $E_{j,ion}$ obtained from the new formulation might reduce the $E_{j,s}$ contribution in E_j calculations, our results show that just the opposite is true: we observe higher $E_{j,s}$(new) than $E_{j,s}$(old) for the entire range of methanol-water compositions.

TABLE 29

Experimental and Calculated Parameters for the Calculation of $E_{j,s}$ in NaCl in Methanol-Water Solvents. (Molar Scale, 25°C)

NaCl | NaCl

H_2O MeOH- H_2O

Wt% MeOH	~C_{NaCl}	E_{exp}[a]	E_l[a]	$E_{j,ion}$ New	$E_{j,ion}$ Old (mV)	$E_{j,s}$ New	$E_{j,s}$ Old
50	$1x10^{-1}$	-26.7	-36.7	-3.6	-1.2	13.6	11.2
	$3x10^{-2}$	-27.2	-37.8			14.2	11.8
	$3x10^{-2}$	-27.9	-38.7			14.4	12.0
	$3x10^{-3}$	-26.8	-39.3			16.1	13.7
	$3x10^{-3}$	-29.9	-40.2			13.9	11.5
60	$1x10^{-1}$	-34.7	-48.4	-0.9	1.6	14.6	12.1
	$3x10^{-2}$	-34.6	-50.0			16.3	13.8
	$3x10^{-2}$	-36.3	-51.6			16.2	13.7
	$3x10^{-3}$	-34.2	-53.2			19.9	17.4
	$3x10^{-3}$	-35.7	-53.7			18.9	16.4
70	$1x10^{-1}$	-39.4	-61.4	3.2	5.6	18.5	16.4
	$3x10^{-2}$	-38.3	-61.9			20.1	18.0
	$3x10^{-2}$	-40.7	-62.6			18.4	16.3
	$3x10^{-3}$	-38.7	-64.4			22.2	20.1
	$3x10^{-3}$	-42.0	-65.2			19.7	17.6

Wt% MeOH	~C_{NaCl}	E_{exp}[a]	E_l[a]	$E_{j,ion}$ New	$E_{j,ion}$ Old	$E_{j,s}$ New	$E_{j,s}$ Old
				(mV)			
80	$1x10^{-1}$	-44.9	-77.9	10.9	13.6	22.8	19.4
	$3x10^{-2}$	-44.3	-78.9			24.4	21.0
	$3x10^{-2}$	-49.2	-84.1			24.7	21.3
	$3x10^{-3}$	-44.6	-82.1			27.3	23.9
	$3x10^{-3}$	-51.4	-87.5			26.0	22.5
90	$1x10^{-1}$	-50.8	-99.2	20.9	25.0	27.5	23.5
	$3x10^{-2}$	-51.2	-102.5			30.4	26.4
	$3x10^{-2}$	-51.1	-100.5			28.5	24.5
	$3x10^{-3}$	-52.4	-106.8			33.5	29.5
	$3x10^{-3}$	-54.2	-104.7			29.6	25.6

(a) Reference [4]

FIGURE 38

$E_{j,s}$ Values Calculated for NaCl|NaCl Junctions in Methanol-Water Solvents.

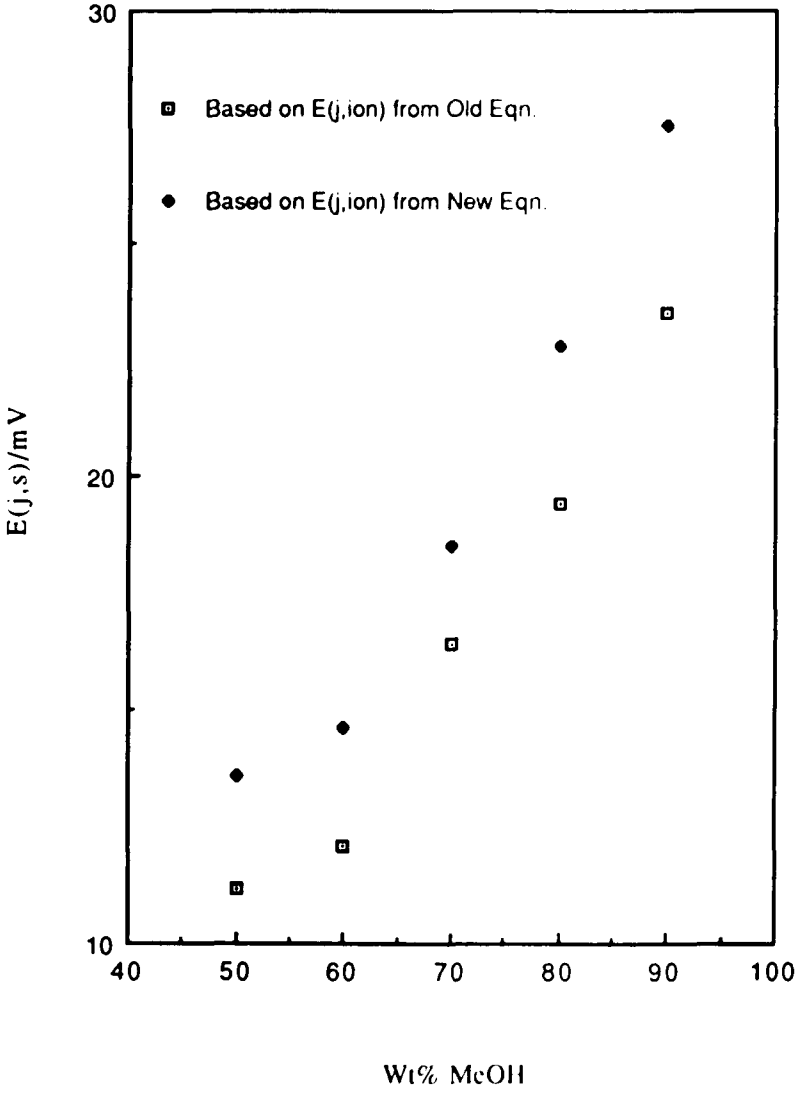


TABLE 30

Comparison of Calculated $E_{j,s}$ Values for NaCl|NaCl Junctions in Methanol-Water Solvents. (in millivolts)

Wt%	Goldberg[48]		Berne[4]		This Study	
MeOH	C_{NaCl}	$E_{j,s}$	C_{NaCl}	$E_{j,s}$	$E_{j,s}$(new)	$E_{j,s}$(old)
90	Saturated	14	$1x10^{-1}$	25.4	27.5	23.5
	$3x10^{-2}$	40	$3x10^{-2}$	27.3	30.4	26.4
	$3x10^{-3}$	45	$3x10^{-3}$	28.8	33.5	29.5
80	Saturated	7	$1x10^{-1}$	21.0	22.8	19.4
	$3x10^{-2}$	32	$3x10^{-2}$	22.0	24.4	21.0
	$3x10^{-3}$	39	$3x10^{-3}$	23.6	27.3	23.9
70	Saturated	7	$1x10^{-1}$	17.6	18.5	16.4
	$3x10^{-2}$	26	$3x10^{-2}$	18.4	20.1	18.0
	$3x10^{-3}$	32	$3x10^{-3}$	19.6	22.2	20.1
60	Saturated	2	$1x10^{-1}$	12.8	14.6	12.1
	$3x10^{-2}$	21	$3x10^{-2}$	14.0	16.3	13.8
	$3x10^{-3}$	20	$3x10^{-3}$	16.8	19.9	17.4
50			$1x10^{-1}$	11.7	13.6	11.2
			$3x10^{-2}$	12.1	14.2	11.8
			$3x10^{-3}$	12.5	16.1	13.7

HCl|HCl Junctions in Methanol-Water Solvents

The results are tabulated in Table 31. In this study, $E_{j,s}$ values were calculated by using both the $E_{j,ion}$ from the new equations and the old equation. The $E_{j,s}$(new) values decrease from 13 to 7 mV when increasing the composition of methanol from 30 to 60 wt% and then increase up to 60 mV for 90 wt% MeOH. In contrast, the $E_{j,s}$(old) values increase smoothly from 1 to 30 mV when increasing the composition of methanol from 30 to 90 wt%. In order to illustrate and to determine the extent of change in $E_{j,s}$ values in terms of using $E_{j,ion}$ values from the old and the new equations, a graph (Figure 39) was drawn of $E_{j,s}$ values as a function of methanol composition.

TABLE 31.

Experimental and Calculated Parameters for the Calculation of $E_{j,s}$ in HCl in Methanol-Water Solvents. (Molar Scale, 25° C)

HCl | HCl

H_2O MeOH- H_2O

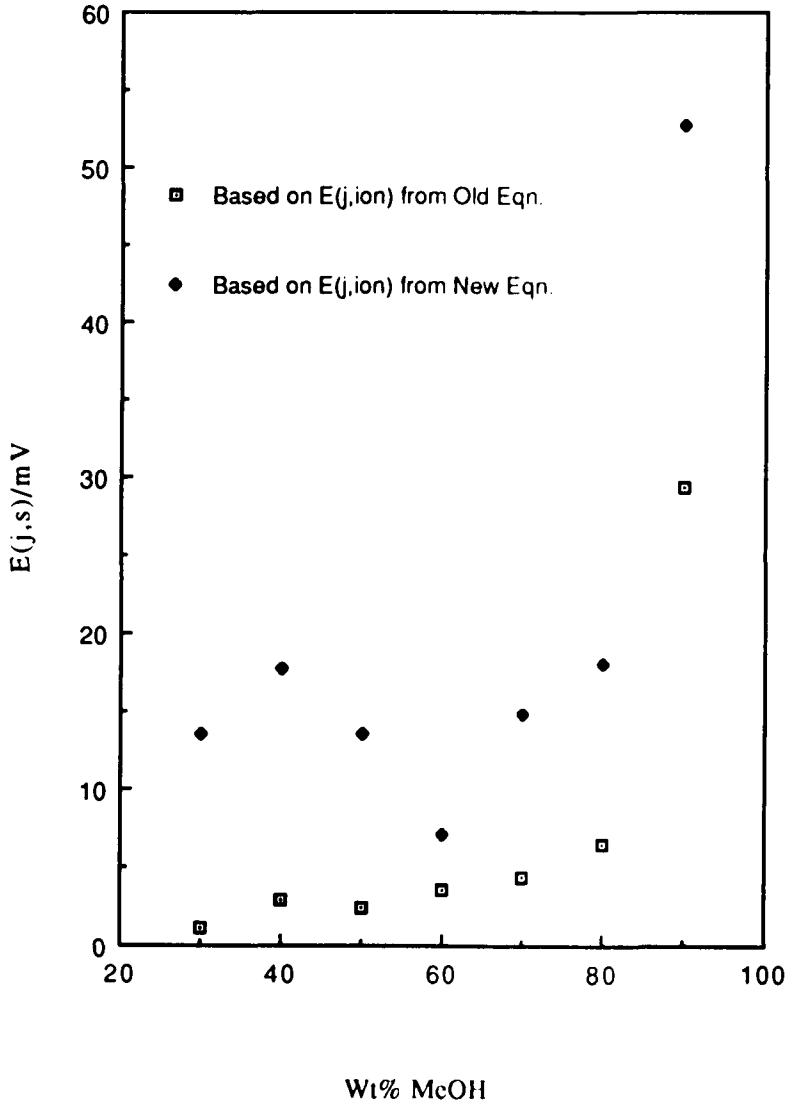
Wt% MeOH	~C_{HCl}	E_{Exp}[a]	E_l[a]	$E_{j,ion}$ New (mV)	$E_{j,ion}$ Old (mV)	$E_{j,s}$ New (mV)	$E_{j,s}$ Old (mV)
30	$1x10^{-1}$	-15.0	-13.8	-14.8	-2.4	13.6	1.2
	$1x10^{-2}$	-16.8	-14.2			12.2	-0.3
	$1x10^{-3}$	-10.6	-15.3			19.5	7.1
40	$1x10^{-1}$	-18.3	-22.5	-13.6	1.4	17.8	2.9
	$1x10^{-2}$	-20.1	-23.9			17.4	2.4
	$1x10^{-3}$	-20.1	-24.6			18.1	3.1
50	$1x10^{-1}$	-23.6	-37.3	0.2	11.3	13.5	2.4
	$1x10^{-2}$	-27.7	-39.3			11.4	0.3
	$1x10^{-3}$	-38.0	-40.3			2.1	-0.9
60	$1x10^{-1}$	-28.2	-47.8	12.5	16.1	7.1	3.5
	$1x10^{-2}$	-31.1	-50.4			6.8	3.2
	$1x10^{-3}$	-34.2	-51.8			5.1	1.5
70	$1x10^{-1}$	-36.0	-62.1	11.2	21.7	14.9	4.4
	$1x10^{-2}$	-39.2	-65.5			15.1	4.6
	$1x10^{-3}$	-45.3	-67.3			10.8	0.3

Wt% MeOH	~C_{HCl}	E_{Exp}[a]	E_1[a]	$E_{j,ion}$ New (mV)	$E_{j,ion}$ Old	$E_{j,s}$ New	$E_{j,s}$ Old
80	$1x10^{-1}$	-46.0	-79.9	15.9	27.5	18.0	6.4
	$1x10^{-1}$	-46.8	-80.0			17.3	5.7
	$1x10^{-2}$	-49.8	-84.2			18.5	6.9
	$1x10^{-2}$	-50.0	-83.4			17.5	5.9
	$1x10^{-3}$	-49.2	-86.6			21.5	9.9
	$1x10^{-3}$	-50.8	-86.2			19.5	7.9
90	$1x10^{-1}$	-59.0	-99.9	-11.9	11.6	52.8	29.3
	$1x10^{-1}$	-58.9	-99.8			52.8	29.3
	$1x10^{-2}$	-61.1	-105.1			56.4	32.9
	$1x10^{-2}$	-63.0	-105.4			54.3	30.8
	$1x10^{-3}$	-63.0	-108.6			57.5	34.0
	$1x10^{-3}$	-55.6	-108.9			64.7	41.2

(a) Reference [4]

FIGURE 39

$E_{j,s}$ Values Calculated for HCl\|HCl Junction in Methanol-Water Solvents.



Bates, Paabo and Robinson [73] and de Ligny and Rehbach [74] studied the e.m.f. of a cell in which a liquid junction was formed between a saturated KCl solution in water and dilute solutions of hydrogen ions (in buffers) in methanol-water solvents. From the experimental data, a value of δ was calculated for each methanol-water solvent, where δ was defined by

$$\delta = E_j - \log {}_m\gamma_H \qquad (49)$$

where E_j was in pH units. The liquid-junction potential E_j' for this interface can be calculated if we assume that the contributions to E_j from the buffer constituents can be ignored, relative to that of the saturated KCl. Since the transfer activity coefficients for hydrogen ion are also known, we can calculate $E_{j,s}$ values from:

$$E_{j,s} = \delta + \log {}_m\gamma_H - E_j' \qquad (50)$$

Using these literature data [73,74] the $E_{j,s}$ values were calculated. Berne [4] used cell (XXII) to estimate $E_{j,s}$ values for HCl solutions ranging from $1x10^{-3}$ to $1x10^{-1}$M in water and methanol-water solutions. In her calculations of $E_{j,s}$, she used $E_{j,ion}$ values from the old equation. In Figure 40 and Table 32, the $E_{j,s}$ values from the literature and this study are compared. Even though there is a general trend among the $E_{j,s}$ values of first increasing, and then decreasing with the increasing methanol composition, the individual values are rather scattered. From Figure 40, we can see that there is a poor correlation between the $E_{j,s}$ values for HCl|HCl junction from the literature and this study. In this study, the $E_{j,s}$ value is relatively

high for the composition of 90 wt% methanol. At that composition of MeOH, the transport number of the hydrogen ion goes through a minimum.

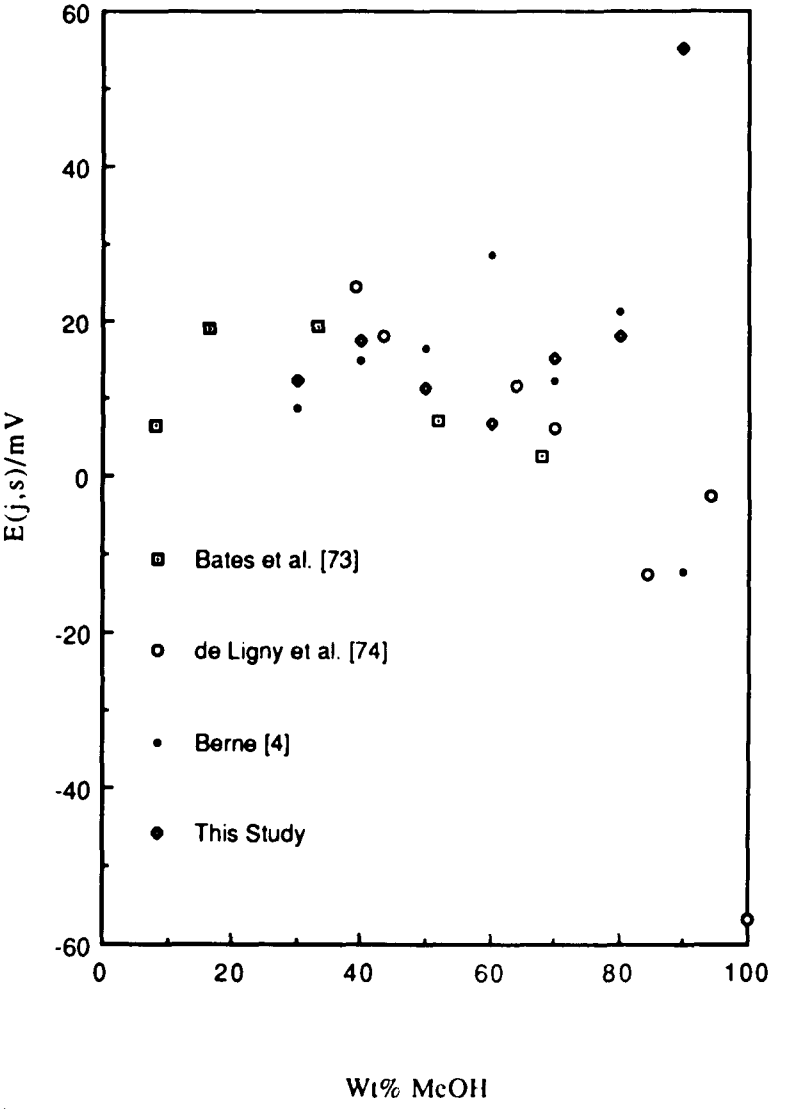
TABLE 32

A Comparison of the Literature Values of $E_{j,s}$ in Methanol-Water Solvents.

Wt% MeOH	$E_{j,s}$ (mV)	
	Bates et. al. [73]	
8.1	6.5	
16.3	19.1	
33.3	19.4	
52.1	7.2	
68.1	2.7	
	de Ligny et. al. [74]	
39.1	24.4	
43.3	18.1	
64.2	11.7	
70.0	6.0	
84.2	-12.5	
94.2	-2.6	
100	-56.9	
	Berne [4]	This Study
30	8.7	12.2
40	14.7	17.4
50	16.6	11.4
60	28.8	6.8
70	12.3	15.1
80	21.2	18.0
90	-12.2	55.3

FIGURE 40

Comparison of the $E_{j,s}$ Values in this Study with the Literature in Methanol-Water Solvents.



Comparison of $E_{j,s}$ Values of NaCl, KCl and HCl in MeOH-Water Solvents.

Table 33 contains the $E_{j,s}$ values for the NaCl|NaCl, KCl|KCl and HCl|HCl junctions in methanol-water solvents and the transfer activity coefficients of the corresponding cations. The calculations of $E_{j,s}$ for the NaCl|NaCl and HCl|HCl junctions in methanol-water solvents were discussed earlier. The following cell was used to measure $E_{j,s}$ directly:

$$\underset{}{Hg(l)\,,\,Hg_2Cl_2\,(s)\,|\,KCl\,(Satd.)}\;\underset{H_2O}{|}\;\underset{MeOH\text{-}H_2O}{KCl\,(Satd.)\,|\,Hg_2Cl_2\,(s)\,,\,Hg(l)} \qquad (XXIII)$$

It consists of two saturated calomel electrodes immersed in saturated solutions of KCl in water and methanol-water, respectively. The e.m.f. of this cell can be represented by:

$$E(XXIII) = -(t_k/F)\,\Delta G_t(KCl)\ \text{Satd.} + E_{j,s} \qquad (34b)$$

As discussed earlier, in the absence of any crystal solvates, the (partial molar) free energies of any two saturated solutions of a solute i, are equal. Thus, the free energies of the two saturated solutions of KCl in water and methanol-water media must be equal and the corresponding $\Delta G_t(KCl)$ is equal to zero, leaving

$$E(XXIII) = E_{j,s} \qquad (50)$$

The transfer activity coefficients of Na^+ and K^+ ions increase with increasing composition of methanol. With the increasing

concentration of methanol, the $E_{j,s}$ values increased linearly for the NaCl|NaCl and KCl|KCl junctions. The transfer activity coefficients of Na^+ and K^+ ions are very similar. As was shown earlier, the transfer activity coefficient of the hydrogen ion does not follow the above behavior. The $E_{j,s}$ values decreased with the addition of methanol and then increased with a minimum $E_{j,s}$ value at 60 wt% methanol, which is the composition corresponding to the maximum basicity.

TABLE 33

Transfer Activity Coefficients and $E_{j,s}$ Values in MeOH-Water Mixtures. (25°C)

Wt% MeOH	$\log_m \gamma_H$	$E_{j,s}$(mV) HCl | HCl H_2O S-H_2O	$\log_m \gamma_{Na}$	$E_{j,s}$(mV) NaCl | NaCl H_2O S-H_2O	$\log_m \gamma_K$	$E_{j,s}$[a](mV) KCl* | KCl* H_2O S-H_2O
100	1.80		1.57	34.1[b]	1.72	18.7
90	0.53	52.8	1.51	27.5	1.70	15.1
80	-0.08	18.0	1.44	22.8	1.58	11.7
70	-0.11	14.9	1.35	18.5	1.39	8.8
60	-0.10	7.1	1.16	14.6	1.22	6.3
50	-0.06	13.5	1.00	13.6	0.99	4.3
40	0.07	17.8	0.89	12.5[b]	0.87	2.8
30	0.11	13.6			0.70	1.7
20	0.20				0.48	0.9
10	0.08				0.20	0.3

a Zhou, L., Unpublished data from our laboratory

b Interpolated values

* Saturated KCl Solutions

A Comparison of $E_{j,s}$ values Obtained in this Study with the Literature Values in Ethanol-Water solvents.

KCl|KCl Junctions

Murray and Aikens [1] reported a value of $E_{j,s}$ equal to 38 mV for a junction between saturated solutions of KCl in water and ethanol. In this study, the e.m.f. measurements were taken for the entire range of ethanol-water solvents for the concentration of KCl solutions varied from $2x10^{-2}$ M to $2x10^{-4}$ M using cell (XXII). For the system of KCl|KCl junctions in EtOH-water solvents we observed the same behavior as discussed in NaCl in methanol-water solvents. The $E_{j,s}$(new) and $E_{j,s}$(old) values are very similar for each solvent composition and vary from 0.5 mV to 33 mV for the entire range of ethanol-water solvents. These results are listed in Table 34. It can be seen from these results that $E_{j,s}$ tends to increase with increasing wt% ethanol.

TABLE 34.

Experimental and Calculated Parameters for the Calculation of $E_{j,s}$ in KCl in Ethanol-Water Solvents. (Molar Scale, 25°C)

KCl | KCl
H_2O EtOH- H_2O

Wt% EtOH	~C_{KCl}	E_{cell}	E_l	$E_{j,ion}$ New	$E_{j,ion}$ Old	$E_{j,s}$ New	$E_{j,s}$ Old
				(mV)			
12.0	$2x10^{-2}$	-8.5	-4.2	-4.8	-4.7	0.5	0.4
	$2x10^{-3}$	-8.7	-4.1			0.3	0.1
	$2x10^{-4}$	-22.8	-4.2			13.8	-14.0
18.9	$3x10^{-2}$	-15.6	-9.8	-5.9	-5.9	0.1	0.1
	$3x10^{-3}$	-15.7	-9.7			-0.1	-0.1
	$3x10^{-4}$	-23.3	-9.7			-7.8	-7.8
30.4	$3x10^{-2}$	-25.1	-25.7	-3.0	-2.8	3.6	3.4
	$3x10^{-3}$	-24.8	-25.7			3.9	3.7
	$3x10^{-4}$	-38.6	-25.7			-9.9	-10.1
38.1	$2x10^{-2}$	-31.5	-40.1	3.4	3.2	5.2	5.2
	$2x10^{-3}$	-31.2	-40.1			5.5	5.7
	$2x10^{-4}$	-39.0	-40.1			-2.3	-2.1
46.7	$2x10^{-2}$	-40.1	-57.4	13.8	14.0	3.5	3.3
	$2x10^{-3}$	-40.0	-57.3			3.5	3.3
	$2x10^{-4}$	-55.2	-57.3			-11.7	-11.9

Wt% EtOH	~C_{KCl}	E_{cell}	E_l	$E_{j,ion}$ New	$E_{j,ion}$ Old	$E_{j,s}$ New	$E_{j,s}$ Old
				(mV)			
56.5	$2x10^{-2}$	-49.7	-77.2	20.3	20.7	7.1	6.8
	$2x10^{-3}$	-50.8	-77.2			6.0	5.7
	$2x10^{-4}$	-60.1	-77.2			-8.3	-3.6
65.5	$2x10^{-2}$	-65.2	-91.7	22.9	25.0	3.6	1.5
	$2x10^{-3}$	-61.5	-91.4			7.1	5.0
	$2x10^{-4}$	-71.3	-91.5			-2.7	-4.7
74.2	$2x10^{-3}$	-79.2	-103.6	23.1	24.6	1.3	1.3
	$2x10^{-4}$	-80.5	-103.6			0.1	-1.5
	$2x10^{-5}$	-93.5	-103.6			-12.9	-14.5
84.0	$2x10^{-3}$	-94.3	-117.6	17.3	17.3	6.1	6.1
	$2x10^{-4}$	-91.2	-117.6			9.2	9.1
	$2x10^{-5}$	-115.6	-117.6			-14.7	-14.7
100	$3x10^{-4}$	-107.2	-153.2	14.6	13.3	31.5	32.8
	$4x10^{-4}$	-108.2	-149.6			26.8	28.1
	$9x10^{-4}$	-110.2	-155.9			31.5	32.5

HCl|HCl Junctions in EtOH-Water Solvents.

For the HCl|HCl junction in ethanol-water solvents, the calculated $E_{j,s}$ values varied from 1 to 129 mV for the entire solvent range. A sudden increase in $E_{j,s}$ values for the composition of 75 - 100 wt% EtOH was observed. Great differences between the values of $E_{j,s}$(new) and $E_{j,s}$(old) were observed and these differences increased with increasing composition of ethanol. Table 35 shows these results. Figures 41 and 42 illustrate the $E_{j,s}$ values for KCl|KCl and HCl|HCl junctions in ethanol-water solvents, and they show the effect on $E_{j,s}$ values when using $E_{j,ion}$ values from the old and the new equations.

Bates, Paabo and Robinson [73] studied the e.m.f. of cells in which a liquid junction was formed between a saturated KCl solution in water and dilute solutions of hydrogen ions (in buffers) in ethanol-water solvents. Using the above results, the values of $E_{j,s}$ were calculated by Goldberg [25]. These results are shown in Table 36 and Figure 43. In Figure 43, the $E_{j,s}$ values from this study and the calculated $E_{j,s}$ values from the data of Bates, Paabo and Robinson [73] are compared. As can be seen from Figure 43, there is poor correlation between the results from these two studies.

TABLE 35

Experimental and Calculated Parameters for the Calculations of $E_{j,s}$ in HCl in Ethanol-Water Solvents. (Molar Scale, 25°C)

HCl | HCl
H_2O EtOH- H_2O

Wt% EtOH	$\sim C_{HCl}$	E_{cell}	E_l	$E_{j,ion}$ New	$E_{j,ion}$ Old	$E_{j,s}$ New	$E_{j,s}$ Old
			(mV)				
11.6	$1x10^{-2}$	-4.9	-4.6	-0.1	-3.4	-0.2	3.1
	$1x10^{-3}$	-6.5	-4.7			-1.8	1.6
	$1x10^{-4}$	-21.2	-4.6			-16.5	-13.2
19.3	$1x10^{-2}$	-9.3	-10.2	2.7	-1.5	-1.8	2.4
	$1x10^{-3}$	-13.5	-10.2			-6.0	-1.8
	$1x10^{-4}$	-27.0	-10.2			-19.5	-15.3
27.3	$1x10^{-2}$	-11.7	-20.9	9.5	4.0	-0.3	5.1
	$1x10^{-3}$	-15.6	-20.9			-4.2	1.3
	$1x10^{-4}$	-23.2	-20.9			-11.8	-6.3
36.1	$1x10^{-2}$	-15.6	-36.1	31.5	15.5	-11.1	5.0
	$1x10^{-3}$	-20.8	-36.1			-16.2	-0.2
	$1x10^{-4}$	-26.5	-36.2			-21.9	-5.9
46.3	$1x10^{-2}$	-19.5	-56.5	30.0	34.0	7.0	3.0
	$1x10^{-3}$	-27.5	-56.5			-1.0	-5.0
	$1x10^{-4}$	-45.2	-56.5			-18.7	-22.7

Wt% EtOH	~C_{HCl}	E_{cell}	E_l (mV)	$E_{j,ion}$ New	$E_{j,ion}$ Old	$E_{j,s}$ New	$E_{j,s}$ Old
55.6	$1x10^{-2}$	-24.3	-75.4	49.0	46.0	2.1	5.1
	$1x10^{-3}$	-35.7	-75.4			-9.3	-6.3
	$1x10^{-4}$	-60.2	-75.4			-33.8	-30.8
63.8	$1x10^{-2}$	-28.1	-89.3	60.5	53.8	0.7	7.4
	$1x10^{-3}$	-41.1	-89.3			-12.3	-5.6
	$1x10^{-4}$	-53.6	-89.3			-24.8	-18.1
74.1	$1x10^{-2}$	-35.5	-102.9	76.0	57.8	-8.6	9.6
	$1x10^{-2}$	-51.3	-102.9			-24.4	-6.2
	$1x10^{-4}$	-65.5	-102.9			-38.6	-20.4
82.8	$1x10^{-2}$	-48.8	-115.7	26.5	55.3	40.4	11.6
	$1x10^{-3}$	-65.7	-115.5			23.3	-5.5
	$1x10^{-4}$	-71.5	-115.6			17.6	-11.2
100	$1x10^{-2}$	-58.6	-160.3	7.3	-27.6	94.5	129.3
	$1x10^{-3}$	-86.3	-160.3			66.7	101.6
	$1x10^{-4}$	-95.5	-160.3			57.5	92.4

FIGURE 41

$E_{j,s}$ Values Calculated for KCl|KCl Junction in Ethanol-Water Solvents.

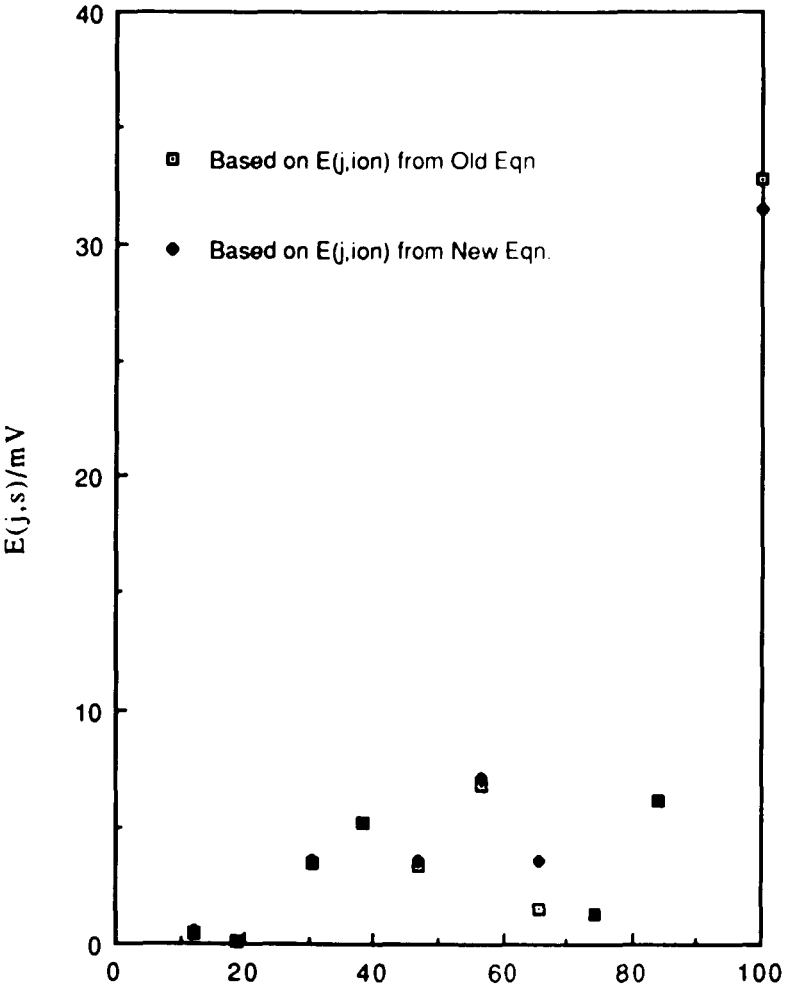


FIGURE 42

$E_{j,s}$ Values Calculated for HCl|HCl Junction in Ethanol-Water Solvents.

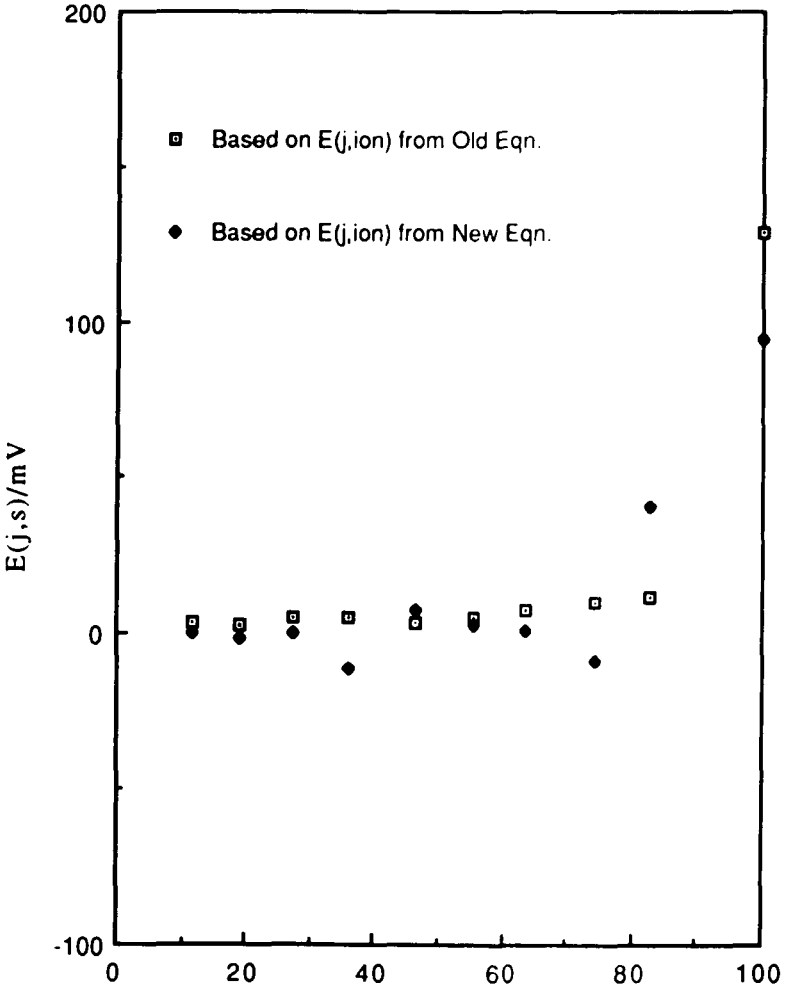


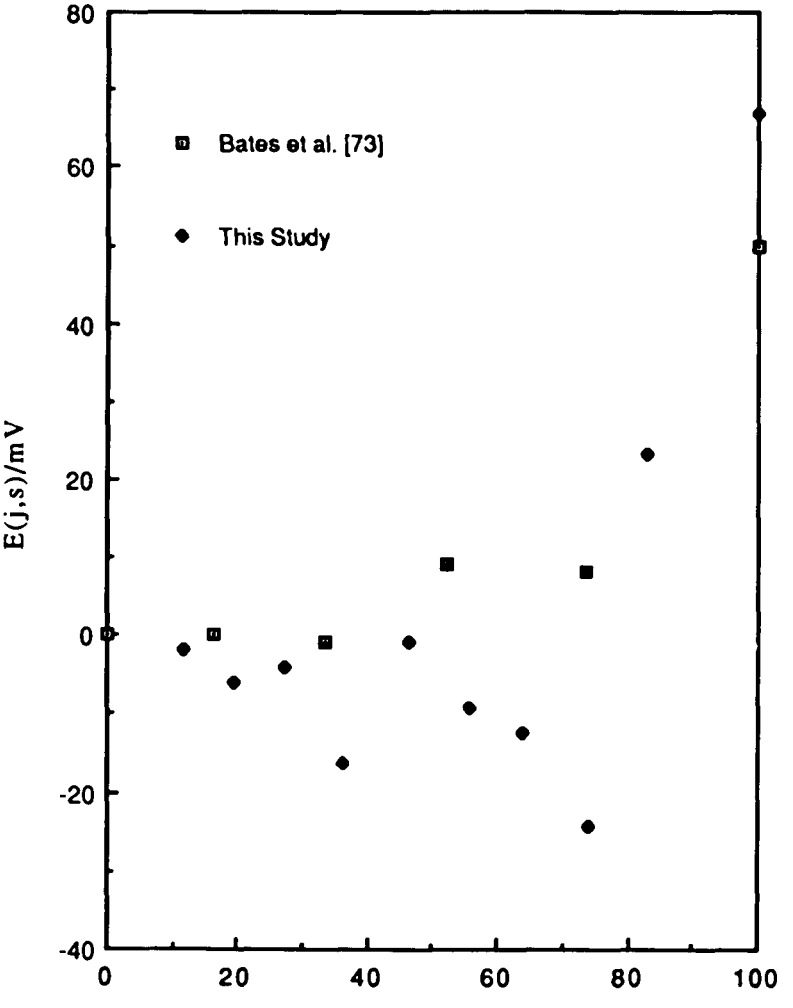
TABLE 36

The $E_{j,s}$ Values Based on the Literature Data(73) and from this Study in Ethanol-Water Solvents.

Wt% EtOH	$E_{j,s}$
Bates et al [73]	(mV)
0	0
16.2	0
33.3	-1
52.1	9
73.4	8
100	50
This Study	
11.6	-1.8
19.3	-6.0
27.3	-4.2
36.1	-16.2
46.3	-1.0
55.6	-9.3
63.8	-12.3
74.1	-24.4
82.8	23.3
100	66.7

FIGURE 43

Comparison of the $E_{j,s}$ Values in this Study with the Literature [73] in Ethanol-Water Solvents.



Calculated $E_{j,s}$ Values for the $AgNO_3|AgNO_3$ Junctions in Acetonitrile-Water Solvents.

Acetonitrile, unlike water and AN-water mixtures, has weak solvent-solvent interactions, it is not extensively ordered and is a solvent of relatively high entropy [76].

The calculated $E_{j,s}$ values for $AgNO_3|AgNO_3$ junctions in AN-water solvents are noteworthy. The most striking feature of the calculated solvent components of the liquid-junction potential, $E_{j,s}$, is that their values are not only appreciable, but generally larger than the $E_{j,ion}$ values. The calculated results for the $E_{j,s}$ values of $AgNO_3|AgNO_3$ junctions in AN-water solvents are listed in Table 37. The $E_{j,s}$ values range from -67 mV to -403 mV, when the composition of the AN-water solvents varies from 10 - 100 wt%. From the above results it has been shown that the $E_{j,s}$ values are significant for the $AgNO_3|AgNO_3$ junctions in AN-water solvents, since the ion-solvent interactions are larger. The solvation behavior of silver ion is of interest in mixed solvents because of a special interaction between the ion and AN. The silver ions are more strongly solvated by AN than by water and so will tend to transport AN into water. This happens because the silver ion forms strong complexes with AN, through $p\pi - d\pi$ back bonding interactions. It can be seen, that the sharp decrease in the Walden product (the Walden product is inversely dependent on the radius of the solvated ion) upon transfer of $AgNO_3$ from water to AN-water is an indication of a large increase in the radius of the solvated ion. Because of the large molar volumes of AN, the nitrile-solvated ions are bulkier than the water-solvated ions. We know from the literature [77] that the solvation shell of the silver ion contains approximately 7 AN and 2

water molecules. The nitrate ion, however, is surrounded by 2 AN and 4 water molecules. We interpret the significant values of $E_{j,s}$ to be the result of this solvation behavior of silver and nitrate ions in AN-water solvents.

TABLE 37

Experimental and Calculated Parameters for $AgNO_3$ in Acetonitrile - Water Solvents. (Molar Scale, 25°C)

$AgNO_3$ | $AgNO_3$
H_2O AN-H_2O

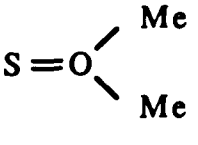
Wt%AN	~C_{AgNO3}	E_{exp}	E_l (mV)	$E_{j,ion}$ New	$E_{j,ion}$ Old	$E_{j,s}$ New	$E_{j,s}$ Old
9.4	$1x10^{-2}$	-70.8	32.9	-36.7	-32.5	-66.9	-71.2
	$1x10^{-3}$	-72.5	33.0			-68.8	-73.0
	$1x10^{-4}$	-73.5	33.1			-69.8	-74.1
19.1	$1x10^{-2}$	-96.7	66.8	-51.0	-45.6	-107.7	-109.2
	$1x10^{-3}$	-94.5	66.6			-110.1	-115.5
	$1x10^{-4}$	-98.8	66.7			-114.5	-119.9
26.5	$1x10^{-2}$	-103.4	93.7	-51.8	-45.5	-145.3	-151.6
	$1x10^{-3}$	-104.7	94.3			-147.5	-153.5
	$1x10^{-4}$	-112.2	94.5			-154.9	-161.2
36.1	$1x10^{-2}$	-114.2	128.4	-48.8	-39.0	-193.8	-203.6
	$1x10^{-3}$	-117.3	129.2			-197.6	-207.4
	$1x10^{-4}$	-119.1	129.4			-199.7	-209.5
47.1	$1x10^{-2}$	-113.2	161.2	-51.3	-27.0	-223.1	-247.4
	$1x10^{-3}$	-115.5	162.5			-226.8	-251.0
	$1x10^{-4}$	-117.8	163.0			-229.5	-253.8

Wt%AN	~C_{AgNO3}	E_{exp}	E_1	$E_{j,ion}$ New	$E_{j,ion}$ Old	$E_{j,s}$ New	$E_{j,s}$ Old
58.9	$1x10^{-2}$	-115.3	195.3	-1.0	1.0	-309.6	-311.6
	$1x10^{-3}$	-113.9	197.2			-310.1	-312.1
	$1x10^{-4}$	-111.9	197.8			-308.7	-310.7
76.7	$1x10^{-2}$	-97.1	238.8	5.5	29.3	-341.4	-365.2
	$1x10^{-3}$	-101.8	241.6			-348.9	-372.7
	$1x10^{-4}$	-105.8	242.5			-353.8	-377.6
86.7	$1x10^{-2}$	-95.2	258.9	36.0	47.0	-390.2	-401.2
	$1x10^{-3}$	-96.2	255.1			-387.3	-398.3
	$1x10^{-4}$	-102.2	256.2			-394.4	-405.4
100	$1x10^{-2}$	-75.8	257.7	36.4	56.0	-369.9	-389.5
	$1x10^{-3}$	-81.8	262.2			-380.4	-399.9
	$1x10^{-4}$	-83.6	263.8			-396.5	-403.4

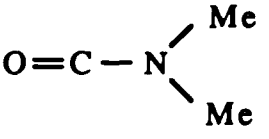
Calculated $E_{j,s}$ Values for KCl|KCl and HCl|HCl junctions in Dimethylformamide-Water and Dimethylsulfoxide-Water Solvents.

In dipolar aprotic solvents, like DMF and DMSO, the positive charge of the cation may be shielded from the bulk solvent by methyl groups. We expect that for any cation. The presence of the more electronegative oxygen atom and the electron push by two methyl groups make DMF and DMSO more effective cation solvators.

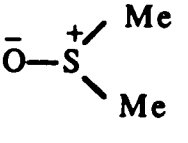
The most strongly solvating solvents for the potassium cation are DMF and DMSO. The sulfur-oxygen and carbon-oxygen bonds in these sulfoxides and amides have less than full double-bond character; indeed, their structures in the first solvation sphere about the potassium cation may well be more like III and IV than I and II.



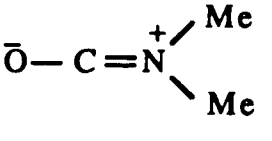
I



II



III



IV

The oxygens of the alcohols and water are more shielded and carry less partial negative charge than do the oxygens of the sulfoxides and amides. Thus, the former set of solvents are weaker solvators of cations than the latter. The hydrogen ion always has to be more solvated in mixed media than in water, and much more so by basic co-solvents. DMSO turns out to be the most basic solvent for hydrogen ion, followed by DMF. From this study, the calculated $E_{j,s}$ values for HCl|HCl junctions in DMSO-water are greater than those in

DMF-water, MeOH-water and EtOH-water solvents.

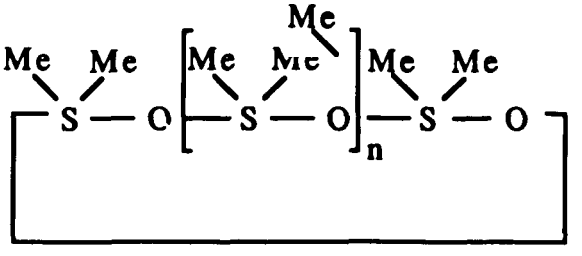
Anion solvation data [78] point to water, MeOH and EtOH, all solvents capable of donating strong hydrogen bonds as being strong solvators of most monovalent anions in a free-energy sense, whereas DMF, DMSO are relatively poor solvators of all but the largest and the most polarizable anions.

The calculated results for the $E_{j,s}$ values of KCl|KCl and HCl|HCl junctions in DMF-water and DMSO-water solvents are listed in Tables 38-41. The values of $E_{j,s}$ for KCl|KCl junctions in DMF-water and DMSO-water solvents range from -2 mV to 29 mV and from 2 mV to 30 mV, respectively, through the entire range of solvent compositions. The ranges of $E_{j,s}$ values for KCl|KCl junctions in DMF-water and DMSO-water solvents are very similar because of the similar solvating properties of potassium and chloride ions in these solvents. Also, we observed that the values of $E_{j,s}$ grow increasingly positive with the decreasing concentration of KCl for both solvent systems.

However, the $E_{j,s}$ values of HCl|HCl junctions are different from KCl|KCl junctions due to the solvation properties of protons. The $E_{j,s}$ values of HCl|HCl junctions in DMF-water and DMSO-water solvents range from -66 mV to 107 mV and from -101 mV to 87 mV, respectively, through the entire range of solvent composition. It has been reported [68] that HCl is quite strongly associated in DMSO but that the association constant falls quickly with the addition of water. From these results we can see that the $E_{j,s}$ value for HCl (7×10^{-4} M) in DMSO (-101 mV) changes quickly with the addition of small amount of water to 87 mV (90.2 wt% DMF) for the same concentration of HCl. The $E_{j,s}$ values of HCl|HCl junctions in DMF-water and DMSO-water solvents are relatively greater than those of EtOH-

water and MeOH-water solvents. This is so because in the DMF or DMSO, there is no possibility of a "jump" mechanism of proton transport and consequently the addition of small amounts of water has a less dramatic effect on conductivity. The value of conductivity for the water-solvated proton does seem very low when compared with that for the DMF or DMSO solvated proton. This can be explained by using the following structures.

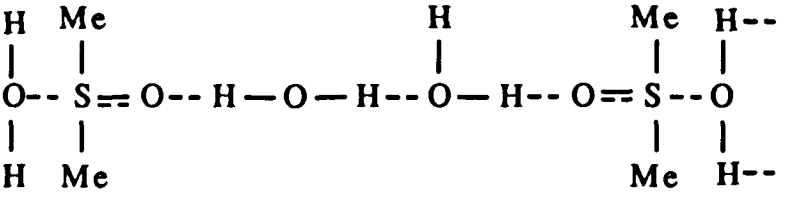
Schafer and Schaffernicht [79] suggested that the structure of DMSO involves hydrogen bonds between polar oxygen and the hydrogen of the methyl groups. Although the molecules do not dimerize, it is not unlikely that the structure may involve chains of sulfur and oxygen atoms of variable size such as V.



V

These could break down on heating or rearrange when a hydrogen donor is added. When water is mixed with strong hydrogen acceptors, such as DMF and DMSO, much heat is evolved, and under certain conditions, the mixture becomes viscous for a short time. This may result from a breakdown of the sulfoxide rings and the formation of a hydrogen-bonded structure such as VI, thus lowering the conductivity of solvated protons [80]. For this reason, we observe

a drastic change in $E_{j,s}$ values from -101 mV to 87 mV when the composition changes from pure DMSO to 90.2 wt% DMSO.



VI

In DMF-water solvents, the limiting equivalent conductance of an electrolytes decreases with the corresponding increase in viscosity of the solvent mixtures. The maximum in viscosity does not coincide with the observed minimum in equivalent conductance. The shift of minimum in conductance towards the DMF-rich region can be explained partially by the ion-solvent interaction. Since water molecules (r_{water} = 1.93 A) are smaller than DMF molecules (r_{DMF} = 3.13 A), the hydrodynamic entity of an ion solvated with water will be smaller than a DMF-solvated one, provided the solvation numbers are almost the same.

The mobility of solvated ions in DMF-rich region will be smaller than in water-rich region, resulting in a further decrease in the conductance in DMF-rich region. Pure and Sherrington [80] have compared the Stokes radii of anions and cations in solvents with their crystallographic radii, and concluded that cations carry a large solvation sheath in DMF and DMSO, whereas anions are naked in these dipolar aprotic solvents. Because of this, anions are much more conducting than cations in the DMF and DMSO solvents.

The Walden product should be inversely related to the size of the moving ion (including the solvation sphere), which in turn should be related to the strengths of the ion-solvent interactions. For example, in water, potassium and chloride, have almost equal Walden products, whereas in DMF and DMSO, Walden products of potassium ion is smaller than that of chloride ion. This suggests a large decrease in the size of solvated chloride relative to potassium ion on transfer from water to the above solvents.

TABLE 38

Experimental and Calculated Parameters for KCl in Dimethyl formamide -Water Solvents. (Molar Scale, 25°C)

KCl | KCl
H_2O DMF-H_2O

Wt% DMF	~C_{KCl}	E_{exp}	E_l	$E_{j,ion}$ New	$E_{j,ion}$ Old	$E_{j,s}$ New	$E_{j,s}$ Old
				(mV)			
10.1	$2x10^{-2}$	-6.4	-8.9	3.5	3.5	-1.0	-1.0
	$2x10^{-3}$	-5.7	-8.9			-0.3	-0.3
	$2x10^{-4}$	-2.1	-8.9			3.3	3.3
22.3	$2x10^{-2}$	-12.1	-22.5	12.5	11.5	-2.1	-1.1
	$2x10^{-3}$	-12.7	-22.5			2.7	-1.7
	$2x10^{-4}$	-3.5	-22.5			6.5	7.5
31.5	$2x10^{-2}$	-25.4	-45.0	7.0	27.7	12.6	-8.1
	$2x10^{-3}$	-24.4	-44.9			13.6	-7.2
	$2x10^{-4}$	-13.5	-44.9			15.6	-5.1
42.5	$2x10^{-2}$	-31.2	-79.2	23.2	65.0	24.8	-16.9
	$2x10^{-3}$	-30.6	-79.2			25.4	-16.4
	$2x10^{-4}$	-29.4	-79.2			26.6	-15.2
51.2	$2x10^{-2}$	-41.2	-109.6	42.5	75.0	25.9	-6.6
	$2x10^{-3}$	-40.4	-109.5			26.6	-5.9
	$2x10^{-4}$	-38.7	-109.5			28.3	-4.2

Wt% DMF	~C_{KCl}	E_{exp}	E_l (mV)	$E_{j,ion}$ New	$E_{j,ion}$ Old	$E_{j,s}$ New	$E_{j,s}$ Old
60.8	$2x10^{-2}$	-61.5	-148.8	64.0	97.0	23.3	-9.7
	$2x10^{-3}$	-59.2	-149.1			25.9	-7.1
	$2x10^{-4}$	-56.8	-149.3			28.5	-4.5
67.8	$7x10^{-3}$	-67.9	-157.9	71.0	106.0	18.9	-16.1
	$7x10^{-4}$	-66.4	-157.8			20.4	-14.6
	$7x10^{-5}$	-59.4	-157.9			27.5	-7.5
77.0	$7x10^{-3}$	-68.6	-182.2	93.5	117.0	20.1	-3.4
	$7x10^{-4}$	-66.9	-182.2			21.8	-1.7
	$7x10^{-5}$	-61.8	-182.2			26.9	3.4
92.4	$7x10^{-3}$	-125.8	-334.7	183.0	227.0	25.9	-18.1
	$7x10^{-4}$	-123.0	-334.7			28.7	-15.3
	$7x10^{-5}$	-125.0	-334.7			26.7	-17.3
100	$7x10^{-4}$	-151.8	-476.5	305.5	355.0	19.2	-30.3
	$7x10^{-5}$	-144.3	-476.4			26.7	-22.9
	$7x10^{-6}$	-143.0	-476.3			27.8	-21.7

TABLE 39

Experimental and Calculated Parameters for HCl in Dimethyl formamide-Water Solvents. (Molar Scale, 25°C)

HCl | HCl
H_2O DMF-H_2O

Wt% DMF	~C_{HCl}	E_{exp}	E_l	$E_{j,ion}$ New (mV)	$E_{j,ion}$ Old (mV)	$E_{j,s}$ New (mV)	$E_{j,s}$ Old (mV)
10.1	$7X10^{-2}$	4.4	-8.9	8.7	8.7	4.6	4.6
	$7X10^{-3}$	3.7	-8.9			4.0	3.9
	$7X10^{-4}$	3.4	-8.9			3.6	3.6
22.3	$7X10^{-2}$	16.3	-22.5	-5.0	21.0	43.8	17.8
	$7X10^{-3}$	13.0	-22.5			40.4	14.4
	$7X10^{-4}$	0.7	-22.5			28.2	2.2
31.5	$7X10^{-2}$	1.4	-44.9	12.0	41.5	34.3	4.8
	$7X10^{-3}$	-0.8	-45.0			32.2	2.7
	$7X10^{-4}$	-17.2	-45.0			15.8	-13.7
42.5	$7X10^{-2}$	11.5	-79.3	16.2	75.5	74.6	15.3
	$7X10^{-3}$	1.0	-79.3			64.1	4.8
	$7X10^{-4}$	0.9	-79.3			63.9	4.7
51.2	$7X10^{-2}$	7.9	-109.4	110.0	99.0	7.3	18.3
	$7X10^{-3}$	12.1	-109.4			11.5	22.5
	$7X10^{-4}$	18.0	-109.4			17.4	28.4

Wt% DMF	~C_{HCl}	E_{exp}	E_l	$E_{j,ion}$ New (mV)	$E_{j,ion}$ Old (mV)	$E_{j,s}$ New (mV)	$E_{j,s}$ Old (mV)
60.8	$7X10^{-2}$	-8.0	-141.3	154.9	122.0	-21.6	11.3
	$7X10^{-3}$	-2.0	-141.4			-15.6	17.4
	$7X10^{-4}$	79.0	-141.3			65.4	98.3
67.8	$7X10^{-2}$	-23.0	-157.7	166.2	125.2	-31.5	9.5
	$7X10^{-3}$	-13.9	-157.9			-22.2	18.8
	$7X10^{-4}$	45.0	-157.9			36.7	77.7
77.0	$7X10^{-2}$	-26.2	-182.2	222.1	132.0	-66.1	24.0
	$7X10^{-3}$	-18.5	-182.2			-58.4	31.7
	$7X10^{-4}$	31.5	-182.2			-8.4	81.7
92.4	$7X10^{-2}$	-107.5	-334.8	190.2	199.0	37.1	28.3
	$7X10^{-3}$	-91.5	-334.8			53.1	44.3
	$7X10^{-4}$	-68.0	-334.8			76.6	67.8
100	$7X10^{-2}$	-148.3	-477.4	267.9	278.3	61.2	50.8
	$7X10^{-3}$	-114.4	-447.5			95.2	84.8
	$7X10^{-4}$	-102.3	-477.5			107.3	96.9

TABLE 40

Experimental and Calculated Parameters for KCl in Dimethyl sulfoxide-Water Solvents. (Molar Scale, 25°C)

KCl | KCl
H_2O DMSO-H_2O

Wt% DMSO	~C_{KCl}	E_{exp}	E_l	$E_{j,ion}$ New (mV)	$E_{j,ion}$ Old (mV)	$E_{j,s}$ New (mV)	$E_{j,s}$ Old (mV)
10.5	$3X10^{-2}$	-3.3	-10.0	-8.0	6.0	14.7	0.7
	$3X10^{-3}$	-0.1	-10.0			17.9	3.9
	$3X10^{-4}$	0.4	-10.0			18.4	4.4
18.8	$2X10^{-2}$	-7.6	-19.5	-1.7	15.5	13.6	-3.6
	$2X10^{-3}$	-8.2	-19.5			13.0	-4.2
	$2X10^{-4}$	-7.0	-19.5			14.2	-3.0
29.7	$2X10^{-2}$	-14.5	-40.2	23.7	23.8	2.0	2.0
	$2X10^{-3}$	-12.0	-40.3			4.6	4.5
	$2X10^{-4}$	-10.1	-40.3			6.5	6.4
39.8	$1X10^{-2}$	-25.8	-64.5	29.0	38.7	9.7	-0.1
	$1X10^{-3}$	-25.1	-64.5			10.4	0.7
	$1X10^{-4}$	-23.3	-64.5			12.2	2.5
50.3	$1X10^{-2}$	-38.2	-78.7	26.5	40.0	14.0	0.5
	$1X10^{-3}$	-33.0	-78.7			19.2	5.7
	$1X10^{-4}$	-34.1	-78.7			18.1	4.6

Wt% DMSO	~C_{KCl}	E_{exp}	E_l	$E_{j,ion}$ (mV) New	$E_{j,ion}$ (mV) Old	$E_{j,s}$ (mV) New	$E_{j,s}$ (mV) Old
58.8	$1X10^{-2}$	-49.9	-121.9	57.0	70.0	14.9	2.0
	$1X10^{-3}$	-48.0	-121.9			16.9	3.9
	$1X10^{-4}$	-46.0	-121.8			18.8	5.8
66.8	$7X10^{-3}$	-66.7	-171.6	96.5	110.5	8.4	-5.6
	$7X10^{-4}$	-65.2	-171.5			9.8	-4.2
	$7X10^{-5}$	-64.2	-171.5			10.8	-3.2
77.4	$7X10^{-3}$	-83.3	-224.8	130.5	148.7	11.0	-7.2
	$7X10^{-4}$	-80.3	-224.8			14.0	-4.2
	$7X10^{-5}$	-75.8	-224.8			18.5	0.3
90.2	$2X10^{-3}$	-102.0	-312.1	197.0	220.5	13.1	-10.4
	$2X10^{-4}$	-102.2	-312.1			12.9	-10.6
	$2X10^{-5}$	-99.7	-312.1			15.4	-8.1
100	$2X10^{-3}$	-114.3	-399.1	265.2	293.0	19.9	-7.9
	$2X10^{-4}$	-108.0	-399.1			25.9	-1.9
	$2X10^{-5}$	-103.8	-399.1			30.1	2.3

TABLE 41

Experimental and Calculated Parameters for HCl in Dimethyl sulfoxide-Water Solvents. (Molar Scale, 25°C)

HCl | HCl
H_2O DMSO-H_2O

Wt% DMSO	~C_{HCl}	E_{exp}	E_l	$E_{j,ion}$ New (mV)	$E_{j,ion}$ Old (mV)	$E_{j,s}$ New (mV)	$E_{j,s}$ Old (mV)
10.5	$7X10^{-2}$	-1.3	-10.1	18.7	26.5	-10.0	-17.8
	$7X10^{-3}$	-3.6	-10.1			-12.3	-20.1
	$7X10^{-4}$	-3.6	-10.1			-12.2	-20.0
18.8	$7X10^{-2}$	-1.5	-19.5	58.5	46.2	-40.8	-28.2
	$7X10^{-3}$	-4.0	-19.5			-43.0	-30.7
	$7X10^{-4}$	-4.5	-19.5			-43.5	-31.2
29.7	$7X10^{-2}$	0.7	-40.2	73.8	67.5	-34.3	-28.0
	$7X10^{-3}$	-2.6	-40.2			-36.2	-29.9
	$7X10^{-4}$	-1.8	-40.2			-35.4	-29.1
39.8	$7X10^{-2}$	-2.6	-64.5	99.0	92.3	-37.2	-30.4
	$7X10^{-3}$	-1.4	-64.5			-36.0	-29.3
	$7X10^{-4}$	-13.1	-64.5			-47.7	-41.0
50.3	$7X10^{-2}$	0.1	-78.7	117.5	110.5	-38.9	-31.9
	$7X10^{-3}$	-5.4	-78.7			-44.2	-37.2
	$7X10^{-4}$	-6.5	-78.7			-45.3	-38.3

Wt% DMSO	~C_{HCl}	E_{exp}	E_l	$E_{j,ion}$ (mV) New	Old	$E_{j,s}$ New	Old
58.8	$7X10^{-2}$	-3.8	-121.9	177.0	130.5	-58.9	-11.3
	$7X10^{-3}$	-7.9	-121.9			-63.0	-16.5
	$7X10^{-4}$	-8.6	-121.8			63.8	-17.3
66.8	$7X10^{-2}$	-12.3	-171.6	181.3	151.5	-22.0	-7.8
	$7X10^{-3}$	-21.9	-171.6			-31.6	-1.8
	$7X10^{-4}$	-23.6	-171.6			33.3	-3.5
77.4	$7X10^{-2}$	-47.4	-224.8	150.0	179.5	-27.4	-2.1
	$7X10^{-3}$	-72.4	-224.8			-2.4	-27.1
	$7X10^{-4}$	-85.9	-224.8			-11.1	-40.6
90.2	$7X10^{-2}$	-135.9	-312.4	168.5	228.6	8.0	-52.2
	$7X10^{-3}$	-121.8	-312.4			22.1	-38.0
	$7X10^{-4}$	-56.5	-312.4			87.4	27.3
100	$7X10^{-2}$	-205.9	-399.4	288.1	276.1	-94.7	-82.7
	$7X10^{-3}$	-272.6	-399.4			-161.3	-149.3
	$7X10^{-4}$	-212.7	-399.4			-101.4	-89.4

Cox, Parker and Waghorne [3] used the following cell to evaluate $E_{j,s}$. In their studies, e.m.f. cells with Et_4NPi and Bu_4NBPh_4 salt-bridges between dipolar aprotic solvents were used, e.g.:

$$\underset{\text{AN}}{\text{Ag (s) | AgClO}_4\text{ (0.01M) | Et}_4\text{NPi (0.1) | AgClO}_4\text{ (0.01M) | Ag (s)}}\quad (X)$$
$$\text{S}$$

They studied the relationship between the measured e.m.f. of cell(X) and the corresponding total heats of transfer of solvents. The heats of solution required for the calculation of total heats of transfer are listed in Table 42. They found a direct correlation between the $E_{j,s}$ and the mutual heats of solution of the solvent forming the junction [3].

Since the interactions between acetonitrile and water are small (Table 42), the $E_{j,s}$ for the AN|H_2O junction in cell (X) might be expected to be negligible. But the $E_{j,s}$ is significant in cell (X) with water as S due to the appreciable ion-solvent interactions. The silver ion is more strongly solvated by AN than by water and so will tend to transport AN into the aqueous half cell (ΔH_s = -0.45 KCal mol^{-1}) whereas the nitrate ions, which are much more strongly solvated by water will tend to transport water into AN (ΔH_s = 1.47 KCal mol^{-1}).

After a series of extensive studies of cells with liquid junction, Izutsu et al. [30-36] concluded that for a given pair of solvents, the $E_{j,s}$ can be very nearly independent of the nature of electrolyte, if the current-carrying ions are weakly solvated. However, they did not show many results which can verify their conclusion.

Previous work in our laboratory, reported by Berne and Popovych [27], led to the conclusion that the $E_{j,s}$ term was appreciable for junctions between dipolar aprotic solvent and varied

with the concentration of both the electroactive and the salt-bridge electrolyte. The maximum value of $E_{j,s}$ observed was 172 mV for an acetonitrile-propylene carbonate junction in their study. In the present study, the $E_{j,s}$ values in dipolar aprotic solvents were found to be more significant than in the protic solvents and the $E_{j,s}$ values in acetonitrile-water solvents are much greater than the $E_{j,ion}$ for the entire range. The maximum value of $E_{j,s}$ observed was 403 mV for an water-acetonitrile junction in this study.

TABLE 42

Mutual Heats of Solution (ΔH_s , KCal mol^{-1}) of Solvents at 23°C [3]

	Solvent				
Solute	H_2O	MeOH	AN	DMF	DMSO
H_2O		-0.80	1.47	0.91	-1.28
MeOH	-1.78				
AN	-0.45				
DMF	-3.92				
DMSO	-4.61				

Recommendations for Future Studies

The new formulation for estimating the component of liquid-junction potential due to the passage of ions, $E_{j,ion}$, needs to be studied further. In this investigation, we studied only systems showing a minimum or a maximum of transport numbers and transfer activity coefficients. For this reason, we were not able to demonstrate the full potential of Equation (13) or (14) to calculate the $E_{j,ion}$ because in Equation (13) we were evaluating the drastically changing slope $\Delta G/\Delta s$ and in Equation (14), $\Delta t/\Delta s$.

However, in DMSO-water solvents, the transport numbers of the hydrogen ion experience a steep drop in the region of 60 - 100 wt% DMSO, while its transfer activity coefficients change smoothly with the entire composition of DMSO. In this case, we can choose which equation is better to calculate $E_{j,ion}$ and Equation (13) is preferred. This is so because in Equation (13) we have to evaluate the smoothly changing $\Delta G/\Delta s$ term, instead of the drastically changing slope $\Delta t/\Delta s$ in Equation (14).

On the other hand, for a system having smoothly changing transport numbers and drastically changing transfer activity coefficients of the ion with the solvent composition, Equation (14) would be preferred for the calculation of $E_{j,ion}$, because we would be estimating the $\Delta t/\Delta s$ term, and not Equation (13).

Further studies are required in acetonitrile-water solvents regarding the variation of transport numbers of nitrate ion with the composition of acetonitrile in the region where a maximum is occurred. The transport numbers of nitrate ion increased rapidly when small amounts of AN are added to water. Very accurate data for transport numbers of nitrate ions are needed in order to calculate

$E_{j,ion}$ from the new equation for the AN-water solvents especially for the region of 0 - 50 wt% AN.

We have seen that the presence of the solvent contribution to liquid-junction potential at the interface of two solvent media, $E_{j,s}$, is an important factor in the interpretation of e.m.f. of cells. $E_{j,s}$ values can be obtained from the e.m.f. of cell (IX) containing saturated solutions of an electroactive electrolyte in two solvents. Then, the calculated $E_{j,s}$ values could be compared with the corresponding values obtained from experiments with the saturated electrolyte systems. Furthermore, e.m.f. measurements can be done with KCl, NaCl, LiCl, HCl and KBr as the saturated electrolytes using cell (IX) for different solvent systems. The results would shed additional light on the effect of solvation on $E_{j,s}$.

Appendix 1

Densities of Methanol-Water Solvents at 25°C [37].

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.

Densities of Ethanol-Water Solvents at 25°C [38].

Wt% EtOH	Density
0.0	0.9971
10.0	0.9804
20.0	0.9664
30.0	0.9507
40.0	0.9315
50.0	0.9099
60.0	0.8870
70.0	0.8634
80.0	0.8391
90.0	0.8136
100.0	0.7851

Appendix 3.

Densities of Acetonitrile-Water Solvents at 25°C [40].

Wt% AN	Density
0.0	0.9971
10.7	0.9779
20.2	0.9586
28.7	0.9399
36.3	0.9223
49.4	0.8915
60.3	0.8662
69.5	0.8451
77.4	0.8270
84.2	0.8111
90.1	0.7975
95.4	0.7863
100.0	0.7767

Appendix 4.

Densities of Dimethylformamide-Water Solvents at 25°C [41].

Wt% DMF	Density
0.0	0.9971
10.1	0.9951
22.3	0.9950
31.5	0.9957
42.8	0.9955
51.2	0.9950
60.8	0.9926
67.8	0.9884
77.0	0.9798
92.4	0.9579
100.0	0.9429

Appendix 5.

Densities of Dimethylsulfoxide-Water Solvents at 25°C [42].

Wt% DMSO	Density
0.0	0.9971
10.0	1.0105
20.0	1.0242
30.0	1.0387
40.0	1.0535
50.0	1.0682
60.0	1.0823
70.0	1.0926
80.0	1.0960
90.0	1.0960
100.0	1.0958

Appendix 6

The Molar Concentration (C) and Equivalent Conductance (Λ) of the NaCl in Methanol-Water Solvents.

65.2% MeOH

Molar Concentration $C \times 10^3$ moles/L	Equivalent Conductance Λ
1.8540	62.84
2.7113	62.49
3.6013	61.98
4.5378	61.21
5.4460	60.61
6.3910	60.37
7.3274	59.79
8.2176	59.42

72.2% MeOH

1.7868	65.85
2.7124	64.61
3.6679	63.37
4.5349	62.86
5.4462	62.58
6.4041	62.09
7.3084	61.66
8.1684	61.20

The Molar Concentration (C) and Equivalent Conductance (Λ) of the NaCl in Methanol-Water Solvents.

82.5% MeOH

Molar Concentration $C \times 10^3$ moles/L	Equivalent Conductance Λ
1.9867	69.83
3.0073	68.55
3.9951	67.26
4.9970	66.25
5.9997	65.56
6.9475	65.30
8.0414	64.38
10.2372	63.45

95.4% MeOH

0.7476	81.13
1.5045	81.41
2.6460	79.87
3.8140	77.62
4.9505	76.46
6.1118	75.05
7.2683	74.09
8.3368	73.88

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