Evaluation of Diffusivities in Electrolyte Solutions using Stefan-Maxwell Equations

The Stefan-Maxwell equations have been used to predict single-electrolyte diffusion and ternary tracer diffusion in concentrated electrolyte solutions. Variations in diffusivity due to concentration have been shown to be related to the relaxation effect and viscosity changes of solution. Specific equations are presented to evaluate the ion-ion and ion-solvent interaction coefficients appearing in the Stefan-Maxwell equations. These equations, when tested against experimental data, gave an accurate description of the process at up to 4.0 M concentrations and for trace species mobilities differing by a factor of ten.

N. deG. PINTO and E. E. GRAHAM

Department of Chemical Engineering
The Pennsylvania State University
University Park, PA 16802

SCOPE

Electrolyte solutions are currently used in numerous industrial and laboratory operations. The design of processes for a number of these applications, such as ion exchange and hydrometallurgy, involves an understanding of the mechanism of ionic transport in solution. While the fundamental flux equations are well-developed, their use is limited by the lack of methods of evaluating the phenomenological coefficients appearing in these equations. Current methods available for predicting these coefficients are applicable only at very low ionic concentrations and usually have no more than theoretical importance. This paper examines the use of the Stefan-Maxwell flux equations to predict multicomponent electrolyte diffusion at high concentrations (up to 4.0 M). The coefficients of these equations have special characteristics (Graham and Dranoff, 1982) that facilitate their evaluation from fundamental physical properties of the ions. Well-established binary electrolyte and ternary tracer diffusion data have been used to test the predictions.

CONCLUSIONS AND SIGNIFICANCE

Using the Stefan-Maxwell flux equations, a method has been developed to determine ternary tracer diffusion coefficients at high electrolyte concentrations. The phenomenological coefficients of these equations have been related to properties such as solution viscosity and limiting ionic mobilities. This development was possible because unlike other flux equations, the coefficients of the Stefan-Maxwell equations can be individually identified with physical phenomena occuring during the diffusion process. The method has been tested for the univalent ions Na^+, K^+, Li^+, H^+, I^-, and Cl^-. Although the ionic mobilities of these ions differ by an order of magnitude, the equations describe the diffusion process accurately at up to a 4.0 M ionic concentration.

The Stefan-Maxwell equations have also been applied to the diffusion of a single electrolyte. For this case Robinson and Stokes (1968) have shown that the behavior at low concentrations is well-represented by the Nernst-Hartley equation. The Stefan-Maxwell equations reduce directly to the Nernst-Hartley equation, and it has been shown that with an appropriate viscosity correction this equation is fairly accurate at high concentrations.

The present work is a first step in the evaluation of multicomponent diffusivities in free solution and subsequently in ion exchangers and membranes. When additional effects such as solvent flux and tortuosity are present, the Stefan-Maxwell equations isolate these effects so that each can be studied separately.

INTRODUCTION

The diffusion of nonelectrolytes or electrolytes in liquid solvents is rigorously described by flux equations obtained from the theory of the thermodynamics of irreversible processes. The use of these equations requires the evaluation of phenomenological coefficients from fundamental physical data. The modern theory of electrolyte conduction and diffusion is based on the physical model developed by Debye and Hückel (1923). Onsager and Fuoss (1932) first used this model to evaluate phenomenological coefficients at low ionic concentrations. The model of Debye and Hückel assumes that the ionic distribution

---

E. E. Graham is presently at the Cleveland State University, Cleveland, OH 44115.
N. deG. Pinto is presently at the University of Cincinnati, Cincinnati, OH 45221.

in free solution is described by the Boltzmann distribution law. However, this distribution is inconsistent with the principle of linear superposition of fields. To circumvent this problem, the Boltzmann distribution is expanded to an infinite series truncated beyond the linear term. This is equivalent to assuming that the potential energy of an ion is small compared to its thermal energy, a situation approximately valid only for dilute solutions. The original equations of Onsager and Fuoss have since been refined (Miller, 1966, 1981; Leaist and Lyons, 1980; Chen and Onsager, 1977; Pikal, 1971), but the fundamental assumption made about the ionic distribution has not been removed. Consequently, all predictive equations presently available are valid at concentrations far below most engineering applications of electrolyte solutions.

The prediction of phenomenological coefficients requires an evaluation of two effects, a relaxation effect and an electrophoretic effect. The problem is most conveniently approached by considering situations where the two can be isolated from each other. In this paper, special properties of the Stefan-Maxwell form of the phenomenological flux equations have been exploited to develop equations that predict binary electrolyte diffusion and ternary tracer diffusion at high ionic concentrations.

THEORY

In electrolyte diffusion, the most commonly used form of the phenomenological equations derived from the thermodynamics of irreversible processes is:

$$\vec{J}_i = -\sum_{j=1}^{n} \ell_{ij} \vec{\nabla} \mu_j'; \; i = 1, 2, \; . \; . \; . \; , n \tag{1}$$

These equations can be written in a number of alternative ways, all consistent with the tenets of nonequilibrium thermodynamics. Of particular interest are the Stefan-Maxwell equations:

$$-x_i \vec{\nabla} \mu_i' = \frac{RT}{C} \sum_{j=0}^{n} \left(\frac{x_j \vec{J}_i - x_i \vec{J}_j}{a_{ij}} \right); \; i = 1, \; . \; . \; . \; , n \tag{2}$$

The coefficients of Eqs. 1 and 2 can be related to each other, so the choice of a particular formulation depends on such factors as its convenience for a given situation, the physical significance of its coefficients, and the relation of the coefficients to basic electrochemical properties (in particular how these relationships depend on ionic concentration and composition).

Graham and Dranoff (1982) have drawn two important conclusions in a comparison of Eqs. 1 and 2. They found that the coefficients of Eq. 2 are less concentration-dependent than those of Eq. 1, and that the Stefan-Maxwell coefficients are independent of the other ions present in the system. These factors are of crucial importance in the development of predictive expressions for the coefficients at high concentrations.

Diffusion of a Single Electrolyte

The physical significance of the coefficients of the Stefan-Maxwell equations is made clear by analyzing the diffusion of a single electrolyte. For this system containing a single cation, subscript 1, and a single anion, subscript 2, in water, subscript 0, Eq. 2 becomes

$$-x_1 \vec{\nabla} \mu_1' = \frac{RT}{C} \left[\frac{x_0 \vec{J}_1}{a_{10}} + \frac{x_2 \vec{J}_1 - x_1 \vec{J}_2}{a_{12}} \right] \tag{3}$$

$$-x_2 \vec{\nabla} \mu_2' = \frac{RT}{C} \left[\frac{x_0 \vec{J}_2}{a_{20}} + \frac{x_1 \vec{J}_2 - x_2 \vec{J}_1}{a_{21}} \right] \tag{4}$$

Substituting the condition of no current

$$\vec{J}_1 \nu_2 = \vec{J}_2 \nu_1 \tag{5}$$

and electroneutrality

$$x_2 \nu_1 = x_1 \nu_2 \tag{6}$$

into Eqs. 3 and 4, and eliminating electrical potential gives

$$\vec{J}_1 = \frac{(\nu_1 + \nu_2) a_{10} a_{20}}{x_o (\nu_2 a_{10} + \nu_1 a_{20})} \left[1 + \frac{d \ln \gamma \pm}{d \ln C_I} \right] \vec{\nabla} C_I \tag{7}$$

For diffusion of a single electrolyte at low concentrations Robinson and Stokes (1968) have shown that the behavior is well-represented by the Nernst-Hartley relation

$$\vec{J}_1 = kT \frac{(\nu_1 + \nu_2) \omega_1 \omega_2}{\nu_2 \omega_1 + \nu_1 \omega_2} \left[1 + \frac{d \ln \gamma \pm}{d \ln C_I} \right] \vec{\nabla} C_I \tag{8}$$

The diffusion of a single electrolyte involves no relaxation effect, because the electroneutrality condition guarantees no relative motion between the ions, but it does involve an electrophoretic effect. Equation 8 when corrected for this takes the form

$$\vec{J}_1 = kT \frac{(\nu_1 + \nu_2)(\omega_1 + \delta_1)(\omega_2 + \delta_2)}{\nu_2 (\omega_1 + \delta_1) + \nu_1 (\omega_2 + \delta_2)} \left[1 + \frac{d \ln \gamma \pm}{d \ln C_I} \right] \vec{\nabla} C_I \tag{9}$$

In the low-concentration region, where the Onsager expressions for δ_1 and δ_2 apply, Eq. 9 gives an accurate representation of the electrolyte flux. If Eq. 9 is to be extended to high concentrations, another important effect has to be considered. Since the viscosity of the solution changes with ionic concentration, it is incorrect to use limiting ionic mobilities in Eq. 9. Conventionally, ionic mobilities at finite concentrations are obtained by using Stokes' law.

$$\omega = \omega^o \left(\frac{\eta^o}{\eta} \right) \tag{10}$$

However, it has been found that this equation tends to overcorrect for small ions, such as Na^+, Cl^-, K^+, I^-, etc. (Guggenheim et al., 1965), and use of the equation

$$\omega = \omega^o \left(\frac{\eta^o}{\eta} \right)^{.7} \tag{11}$$

usually gives more accurate results. Combining Eqs. 9 and 11 gives

$$\vec{J}_1 = kT \frac{(\nu_1 + \nu_2)(\omega_1^o + \delta_1)(\omega_2^o + \delta_2)}{\nu_2 (\omega_1^o + \delta_1) + \nu_1 (\omega_2^o + \delta_2)} \left[1 + \frac{d \ln \gamma \pm}{d \ln C_I} \right] \vec{\nabla} C_I \left(\frac{\eta^o}{\eta} \right)^{.7} \tag{12}$$

It is clear that Eq. 7 and 12 are equivalent when

$$a_{io} = kT x_o (\omega_i^o + \delta_i) \left(\frac{\eta^o}{\eta} \right)^{.7} \tag{13}$$

The preceding development has clearly shown an advantage of the Stefan-Maxwell equations. While Eq. 2 reduces directly to the form of the Nernst-Hartley equaton, the same is not possible with Eq. 1 without restrictions on the values of certain coefficients. Also, for the Stefan-Maxwell equations the electrophoretic effect, physically an ion-ion interaction through the solvent, is accounted for by the ion-solvent coefficients a_{io}. Equation 1 does not contain ion-solvent phenomenological coefficients, which makes the physical significance of the ion-ion coefficients unclear.

Tracer Diffusion

The diffusion of a trace component represents a special case of free diffusion in which there is only the interchange or diffusion of the trace component in a system essentially in equilibrium. The result is that there are no gradients in activity coefficients or solvent flux, which greatly simplifies the analysis. Since in this case there is no net motion of the ionic species, the electrophoretic effect is negligible. However, since the radioactive isotope is moving relative to a fixed background, there is a distortion of the ionic atmosphere, making the relaxation effect important. For a radioactive tracer, subscript 1, diffusing in an electrolyte solution made up of ions, subscripts 2 and 3, Eq. 2 reduces to

$$-x_1\vec{\nabla}\mu_1' = \frac{RT}{C}\left[\vec{J}_1\left(\frac{x_0}{a_{10}} + \frac{x_2}{a_{12}} + \frac{x_3}{a_{13}}\right)\right] \qquad (14)$$

On rearrangement Eq. 14 gives:

$$\vec{J}_1 = -\frac{C_1}{RT}\left[\frac{1}{\dfrac{x_0}{a_{10}} + \dfrac{x_2}{a_{12}} + \dfrac{x_3}{a_{13}}}\right]\vec{\nabla}\mu_1' \qquad (15)$$

Equation 15 involves an ion-solvent interaction coefficient, a_{10}, as well as ion-ion coefficients a_{12} and a_{13}. The presence of a relaxation effect, physically a direct ion-ion interaction, accounts for the appearance of ion-ion coefficients in Eq. 15.

In a solution unaffected by external forces, the ionic atmosphere is an equilibrium between electric forces and thermal energy. When in equilibrium, the time-averaged distribution is spherically symmetric and therefore exerts no resultant force on the central ion. The introduction of an external force distorts the ionic atmosphere, resulting in a restoring force $\vec{\nabla}\phi$, the relaxation effect, exerted by the atmosphere on the ion. Evaluation of this relaxation field is mathematically one of the most difficult parts of electrolyte theory. Use of the Stefan-Maxwell equations offers a possible method of circumventing the problem.

Since the ion-ion phenomenological coefficients, for the Stefan-Maxwell equations, are independent of the other ions present in the system, their evaluation involves consideration of only the ion pair described by that coefficient. For example, an analysis of a_{ij} would consider the pseudobinary system consisting of ions i and j. For this system it can be shown that the Stefan-Maxwell ion-ion interaction coefficients are related to the Onsager coefficients by:

$$a_{ij} = \frac{RT}{C}\left[\frac{\ell_{ii}\ell_{jj} - (\ell_{ij})^2}{\ell_{ij}}\right] \qquad (16)$$

The Onsager coefficients can be expressed as the sum of a limiting term, an electrophoretic term and a relaxation term:

$$\ell_{ij} = \ell_{ij}^{\circ} + \ell_{ij}' + \ell_{ij}'' \qquad (17)$$

A number of equations are available (Leaist and Lyons, 1980; Chen and Onsager 1977; Pikal, 1971) to evaluate the relaxation effect at very dilute concentrations. Regardless of the equation used for ℓ_{ij}'', Eq. 16 always takes the form

$$a_{ij} = kTf_1(\omega_i^{\circ}, \omega_j^{\circ})f_2(\kappa d)f_3(\eta) \qquad (18)$$

where $f_1(\omega_i^{\circ}, \omega_j^{\circ})$, referred to as the mobility function, is the resultant mobility of the pseudobinary system, at infinite dilution; $f_2(\kappa d)$ is concentration-dependent and arises due to the relaxation effect; and $f_3(\eta)$ is a correction factor for the viscosity change of the solution with concentration.

To evaluate the mobility function for a pseudobinary system, two distinct cases have to be considered. When ions i and j are oppositely charged, the driving force can be expressed as (Newman, 1973)

$$\vec{F}_i = -\frac{1}{N}\vec{\nabla}\overline{G}_i - z_i\vec{\nabla}\phi \qquad (19)$$

The electric field potential appearing in Eq. 19 is the sum of potentials generated by charge separation and the relaxation effect between ions i and j.

The situation is now similar to the diffusion of a single electrolyte:

$$\vec{v}_i = -\frac{\omega_i}{N}\vec{\nabla}\overline{G}_i - \omega_i z_i\vec{\nabla}\phi \qquad (20)$$

and

$$\vec{v}_j = -\frac{\omega_j}{N}\vec{\nabla}\overline{G}_j - \omega_j z_j\vec{\nabla}\phi \qquad (21)$$

where the chemical potential of the salt as a whole is

$$\overline{G}_s = \nu_i\overline{G}_i + \nu_j\overline{G}_j \qquad (22)$$

Elimination of $\vec{\nabla}\phi$ between Eqs. 20 and 21 and combination with the no-current condition

$$\vec{v}_i = \vec{v}_j$$

and the electroneutrality condition

$$\nu_i z_i + \nu_j z_j = 0$$

gives

$$\vec{v}_i = -\frac{\omega_i\omega_j}{N(\omega_i\nu_j + \omega_j\nu_i)}(\nu_i\vec{\nabla}\overline{G}_i + \nu_j\vec{\nabla}\overline{G}_j) \qquad (23)$$

Finally, substitution of Eq. 22 into Eq. 23 gives

$$\vec{v}_i = -\frac{\omega_i\omega_j}{N(\omega_i\nu_j + \omega_j\nu_i)}\vec{\nabla}\overline{G}_s \qquad (24)$$

When ions i and j have charges of similar sign, the analysis is only slightly more complex. Equations 19, 20, and 21 still apply, but $\vec{\nabla}\overline{G}_i$ and $\vec{\nabla}\overline{G}_j$ have a different significance. If the third ion in solution is designated by k, then $\overline{G}_i$ and $\overline{G}_j$ are the chemical potentials of the salts formed by ions i and k, and j and k, respectively. Also, the electric field is now entirely generated by the relaxation effect between i and j.

Consider a control surface in the system enclosing a volume V of liquid and containing ψ_i ions of i and ψ_j ions of j. The force exerted by the ions on the solvent within the volume is

$$\vec{F} = -\vec{F}_i - \vec{F}_j \qquad (25)$$

Since for isotopic diffusion the solvent flux is zero

$$\vec{F}_i + \vec{F}_j = 0 \qquad (26)$$

or

$$\frac{\psi_i}{N}\vec{\nabla}\overline{G}_i + \psi_i z_i\vec{\nabla}\phi + \frac{\psi_j}{N}\vec{\nabla}\overline{G}_j + \psi_j z_j\vec{\nabla}\phi = 0 \qquad (27)$$

For isotopic diffusion, conservation of charge within the control volume requires

$$\psi_i z_i\vec{v}_i + \psi_j z_j\vec{v}_j = 0 \qquad (28)$$

Solution of Eqs. 20, 21, 27, and 28 in terms of $\vec{v}_i$ and $\vec{\nabla}\overline{G}_i$ gives

$$\vec{v}_i = -\frac{2\omega_i\omega_j}{\omega_i|z_i| + \omega_j|z_j|}P\vec{\nabla}\overline{G}_i \qquad (29)$$

where P is a function of z_i, z_j, ψ_i, and ψ_j.

Equations 24 and 29 clearly show the effect of the electroneutrality and no-solvent flux conditions on the mobility of the tracer ion. For oppositely and similarly charged ions, the mobility functions are

$$f_1(\omega_i^{\circ}, \omega_j^{\circ}) = \frac{\omega_i^{\circ}\omega_j^{\circ}}{(\omega_i^{\circ}\nu_j + \omega_j^{\circ}\nu_i)} \qquad (30)$$

and

$$f_1(\omega_i^{\circ}, \omega_j^{\circ}) = \frac{2\omega_i^{\circ}\omega_j^{\circ}}{(\omega_i^{\circ}|z_i| + \omega_j^{\circ}|z_j|)} \qquad (31)$$

respectively.

Nowhere in the analysis has the ionic distribution in solution been considered. Without such a distribution, the absolute magnitudes of the phenomenological coefficients cannot be evaluated because the value of the concentration-dependent function $f_2(\kappa d)$ is unknown. Unfortunately, there is no method of determining this function from fundamental data, at high concentrations, and best use has to be made of the dilute-solution equations presently available. The importance of selecting an exact distribution function appears to be linked to the concentration dependence of the coefficients. The Stefan-Maxwell coefficients, being less concentration-dependent should not be seriously affected by the distribution linearization assumption of Debye and Hückel. One dilute-solution equation particularly amenable to use in conjunction with the Stefan-Maxwell equations is due to Falkenhagen et al. (1952).

$$f_2(\kappa d) = \frac{\alpha\kappa}{1 + \kappa d} \tag{32}$$

This equation requires a variable minimum ionic distance parameter d to accurately describe tracer diffusivities at high concentrations. For the 1 : 1 electrolytes studied, d was found to obey the equation

$$d = \frac{\alpha}{A}\left[\frac{(\alpha' - A)}{\alpha'\sqrt{x_I}} + 1\right] \tag{33}$$

where A is a constant.

Substitution of Eq. 33 in Eq. 32 gives:

$$f_2(\kappa d) = \frac{A\sqrt{x_I}}{1 + \sqrt{x_I}} \tag{34}$$

This is a surprisingly simply form for the concentration-dependence of the relaxation effect, and involves the evaluation of only one constant per binary.

Explicit expressions for the ion-ion coefficients are now obtained using Eqs. 18, 30, 31, and 34 with an appropriate viscosity correction factor.

When ions i and j are similarly charged

$$a_{ij} = -\frac{2kT\omega_i^o\omega_j^o}{(\omega_i^o|z_i| + \omega_j^o|z_j|)}\left[\frac{A_{ij}\sqrt{x_I}}{1 + \sqrt{x_I}}\right]\left(\frac{\eta^o}{\eta}\right)^{.7} \tag{35}$$

For oppositely charged ions i and k

$$a_{ik} = +\frac{kT\omega_i^o\omega_k^o}{(\omega_i^o v_k + \omega_k^o v_i)}\left[\frac{A_{ik}\sqrt{x_I}}{1 + \sqrt{x_I}}\right]\left(\frac{\eta^o}{\eta}\right)^{.7} \tag{36}$$

Use of either Eq. 35 or Eq. 36 dictates that the constants A_{ij} and A_{ik} be known in advance. However, it should be realized that since the coefficients are independent of the other ions present, once A_{ij} has been determined for a pair of ions, it remains constant regardless of how the other ions in solution are changed.

The ion-solvent interaction coefficients for isotopic diffusion are obtained from Eq. 13 with $\delta_i = 0$

$$a_{io} = kTx_o\omega_i^o\left(\frac{\eta^o}{\eta}\right)^{.7} \tag{37}$$

COMPARISON WITH EXPERIMENTAL RESULTS

Single Electrolyte

To test the validity of Eq. 12, predicted values have been compared with experimental data from the literature for NaCl (Robinson and Stokes, 1968). To make the comparison, the experimental diffusivities have been converted to a solvent-fixed frame by assuming constant molal volumes in solution. This is a good assumption for small concentration gradients of electrolyte, which were the conditions used in the experimental determinations. Table 1 gives a comparison of experimental and predicted values. For the concentration range studied, the estimated diffusivity is within 3% of the observed value. Also, in every case the calculated value is lower than the experimental observation.

TABLE 1. PREDICTION OF NaCl DIFFUSIVITY AT 25°C

Concentration mol/kg solvent	$D_{obs} \times 10^9$ m²/s	Activity Term	$(\eta^o/\eta)^{.7}$	$D_{calc} \times 10^9$ m²/s	D_{obs}/D_{calc}
0.0	1.61	1.000	1.000	1.61	1.000
0.1	1.48	0.917	0.992	1.46	1.011
0.5	1.49	0.927	0.968	1.45	1.028
1.0	1.50	0.970	0.938	1.47	1.023
2.0	1.56	1.096	0.870	1.54	1.012
3.0	1.63	1.245	0.800	1.60	1.016
4.0	1.68	1.410	0.723	1.65	1.018

Two factors were neglected in estimating the diffusivities. Due to the absence of a method for calculating the electrophoretic effect at high concentrations, the δ_1 and δ_2 factors in Eq. 12 were assumed to be zero. Fortunately, the electrophoretic effect is usually a relatively minor effect and its omission should not introduce errors of the magnitude observed. A more important assumption deals with the hydration of ions in solution. All ions have been considered completely unhydrated. While estimates for hydration numbers are available in the literature, widely differing numbers have been reported depending on the method used. Incorporation of a hydration number in calculating the diffusivity improves the accuracy of prediction but introduces a fairly arbitrary factor in the calculations.

Tracer Diffusion

Tracer diffusion data reported in the literature are usually in terms of the diffusion coefficient of the equation

$$\vec{j}_i = -\frac{C_i}{RT} D_i \vec{\nabla}\mu_i' \tag{38}$$

A comparison of Eqs. 15 and 38 gives

$$D_1 = \left[\frac{1}{\frac{x_o}{a_{10}} + \frac{x_2}{a_{12}} + \frac{x_3}{a_{13}}}\right] \tag{39}$$

At infinite dilution,

$$D_1^o = a_{10}^o \tag{40}$$

Division of Eq. 39 by Eq. 40 gives

$$\frac{D_1}{D_1^o} = \left[\frac{1/a_{10}^o}{\frac{x_o}{a_{10}} + \frac{x_2}{a_{12}} + \frac{x_3}{a_{13}}}\right] \tag{41}$$

The ratio D_1/D_1^o can now be predicted using Eqs. 35, 36, 37, and 41, once the constants in Eqs. 35 and 36 are known. Unfortunately, there are presently no appropriate data available in the literature to determine the two constants uniquely. However, Eqs. 35 and 36 can still be used effectively if one additional assumption is made, namely

$$A_{ij} = A_{ik} = A \tag{42}$$

This is tantamount to assuming that d is constant for all ion pairs, and is valid only when the sizes of the ions do not differ considerably. The two constants of Eqs. 35 and 36 have been replaced by one, reducing the experimental data required for evaluation. However, it is clear that the value of the constant will change when any one of the ions in the system is changed.

The validity of Eqs. 35, 36, 37, 41, and 42 was checked using experimental data available in the literature (Woolf, 1960; Mills, 1955, 1957a,b; Stokes et al., 1957) for three electrolytes, NaCl, KCl, and LiCl. Isotopic data for four trace ions, Na^+, Cl^-, I^-, and H^+ are available in the concentration range of 0.5M to 4M. The predicted values have been compared to the experimental data in Tables 2, 3, and 4. The values of the constant A used are also shown. As expected, these values are a function of all three ionic species present. For all three electrolytes A decreases in the order $Na^+ > Cl^- > I^- > H^+$. At this point it is not certain if this trend is in someway related to ionic diameter or is merely a coincidence.

The model predicts the diffusivities of the univalent trace ions accurately for the whole range considered. The theoretical values are within ±2% for 53 of the 56 data points. In fact, for most of these data points the predicted value falls within the experimental error bar of the observations.

CONCLUSIONS

A method is now available to determine the tracer diffusion coefficients of univalent ions in aqueous solutions up to concentrations of 4.0 M; this range includes concentrations used in many practical applications. The method has been successfully tested against experimental data for trace ions where the mobilities differ by an order of magnitude. The use of Eqs. 35, 36, and 42 requires a minimum of experimental data. One accurate tracer diffusion data point in the concentration range of interest is sufficient for the determination of the isotopic diffusivity of an ion in a single electrolyte at any concentration in that range. The equations presented for the evaluation of ion-ion coefficients obey the Onsager reciprocal relation, an experimentally verified relation (Miller, 1960). This implies that for any three ions obeying the condition of electroneutrality, the isotopic diffusivity of all three ions over the whole concentration range can be obtained with only two accurate experimental data points.

Equations 35 and 36, although untested because of a lack of available data, if proven valid offer a powerful method of predicting isotopic diffusivities in multicomponent systems. The constants must be determined only once for any pair of ions present in the system, and can then be used regardless of how the composition of the system changes.

The evaluation of the phenomenological coefficients is a first step in the prediction of mutual diffusivities in free solution and subsequently in ion-exchange particles and membranes. These processes involve additional effects, such as solvent flux and tortuosity, which may now be separated for independent analyses.

NOTATION

a_{ij} = Stefan-Maxwell phenomenological coefficients
A = ternary constant, Eq. 42
A_{ij} = binary constant, Eqs. 35 and 36
C = total molar concentration including solvent
C_i = molar concentration of species i
C_I = molar concentration of all ionic species present
d = distance of minimum approach between ions
D_{calc} = calculated single electrolyte diffusivity
D_i = tracer diffusion coefficient of species i
D_{obs} = experimental single electrolyte diffusivity
$\underline{F}_i$ = driving force exerted on species i
G_i = molar chemical potential of species i
J_i = flux of species i
k = Boltzmann's constant
ℓ_{ij} = phenomenological coefficients, Eq. 1
ℓ'_{ij} = electrophoretic contribution to phenomenological coefficients
ℓ''_{ij} = relaxation contribution to phenomenological coefficients
N = Avogadro number

Table 2. Tracer Diffusion in NaCl Solution at 25°C

		Concentration, M/L				
		0.5	1.0	2.0	3.0	4.0
Tracer	A	D_i/D_i^0 Theoretical (Experimental)				
Na^+	3.16	0.96(0.96)	0.92(0.93)	0.85(0.85)	0.78(0.77)	0.70(0.70)
Cl^-	1.57	0.92(0.91)	0.87(0.87)	0.79(0.79)	0.70(0.71)	0.63(0.62)
I^-	1.26	0.91(0.91)	0.86(0.86)	0.77(0.78)	0.68(0.68)	0.60(0.60)
H^+	0.43	0.81(0.81)	0.73(0.75)	0.62(0.64)	0.53(0.53)	0.45(0.43)

Table 3. Tracer Diffusion in KCl Solution at 25°C

		Concentration, M/L				
		0.5	1.0	2.0	3.0	4.0
Tracer	A	D_i/D_i^0 Theoretical (Experimental)				
Na^+	3.48	0.99(0.99)	0.98(0.98)	0.97(0.96)	0.95(0.94)	0.91(0.92)
Cl^-	1.95	0.97(0.96)	0.96(0.96)	0.94(0.94)	0.91(0.91)	0.87(0.87)
I^-	1.12	0.95(0.95)	0.94(0.94)	0.90(0.91)	0.86(0.86)	—
H^+	0.89	0.87(0.85)	0.82(0.83)	0.75(0.76)	0.69(0.68)	—

Table 4. Tracer Diffusion in LiCl Solution at 25°C

		Concentration, M/L				
		0.5	1.0	2.0	3.0	4.0
Tracer	A	D_i/D_i^0 Theoretical (Experimental)				
Na^+	1.82	0.94(0.93)	0.89(0.88)	0.79(0.79)	0.71(0.72)	—
Cl^-	1.72	0.90(0.90)	0.83(0.83)	0.73(0.74)	0.64(0.64)	—
I^-	1.60	0.89(0.89)	0.83(0.83)	0.72(0.73)	0.63(0.63)	0.56(0.54)
H^+	0.10	0.75(0.76)	0.65(0.68)	0.52(0.51)	0.43(0.39)	0.36(0.28)

R = universal gas constant
T = absolute temperature
v_i = velocity of species i
x_i = mole fraction of species i
x_I = total ionic mole fraction
z_i = valence of ionic species i

Greek Letters

α = constant, Eq. 32
α' = term proportional to $C^{1/2}$, Eq. 33
$\gamma_\pm$ = mean activity coefficient for an electrolyte
δ_i = electrophoretic effect on species i
η = viscosity of solution
κ = inverse Debye length
μ'_j = electrochemical potential of species j
ν_i = stoichiometric number of species i
ϕ = electric potential
ψ_i = number of ions of i in control volume
ω_i = mobility of ion i

Superscript

o = refers to property at infinite dilution

Subscript

o = refers to the solvent

Operator

∇ = gradient

LITERATURE CITED

Chen, M. S., and L. J. Onsager, "The Generalized Conductance Equation," *J. Phys. Chem.*, **81**, 2,017 (1977).

Debye, P., and E. Hückel, "Zur Theorie der Elektrolyte," *Phys. Z.*, **24**, 185 (1923).

Falkenhagen, H., M. Leist, and G. Kelbg, "Zur Theorie der Leitfahigkeit starker nicht assoziierender Elektrolyte bei höheren Konzentrationen," *Ann. Phys.*, **6** (11), 51 (1952).

Graham, E. E., and J. S. Dranoff, "Application of the Stefan-Maxwell Equations to Diffusion in Ion Exchangers. I: Theory," *Ind. Eng. Chem. Fundam.*, 21, 360 (1982).

Guggenheim, E. A., J. E. Mayer, and F. C. Tompkins, Eds., *International Encyclopedia of Physical Chemistry and Chemical Physics*, Pergamon, New York, Topic 16, 3, 58 (1965).

Leaist, D. G., and P. A. Lyons, "Multicomponent Diffusion in Dilute Solutions of Mixed Electrolytes," *Aust. J. Chem*, **33**, 1,869 (1980).

Miller, D. G., "Explicit Relations of Velocity Correlation Coefficients to Onsager ℓ_{ij}'s, to Experimental Quantities, and to Infinite Dilution Limiting Laws for Binary Electrolyte Solutions," *J. Phys. Chem.*, **85**, 1,137 (1981).

——, "Application of Irreversible Thermodynamics to Electrolyte Solutions. I: Determination of Ionic Transport Coefficients for Isothermal Vector Transport Processes in Binary Electrolyte Systems," *J. Phys. Chem.*, **70**, 2,639 (1966).

——, "Thermodynamics of Irreversible Processes," *Chem. Rev.*, **60**, 15 (1960).

Mills, R., "The Tracer-Diffusion of Sodium Ion in Aqueous Potassium Chloride Solutions," *J. Phys. Chem.*, **61**, 1,258 (1957a).

——, "The Self-diffusion of Chloride Ion in Aqueous Alkali Chloride Solutions at 25°C," *J. Phys. Chem.*, **61**, 1,631 (1957b).

——, "A Remeasurement of the Self-diffusion Coefficients of Sodium Ion in Aqueous Sodium Chloride Solutions," *J. Amer. Chem. Soc.*, **77**, 6,116 (1955).

Newman, J. S., *Electrochemical Systems*, Prentice-Hall, Englewood Cliffs, NJ, 217 (1973).

Onsager, L., and R. Fuoss, "Irreversible Processes in Electrolytes. Diffusion, Conductance, and Viscous Flow in Arbitrary Mixtures of Strong Electrolytes," *J. Phys. Chem.*, **36**, 2,689 (1932).

Pikal, M. J., "Theory of the Onsager Transport Coefficients ℓ_{ij} and R_{ij} for Electrolyte Solutions," *J. Phys. Chem.*, **75**, 3,124 (1971).

Robinson, R. A., and R. H. Stokes, *Electrolyte Solutions*, Butterworths, London, 284–335 (1968).

Stokes, R. H., L. A. Woolf, and R. Mills, "Tracer Diffusion of Iodide Ion in Aqueous Alkali Chloride Solutions," *J. Phys. Chem.*, **61**, 1,634 (1957).

Woolf, L. A., "Tracer Diffusion of Hydrogen Ion in Aqueous Alkali Chloride Solutions at 25°C," *J. Phys. Chem.*, **64**, 481 (1960).

Manuscript received Feb. 13, 1985, and revision received May 13, 1985.