Multicomponent Diffusion in Concentrated Electrolyte Solutions: Effect of Solvation

A method is presented to estimate the diffusivities of electrolytes in concentrated multicomponent systems. The method is based on the Stefan-Maxwell flux equations. Explicit expressions have been developed for the phenomenological transport coefficients. These expressions incorporate the effects of solvation, viscosity, and ionic interactions. It has been shown that multicomponent diffusion behavior can be related to corresponding single-electrolyte and tracer diffusion cases. Thus, solvation effects are estimated from single-electrolyte data, and ion-ion interaction effects are obtained from tracer diffusion studies. The method has been tested for the ternary system NaCl-KCl, at concentrations of up to 3.0 M, and for corresponding single-electrolyte and tracer diffusion cases at concentrations of up to 4.0 M. In general, the method predicts phenomenological coefficient values within 1.5% of the experimental values for univalent systems.

N. G. Pinto
Department of Chemical and
Nuclear Engineering
University of Cincinnati
Cincinnati, OH 45221

E. E. Graham
Department of Chemical Engineering
Cleveland State University
Cleveland, OH 44115

Introduction

Electrolyte solutions are of significant importance in the modern industrial economy. Examples can be found in applications such as electrochemical energy converters, extraction of metals from ores, desalination, electroplating, electrorefining, and purification of biomolecules. In many of these applications successful process design is contingent upon knowledge of the equilibrium and transport properties of electrolyte solutions. While significant inroads have been made in the development of methods for estimation of equilibrium properties (Chen et al., 1982), transport properties have largely been neglected; rigorous methods presently available are only applicable at concentrations of less than 0.001 M (Barthel, 1985). Consequently, transport properties when required usually have to be measured experimentally.

The determination of electrolyte properties through exeprimentation is a tedious and expensive task. The problem is compounded as the number of components in solution is increased. In practice, electrolyte solutions are usually present as concentrated multicomponent mixtures, with the result that expensive experimentation is necessary for process design. The development of a reliable estimation technique will therefore considerably simplify process design.

Multicomponent electrolyte transport in concentrated solutions is a complex problem. In addition to the long-range electrical interactions present in dilute solutions, short-range molecular and ionic interactions are important. Also, since diffusion occurs at appreciable concentrations, corrections involving the solvation of ions, the viscosity change of solution, and the flux of solvent have to be incorporated.

The diffusion of a species across a finite electrochemical potential gradient is rigorously described by the phenomenological flux equations obtained from the thermodynamics of irreversible processes. For electrolyte diffusion, the most commonly used form of these equations is:

$$J_i^s = -\sum_{j=1}^{n} \ell_{ij} \nabla \mu_j' \quad i = 1, 2, \ldots, n$$

$$\ell_{ij} = \ell_{ji} \qquad (1)$$

Equations 1 provides a macroscopic description of ionic mass transport and have found wide use in the analysis of diffusion in dilute electrolyte solutions (Schonert, 1984; Tanigaki et al., 1983; Miller, 1981; Leaist and Lyons, 1980; Patterson, 1977; Woolf and Harris, 1977; Kim et al., 1973; Pikal, 1971). However, these equations are not appropriate for modeling multicomponent diffusion at high concentrations. The phenomenological coefficients of Equations 1 are strongly dependent on total ionic strength and composition of the electrolyte solution (Graham and Dranoff, 1982), and consequently, characterization of this concentration dependence based on detailed chemistry or an interpretation of experimental data is not in general possible.

Newman et al. (1965) and recently Pinto and Graham (1986) have shown that an insight into the nature of the macroscopic transport coefficients is more easily obtained by considering an alternative, but equivalent, form of Equations 1:

$$-x_i\nabla\mu_i' = \frac{RT}{c}\sum_{j=0}^{n}\left(\frac{x_jJ_i^s - x_iJ_j^s}{a_{ij}}\right) \quad i = 1, 2, \ldots, n$$

$$a_{ij} = a_{ji} \tag{2}$$

Equations 2 are called the Stefan-Maxwell equations. These equations are extensions of the relations derived from the kinetic theory of gases (Bird et al., 1960), and have been used previously for liquids (Lightfoot et al., 1962). Equations 2, as written, are with respect to the solvent-fixed frame, but it is evident that the phenomenological coefficients a_{ij} are reference-frame independent. The reciprocals of these coefficients are essentially the friction coefficients used by Laity (1959a, b) and Klemm (1962). It should be noted that only $n - 1$ of the n Eqs. 2 are independent. This and other properties of these equations have been discussed by Newman (1973).

The primary advantage of the Stefan-Maxwell equations over Equations 1 is that the coefficients of the former are essentially pseudobinary in nature (Graham and Dranoff, 1982). That is, a particular a_{ij} will be dependent only on the properties of the ions i and j. Pinto and Graham (1986) have used this property to develop a physical model for diffusion in concentrated electrolyte solutions. Explicit expressions have been presented relating the Stefan-Maxwell coefficients to fundamental properties of the ions and solvent. These expressions were obtained by a combination of microscopic theories and empirical interpretation of experimental data.

The model in its present form is restricted to single-electrolyte and tracer diffusion systems with negligible solvation. This paper eliminates the restriction on solvation, and extends the applicability to multicomponent nonequilibrium diffusion. It has been shown that solvation effects in multicomponent systems can be evaluated from limiting single-electrolyte cases, and solvation is not negligible for tracer or self-diffusion. The paper also verifies the binary character of the Stefan-Maxwell coefficients. Ion-ion interactions in multicomponent diffusion can thus be determined from appropriate tracer diffusion data.

Theoretical Development

For an electrolyte solution consisting of n ions in a polar solvent, the Stefan-Maxwell equations accounting for solvation take the form:

$$-\bar{x}_i\nabla\bar{\mu}_i' = \frac{RT}{\bar{c}}\left[\frac{\bar{x}_oJ_i^s}{\bar{a}_{io}} + \sum_{j=1}^{n}\frac{(\bar{x}_jJ_i^s - \bar{x}_iJ_j^s)}{\bar{a}_{ij}}\right]$$

$$i = 1, 2, \ldots, n \tag{3}$$

In these equations, the ionic fluxes refer to fluxes of the solvated species; since ions carry with them a strongly bound layer of solvent that acts as part of the diffusing species. Thus, in order to distinguish between bound and free solvent all concentrations and concentration-dependent terms are defined on the basis of solvated ions and free solvent.

For systems with negligible solvation effects, expressions have been obtained for a_{io} and a_{ij} (Pinto and Graham, 1986). In terms of solvated concentrations, these can be written as:

$$\bar{a}_{io} = kT\bar{x}_o(\omega_i^o + \delta_i)\left(\frac{\eta^o}{\eta}\right)^{0.7} \tag{4}$$

$$\bar{a}_{ij} = \frac{kT(\omega_i^o + \delta_i)(\omega_j^o + \delta_j)}{[(\omega_i^o + \delta_i)\nu_j + (\omega_j^o + \delta_j)\nu_i]}f(\bar{x}_{ij})\left(\frac{\eta^o}{\eta}\right)^{0.7} \tag{5}$$

for oppositely charged i and j, and

$$\bar{a}_{ij} = \frac{-2kT(\omega_i^o + \delta_i)(\omega_j^o + \delta_j)}{[(\omega_i^o + \delta_i)|Z_i| + (\omega_j^o + \delta_j)|Z_j|]}f(\bar{x}_{ij})\left(\frac{\eta^o}{\eta}\right)^{0.7} \tag{6}$$

for similarly charged i and j. Notice that in addition to defining concentrations in terms of solvated species, the ion-ion coefficients a_{ij} have been corrected for the electrophoretic effect through the δ_i and δ_j terms. This is necessary because for nonequilibrium diffusion, unlike tracer diffusion, both the relaxation and electrophoretic effects have to be considered. Also note that the function $f(\bar{x}_{ij})$ is concentration-dependent and is analogous to the function $f_2(\kappa d)$ used by Pinto and Graham (1986) earlier. However, the concentration x_{ij} is not the total ionic concentration but the mole fraction of ions i and j in solution. This is consistent with the binary nature of the Stefan-Maxwell coefficients.

The nonlinear viscosity correction term used in Eqs. 4–6 merits further discussion. Conventionally, Stokes' law, derived for a macroscopic particle in an ideal hydrodynamic medium, is used to estimate the effect of viscosity on limiting ionic mobility. This law gives a linear correction term (η^o/η). However, Guggenheim et al. (1965) have reported that for small ions, such as Na^+, Cl^-, K^+, I^-, etc., the linear term overcompensates for the effect of viscosity and the term used in Eqs. 4–6 gives more accurate results.

Since experimentally measured concentrations are always reported on the basis of total solvent and bare ions, it is necessary to modify Eqs. 3–6 to this basis. The bare-ion concentrations are related to the solvated ion concentrations by the equations:

$$\bar{x}_o = \frac{c_o - \sum_{i=1}^{n} h_ic_i}{\bar{c}}$$

$$\bar{x}_i = \frac{c_i}{\bar{c}}$$

$$\bar{x}_{ij} = \frac{c_iZ_i^2 + c_jZ_j^2}{\bar{c}}$$

$$\bar{c} = c_o + \sum_{i=1}^{n} c_i(1 - h_i) \tag{7}$$

where

$$c_i = \nu_iC_{ij}$$

Substituting Eqs. 7 in Eqs. 3–6 and simplifying,

$$-x_i\nabla\bar{\mu}_i' = \frac{RT}{c}\left[\frac{x_oJ_i^s}{a_{io}} + G\sum_{j=1}^{n}\frac{(x_jJ_i^s - x_iJ_j^s)}{\bar{a}_{ij}}\right]$$

$$i = 1, 2, \ldots, n \tag{8}$$

where

$$G = \left[\frac{c_o + \sum_{i=1}^{n} c_i}{c_o + \sum_{i=1}^{n} c_i(1 - h_i)}\right] \tag{9}$$

$$a_{io} = kTx_o(\omega_i^o + \delta_i)\left(\frac{\eta^o}{\eta}\right)^{0.7} \tag{10}$$

$$\bar{a}_{ij} = \frac{kT(\omega_i^o + \delta_i)(\omega_j^o + \delta_j)}{[(\omega_i^o + \delta_i)\nu_j + (\omega_j^o + \delta_j)\nu_i]} f(Gx_{ij})\left(\frac{\eta^o}{\eta}\right)^{0.7} \tag{11}$$

for oppositely charges i and j, and

$$\bar{a}_{ij} = \frac{-2kT(\omega_i^o + \delta_i)(\omega_j^o + \delta_j)}{[(\omega_i^o + \delta_i)|Z_i| + (\omega_j^o + \delta_j)|Z_j|]} f(Gx_{ij})\left(\frac{\eta^o}{\eta}\right)^{0.7} \tag{12}$$

for similarly charged i and j.

All the terms appearing on the righthand side of Eqs. 8 are now expressed on the basis of total solvent present. However, the electrochemical potential on the lefthand side of these equations is still defined in terms of free solvent. In order to revert to the nonsolvated form of this term, it is convenient to use the neutral species Stefan-Maxwell formulations. Since only the effect of solvation on the electrochemical potential term has yet to be evaluated, for simplicity all terms in the neutral species Stefan-Maxwell equations except the chemical potential term will be written in the nonsolvated form:

$$-X_i\nabla\bar{\mu}_i = \frac{RT}{C}\left[\frac{X_oJ_i^s}{A_{io}} + \sum_{i=1}^{n-1}\frac{(X_jJ_i^s - X_iJ_j^s)}{A_{ij}}\right] \qquad i = 1, 2, \ldots, n-1 \tag{13}$$

The chemical potential can be expressed as (Robinson and Stokes, 1968a):

$$\nabla\bar{\mu}_i = \nabla \ln \bar{q}_i = \nabla \ln q_i + H_i\nabla \ln q_o \tag{14}$$

where, for the neutral species ij

$$H_i = \nu_i h_i + \nu_j h_j \tag{15}$$

From the Gibbs-Duhem equation,

$$\nabla \ln q_o = -\sum_{i=1}^{n-1}\frac{X_i\nabla \ln q_i}{X_o} \tag{16}$$

By the use of Eq. 16, q_o can be eliminated from Eq. 14. The resultant equation for $\nabla\bar{\mu}_i$ is then substituted into Eqs. 13 to give:

$$-X_i\nabla \ln q_i + H_iX_i\sum_{k=1}^{n-1} X_k\nabla \ln q_k = \frac{RT}{C}\left[\frac{X_oJ_i^s}{A_{io}} + \sum_{j=1}^{n-1}\frac{(X_jJ_i^s - X_iJ_j^s)}{A_{ij}}\right] \qquad i = 1, 2, \ldots, n-1 \tag{17}$$

Summation of all $n - 1$ Eqs. 17 yields:

$$-\sum_{i=1}^{n-1} X_i\nabla q_i = \frac{RT}{CF(H)} \cdot \left[X_o\sum_{i=1}^{n-1}\frac{J_i^s}{A_{io}} + \sum_{i=1}^{n-1}\sum_{j=1}^{n-1}\frac{(X_jJ_i^s - X_iJ_j^s)}{A_{ij}}\right] \tag{18}$$

where

$$F(H) = 1 - \sum_{i=1}^{n-1}\frac{H_iX_i}{X} \tag{19}$$

A similar procedure using Eqs. 13 without a solvated chemical potential term will yield:

$$-\sum_{i=1}^{n-1} X_i\nabla q_i = \frac{RT}{C}\left[X_o\sum_{i=1}^{n-1}\frac{J_i^s}{A_{io}} + \sum_{i=1}^{n-1}\sum_{j=1}^{n-1}\frac{(X_jJ_i^s - X_iJ_j^s)}{A_{ij}}\right] \tag{20}$$

From a comparison of Eqs. 18 and 20, it is clear that the net effect of solvation on the chemical potential term can be accounted for by multiplying each neutral species Stefan-Maxwell coefficient by the term $F(H)$.

It is now necessary to relate the neutral-species coefficients to the ionic coefficients. Graham (1970) has shown that for two ions i and j forming neutral salts ik and jk,

$$\frac{1}{A_{ij}} = \frac{x_i}{x_k}\left(\frac{1}{a_{jk}}\right) + \frac{x_j}{x_k}\left(\frac{1}{a_{ik}}\right) - \frac{x_o}{x_k}\left(\frac{1}{a_{ko}}\right) + \left(\frac{1}{a_{ij}}\right) \tag{21}$$

From Eq. 21 it is evident that multiplying the neutral species coefficient by the terms $F(H)$ is equivalent to multiplying each ionic coefficient by this term.

Equations 8 can now be written as:

$$-x_i\nabla\mu_i' = \frac{RT}{cF(H)}\left[\frac{x_oJ_i^s}{a_{io}} + G\sum_{j=1}^{n}\frac{(x_jJ_i^s - x_iJ_j^s)}{\bar{a}_{ij}}\right] \qquad i = 1, 2, \ldots, n \tag{22}$$

Equations 22 are the generalized solvent-fixed flux equations for a multicompnent electrolyte solution.

Analysis

Single electrolyte

In order to study the effect of solvation on single-electrolyte diffusion, Eqs. 22 are applied to a system consisting of a single cation, subscript 1, and a single anion, subscript 2, in a solvent, subscript o. For this system, Eqs. 22 reduce to:

$$-x_1\nabla\mu_1' = \frac{RT}{cF(H_{12})}\left[\frac{x_oJ_1^s}{a_{10}} + \frac{G(x_2J_1^s - x_1J_2^s)}{\bar{a}_{12}}\right] \tag{23}$$

and

$$-x_2\nabla\mu_2' = \frac{RT}{cF(H_{12})}\left[\frac{x_oJ_2^s}{a_{20}} + \frac{G(x_1J_2^s - x_2J_1^s)}{\bar{a}_{21}}\right] \tag{24}$$

Substitution for the condition of no current

$$J_1^s Z_1 + J_2^s Z_2 = 0 \tag{25}$$

and electroneutrality

$$\bar{c}_1 Z_1 + \bar{c}_2 Z_2 = 0 \tag{26}$$

into Eqs. 23 and 24, and elimination of the electric potential gradient gives:

$$J_1^s = \frac{-1}{x_o}\left[\frac{a_{10}a_{20}(\nu_1 + \nu_2)}{\nu_1 a_{20} + \nu_2 a_{10}}\right] F(H_{12})\left(1 + \frac{d \ln \gamma \pm}{d \ln C_{12}}\right)\nabla C_{12} \tag{27}$$

This equation is identical to the modified Nernst-Hartley relation derived by Robinson and Stokes (1968a) for concentrated single-electrolyte solutions, except for the viscosity correction term (Pinto and Graham, 1986). It is thus clear that Eqs. 22 reduce to the correct form required for single-electrolyte diffusion.

In the literature, experimental mass-transport coefficients are usually reported in terms of the diffusion coefficient of the equation:

$$J_1^v = -D_{12}^v \frac{\partial C_{12}}{\partial x} \tag{28}$$

Notice that the coefficient is measured in the volume-fixed frame. Assuming that partial molar volumes are independent of concentration, it has been shown (Pinto, 1985), by a procedure similar to that used by Robinson and Stokes (1968a), that on substitution for the Stefan-Maxwell coefficients with Eq. 10, Eq. 27 in the volume-fixed frame will take the form:

$$D_{12}^v = (D_{12}^o + \Delta_1 + \Delta_2)F(R)F(H_{12})\left(1 + \frac{d \ln \Lambda \pm}{d \ln m_{12}}\right)\left(\frac{\eta^o}{\eta}\right)^{0.7} \tag{29}$$

where

$$D_{12}^o = \frac{kT\omega_1^o\omega_2^o}{\nu_2\omega_1^o + \nu_1\omega_2^o} \tag{30}$$

$$F(R) = \left\{1 + \frac{M_o}{1{,}000} m_{12}\left[\frac{d_o^o(\nu_1 + \nu_2)}{D_{12}^o + \Delta_1 + \Delta_2} - H_{12}\right]\right\} \tag{31}$$

$$\Delta_1 = \frac{-kT}{6\pi\eta^o}(t_2^o - t_1^o)^2 \frac{\kappa}{1 + \kappa d} \tag{32}$$

and

$$\Delta_2 = \frac{kT}{12\pi\eta^o}\frac{\tilde{e}^2}{EkT}\phi_2(\kappa d)\frac{|Z_1 Z_2|}{d^2} \tag{33}$$

The terms Δ_1 and Δ_2 are electrophoretic corrections that arise from the δ_i term in Eq. 10. The function $\phi_2(\kappa d)$ has been tabulated by Robinson and Stokes (1968b). Equations 32 and 33 are valid only for symmetrical electrolytes in dilute solutions. However, since the electrophoretic effect is relatively small, this does not affect the results significantly.

Equation 29 can be used to predict the diffusivity of a single electrolyte if the solvation numbers are known. Unfortunately, solvation numbers are thermodynamically ill-defined terms. It is not possible to say unambiguously how much solvent is bound to the ion and how much is free. Solvation numbers reported in the literature (Robinson and Stokes, 1968c; Gluekauf and Kitt, 1955; Stokes and Robinson, 1948) have been obtained from various experimental measurements and differ significantly from each other. The objective of this analysis is not to establish a "true" set of solvation numbers, but rather to determine if it is possible from Eq. 29 to define a unique set of numbers that can be used consistently to describe various diffusion processes. Thus, experimental single-electrolyte diffusivities were used to obtain best-fit hydration numbers, and the consistency of these numbers was subsequently verified for tracer diffusion and non-equilibrium ternary diffusion.

The hydration numbers for three electrolytes, NaCl, KCl, and LiCl, calculated from experimental diffusion data (Robinson and Stokes, 1968d) and Eq. 29 are reported in Table 1. The least-squares technique was used. Corresponding best-fit diffusivities have been reported in Tables 2, 3, and 4. Experimental activity coefficient (Robinson and Stokes, 1968d) and viscosity data (Guggenheim et al., 1965) were obtained from the literature. Data reported at molar concentrations were converted to required molal concentrations using the Lagrange interpolation method (Pinto, 1985). The small electrophoretic correction was calculated using distances of nearest approach reported by Stokes and Robinson (1948).

The incorporation of hydration significantly improves the accuracy of the estimated diffusivities. For example, for NaCl, neglecting hydration, the estimated coefficients have an average deviation of 1.8% with a maximim deviation of 3% (Pinto and Graham, 1986). Incorporation of the hydration effect reduces the average deviation to 0.6% and the maximum deviation to 1.5%. This improvement is more pronounced for electrolytes such as LiCl that have higher hydration numbers.

The estimated diffusivities obtained from Eq. 29 are comparable to values obtained from the modified Nernst-Hartley relation (Robinson and Stokes, 1968a). However, Eq. 29 gives more realistic hydration numbers, Table 1. Hydration numbers obtained from the modified Nernst-Hartley relation are consistently lower than those obtained by other methods. Equation 29 gives values closer to those obtained from activity coefficient data (Stokes and Robinson, 1948), and almost exactly matches values reported by Glueckauf and Kitt (1955) from ion-exchange studies.

Table 1. Comparison of Electrolyte Hydration Numbers for KCl, NaCl, and LiCl

	Hydration Numbers, mol water/mol electrolyte			
Electrolyte	Eq. 29	Modified Nernst-Hartley Relation*	Ion-Exchange Data**	Activity-Coefficient Data†
KCl	1.1	0.8	1.0	1.9
NaCl	2.2	1.1	1.9	3.5
LiCl	3.7	2.9	3.7	7.1

*Robinson and Stokes (1968c)
**Glueckauf and Kitt (1955)
†Stokes and Robinson (1948)

Table 2. Estimation of Diffusion Coefficients of NaCl in Water at 25°C

m_{12} mol/kg solvent	Δ_1 $\times 10^5$ cm^2/s	Δ_2 $\times 10^5$ cm^2/s	$(\eta^o/\eta)^{0.7}$	$1 + \frac{d \ln \Lambda \pm}{d \ln m_{12}}$	D^v_{12} expt $\times 10^5$ cm^2/s	D^v_{12} calc $\times 10^5$ cm^2/s	$\frac{D^v_{12}\text{ expt}}{D^v_{12}\text{ calc}}$
0.0	0.000	0.000	1.000	1.000	1.610	1.610	1.000
0.1	−0.008	0.032	0.994	0.917	1.484	1.486	0.999
0.5	−0.013	0.049	0.969	0.927	1.474	1.461	1.009
1.0	−0.015	0.052	0.939	0.970	1.482	1.462	1.014
2.0	−0.017	0.051	0.878	1.096	1.511	1.503	1.005
3.0	−0.018	0.049	0.814	1.245	1.538	1.538	1.000
4.0	−0.019	0.047	0.750	1.410	1.567	1.559	1.005

$D^o_{12} = 1.610 \times 10^{-5}$ cm^2/s; $d = 3.97 \times 10^{-8}$ cm; $H_{12} = 2.2$ gmol water/gmol electrolyte

Ternary electrolyte diffusion

From experimental diffusion data availble in the literature, Miller (1967) has determined the Onsager phenomenological coefficients for the ternary aqueous system NaCl-KCl. These results were used to calculate corresponding Stefan-Maxwell coefficients, which could then be compared to the coefficients determined theoretically from Eqs. 9–12 and 22.

From Eqs. 22, it is evident that experimental ion-solvent and ion-ion Stefan-Maxwell coefficients are given by:

$$a'_{io} = a_{io}F(H) \tag{34}$$

and

$$a'_{ij} = \frac{\bar{a}_{ij}F(H)}{G} \tag{35}$$

respectively. Use of either one of these equations requires appropriate solvation numbers. For the NaCl-KCl system, it is assumed that hydration numbers are not affected by ionic interactions; i.e., single-electrolyte hydration numbers will correctly represent solvation effects in multicomponent systems. With this assumption, the $F(H)$ and G values can be determined for the NaCl-KCl system using the hydration numbers obtained from Eq. 29, Table 1.

The terms a_{io} and $\bar{a}_{ij}$ in Eqs. 34 and 35 can be evaluated from Eqs. 10–12. For the NaCl-KCl system, the viscosity corrections were experimentally determined. Details of the methods used are reported elsewhere (Pinto, 1985). The electrophoretic corrections were evaluated using the dilute solution theory of Debye and Huckel (1923). Since the Stefan-Maxwell coefficients are pseudobinary coefficients, the theory need be applied only to binary systems. This considerably simplifies the development. For a symmetrical binary system *i-j*, it can be shown that (Pinto, 1985):

$$\delta_i = \frac{1}{6\pi\eta^o}\left(\frac{n_j}{n_i + n_j}\right)\frac{\kappa}{1 + \kappa d} - \frac{1}{12\pi\eta^o}\left(\frac{Z_j^2\tilde{e}^2}{EkT}\right)\left(\frac{n_j}{n_i + n_j}\right)\frac{\phi_2(\kappa d)}{d^2} \tag{36}$$

where $\phi_2(\kappa d)$ has been tabulated by Robinson and Stokes (1968b).

A difficulty arises in defining the distance of nearest approach for similarly charged ions of the NaCl-KCl system. One possibility is to use crystallographic radii. However, this creates two problems. First, it is known that the ions are hydrated and the hydrated radius is larger than the corresponding bare-ion value. Using crystallographic radii would thus introduce substantial error. Secondly, if crystallographic radii are used, there is an internal inconsistency with d values used in the single-electrolyte analysis. With this in mind, the d values were selected to minimize the error and to maintain an internal consistency.

Since the chloride ion has the largest crystallographic radius, it will have the lowest surface density of charge and hence the lowest hydration number. Thus, for this ion assuming the hydrated radius to be equal to the crystallographic radius will introduce the least error in the computations. The hydrated radii for K^+ and Na^+ can then be calcuated from d values used in single-electrolyte studies of KCl and NaCl, respectively.

A comparison of the estimated and experimental ion-solvent coefficients for the NaCl-KCl system is shown in Table 5. The concentration range is 0.0 to 3.0 M. It should be noted that no fitted parameter has been used in calculating the coefficients.

Table 3. Estimation of Diffusion Coefficients of KCl in Water at 25°C

m_{12} mol/kg solvent	Δ_1 $\times 10^5$ cm^2/s	Δ_2 $\times 10^5$ cm^2/s	$(\eta^o/\eta)^{0.7}$	$1 + \frac{d \ln \Lambda \pm}{d \ln m_{12}}$	D^v_{12} expt $\times 10^5$ cm^2/s	D^v_{12} calc $\times 10^5$ cm^2/s	$\frac{D^v_{12}\text{ expt}}{D^v_{12}\text{ calc}}$
0.0	0.00	0.000	1.000	1.000	1.993	1.993	1.000
0.1	−0.67	0.035	1.000	0.917	1.844	1.859	0.992
0.5	−1.11	0.056	1.001	0.891	1.850	1.831	1.010
1.0	−1.32	0.062	1.002	0.907	1.890	1.875	1.008
2.0	−1.52	0.063	0.996	0.955	1.983	1.971	1.006
3.0	−1.62	0.061	0.982	1.018	2.084	2.078	1.003
4.0	−1.68	0.060	0.966	1.069	2.157	2.154	1.001

$D^o_{12} = 1.993 \times 10^{-5}$ cm^2/s; $d = 3.63 \times 10^{-8}$ cm; $H_{12} = 1.1$ gmol water/gmol electrolyte

Table 4. Estimation of Diffusion Coefficients of LiCl in Water at 25°C

m_{12} mol/kg solvent	$\Delta_1 \times 10^5$ cm²/s	$\Delta_2 \times 10^5$ cm²/s	$(\eta^\circ/\eta)^{0.7}$	$1 + \dfrac{d \ln \Lambda \pm}{d \ln m_{12}}$	D^v_{12} expt $\times 10^5$ cm²/s	D^v_{12} calc $\times 10^5$ cm²/s	$\dfrac{D^v_{12}\text{ expt}}{D^v_{12}\text{ calc}}$
0.0	0.000	0.000	1.000	1.000	1.366	1.366	1.000
0.1	−0.019	0.028	0.989	0.945	1.269	1.276	0.995
0.5	−0.030	0.042	0.951	1.011	1.278	1.279	0.999
1.0	−0.036	0.044	0.908	1.134	1.301	1.316	0.989
2.0	−0.040	0.043	0.826	1.411	1.359	1.374	0.989
3.0	−0.043	0.041	0.750	1.752	1.420	1.417	1.002

$D^o_{12} = 1.366 \times 10^{-5}$ cm²/s; $d = 4.32 \times 10^{-8}$ cm; $H_{12} = 3.7$ gmol water/gmol electrolyte

For the potassium and chloride ion-solvent coefficients, the match between experiment and theory is good. All the computed values are within ±3% of the corresponding experimental data points. The prediction for the sodium coefficient is, unfortuantely, not as good. The error in the predicted values range from +10 to +17%. The reason for this large discrepancy is not known at this time.

The ion-ion coefficients can be evaluted from Eqs. 11, 12, and 35. However, it is first necessary to specify the function $f(Gx_{ij})$.

In an analysis of tracer diffusion neglecting solvation effects, it was suggested (Pinto and Graham, 1986) that

$$f(x_{ij}) = \frac{g_{ij}\sqrt{x_{ij}}}{1 + \sqrt{x_{ij}}} \tag{37}$$

where the relation between g_{ij} and d was given as:

$$d = \frac{|Z_i Z_j| \bar{e}^2}{6EkTg_{ij}}\left(1 + \frac{1}{\sqrt{x_{ij}}}\right) - \left(\frac{EkT}{4\pi\bar{e}^2 N c x_{ij}}\right)^{1/2} \tag{38}$$

However, on expressing concentration terms in Eq. 38 on the basis of solvated species,

$$d = \frac{|Z_i Z_j| \bar{e}^2}{6EkTg_{ij}}\left(1 + \frac{1}{\sqrt{Gx_{ij}}}\right) - \left(\frac{EkT}{4\pi\bar{e}^2 N c x_{ij}}\right)^{1/2} \tag{39}$$

From Eq. 9 it is evident that at a constant solution composition, G increases with increasing solvation. Equation 39 thus gives a decreasing value of d with increasing solvation. This is physically inconsistent and Eq. 37 is inappropriate.

In the absence of a theoretical equation, Miller's (1967) ion-ion interaction data for the NaCl-KCl system were used to develop an empirical equation for $f(x_{ij})$. From Eqs. 9, 11, 12, 19, 35, the simple form

$$f(\bar{x}_{ij}) = g_{ij}\bar{x}_{ij}^{2/3} \tag{40}$$

was found to represent the data adequately. A comparison of experimental and calculated values is shown in Table 6. Also reported in this table are the best-fit binary constants g_{ij}. Since the Stefan-Maxwell coefficients are pseudobinary coefficients, the values of g_{ij} should be independent of other ions present in the system. Thus, once g_{ij} has been determined for a particular ion pair it can be used regardless of how the composition of the system changes. It is therefore possible to verify the form of Eq. 40 and the consistency of the g_{ij} values of Table 6 by analyzing appropriate tracer diffusion systems. This is the objective of the next section.

Tracer diffusion

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

$$N_i = \frac{-c_i}{RT} d_i \nabla c_i \tag{41}$$

For this case, the diffusive fluxes of all species except the trace species are negligible, and gradients of activity coefficients

Table 5. Estimated Values of Ion-Solvent Coefficients in Aqueous NaCl-KCl at 25°C

$a'_{io} \times 10^5$ cm²/s	System*					
	I	I-A	I-B	I-C	I-D	I-E
a'_{Ko} calc	1.96	1.98	1.92	1.98	1.92	1.56
a'_{Ko} exp	1.96	1.92	1.87	1.92	1.88	1.57
a'_{Clo} calc	2.03	2.13	2.08	2.13	2.08	1.70
a'_{Clo} exp	2.03	2.09	2.07	2.07	2.04	1.71
a'_{Nao} calc	1.33	1.42	1.41	1.40	1.39	1.14
a'_{Nao} exp	1.33	1.29	1.25	1.28	1.22	0.97

*System: I, infinite dilution; I-A, 0.25 M NaCl, 0.25 M KCl; I-B, 0.50 M NaCl, 0.25 M KCl; I-C, 0.25 M NaCl, 0.50 M KCl; I-D, 0.50 M NaCl, 0.50 M KCl; I-E, 1.5 M NaCl, 1.5 M KCl

$d_{NaNa} = 4.32 \times 10^{-8}$ cm; $d_{KK} = 3.64 \times 10^{-8}$ cm; $d_{ClCl} = 3.61 \times 10^{-8}$ cm; $H_{NaCl} = 2.2$; $H_{KCl} = 1.1$.

Table 6. Estimated Values of Ion-Ion Coefficients in Aqueous NaCl-KCl at 25°C

$a'_{ij} \times 10^5$ cm²/s	g_{ij}	System*				
		I-A	I-B	I-C	I-D	I-E
a'_{NaK} calc	1.97	−0.14	−0.18	−0.18	−0.21	−0.38
a'_{NaK} exp	—	−0.15	−0.18	−0.18	−0.20	−0.38
a'_{KCl} calc	2.65	0.12	0.12	0.18	0.19	0.32
a'_{KCl} exp	—	0.11	0.14	0.15	0.18	0.34
a'_{NaCl} calc	2.64	0.09	0.15	0.09	0.15	0.25
a'_{NaCl} exp	—	0.09	0.11	0.11	0.14	0.30

*System: I-A, 0.25 M NaCl, 0.25 M KCl; I-B, 0.50 M NaCl, 0.25 M KCl; I-C, 0.25 M NaCl, 0.50 M KCl; I-D, 0.50 M NaCl, 0.50 M KCl; I-E, 1.50 M NaCl, 1.50 M KCl

$H_{NaCl} = 2.2$; $H_{KCl} = 1.1$

Table 7. Tracer Diffusion at 25°C

			Concentration, M/L					
			0.1	0.5	1.0	2.0	3.0	4.0
Electrolyte	Tracer	g_{ij}	d_i/d_i^o Theory (Exp)					
KCl	Na^+	$g_{NaK} = 1.97$ $g_{NaCl} = 2.64$	0.98 (0.99)	0.97 (0.99)	0.97 (0.98)	0.95 (0.96)	0.93 (0.94)	0.90 (0.92)
NaCl	Cl^-	$g_{NaCl} = 2.64$ $g_{ClCl} = 2.10$	0.96 (0.96)	0.91 (0.91)	0.87 (0.87)	0.79 (0.79)	0.71 (0.71)	0.64 (0.62)
KCl	Cl^-	$g_{KCl} = 2.65$ $g_{ClCl} = 2.10$	0.98 (0.97)	0.96 (0.96)	0.96 (0.96)	0.94 (0.94)	0.91 (0.91)	0.88 (0.87)

are absent. Equations 22 can thus be simplified to:

$$J_i^s = N_i = \frac{-c_i F(H) \nabla c_i}{RT\left(\frac{x_o}{a_{io}} + G \sum_{j=1}^{n} \frac{x_j}{\bar{a}_{ij}}\right)} \tag{42}$$

where i is the trace species. A comparison of Eqs. 41 and 42 gives:

$$d_i = \frac{F(H)}{\left(\frac{x_o}{a_{io}} + G \sum_{j=1}^{n} \frac{x_j}{\bar{a}_{ij}}\right)} \tag{43}$$

Normalizing Eq. 43 with the tracer diffusion coefficient at infinite dilution,

$$\frac{d_i}{d_i^o} = \frac{F(H) a_{io}^o}{\left(\frac{x_o}{a_{io}} + G \sum_{j=1}^{n} \frac{x_j}{\bar{a}_{ij}}\right)} \tag{44}$$

Equation 44 incorporates the effect of solvation on tracer diffusion. Conventionally, in treating tracer diffusion or self-diffusion the effect of solvation is neglected. However, from Eq. 44 it is evident that for strongly solvated ions $F(H)$ and G may not be negligible. Physically, solvation manifests itself through a reduction in the cross section available for diffusion, since solvated solvent is not accessible to the diffusing species.

Eqation 44 was used in conjunction with the binary constants reported in Table 6 to predict the tracer diffusivity of Na^+ in KCl solution. The Stefan-Maxwell coefficients in Eq. 44 were calculated using Eqs. 10–12 with $\delta_i = 0$; when a very low fraction of the total ions in solution is diffusing, the electrophoretic effect is negligible. Viscosity data reported in the literature (Guggenheim et al., 1965) were used. The correction for solvation was made using hydration numbers obtained from single-electrolyte diffusion, Table 1.

The predicted diffusivities are compared to experimental values reported by Robinson and Stokes (1968e), in Table 7. The accuracy of the predictions is encouraging (±2.5%). It must be emphasized that no fitted parameters were used in the calculations.

The binary constants of Table 6 can be used to predict the tracer diffusivity of one other system, K^+ in NaCl. Unfortunately, to our knowledge experimental data are not reported in the literature for this system. However, the pseudobinary nature of the Stefan-Maxwell coefficients can be verified using experimental data reported for the trace ion Cl^- in solutions of NaCl and KCl. For both these systems, the binary constant g_{ClCl} is not available. However, one coefficient for each system, g_{NaCl} for Cl^- in NaCl and g_{KCl} for Cl^- in KCl, is available from the ternary nonequilibrium studies. If the constants of Eq. 44 are truly binary, a best-fit value of g_{ClCl} obtained from one system should enable the prediction of the behavior of the other. From Table 7 it is evident that this is indeed the case. The experimental data for the Cl^- in KCl system were used to obtain a best-fit value for g_{ClCl}. This best-fit value was subsequently used to predict the tracer diffusivity of Cl^- in NaCl. From Table 7 it is evident that the theory predicts the variation in diffusivity accurately over the concentration range.

For the tracer systems considered, the average error in the calculated values is less than 1% and the maximum error is 3%. This excellent match between experimental and predicted values confirms the binary nature of the constants g_{ij} and the functional form of Eq. 40.

Notation

a_{ij} = ionic Stefan-Maxwell phenomenological coefficient
a'_{ijk} = experimental ionic Stefan-Maxwell phenomenological coefficient
A_{ij} = neutral species Stefan-Maxwell phenomenological coefficient
$\bar{A}$ = property A evaluated when ionic species are considered solvated; for example, $\bar{\mu}$ is the electrochemical potential evaluated for solvated species.
c = total concentration when electrolyte concentrations are expressed in terms of individual ionic concentration
c_i = concentration of ionic species
c_o = concentration of solvent
C = total concentration when electrolyte concentrations are expressed in terms of neutral species
C_{ij} = concentration of neutral salt made up of ions i and j
d = distance of nearest approach
d_i = tracer diffusion coefficient of species i
D_{ij} = diffusivity of electrolyte made up of ions i and j
$\tilde{e}$ = protonic charge
E = dielectric constant of medium
$f(\bar{x}_{ij})$ = function, Eq. 37 or 40
$F(H)$ = function, Eq. 19
$F(R)$ = function, Eq. 31
g_{ij} = binary constant, Eq. 37 or 40
G = term, Eq. 9
h_i = solvation number of ionic species i
H_i = solvation number of neutral species i
H_{ij} = solvation number of species made up of ions i and j
J_i = flux of species i
k = Boltzmann constant
ℓ_{ij} = ionic Osnager phenomenological coefficient
m_{ij} = molal concentration of neutral species made up of ions i and j
M_o = molecular weight of solvent

n_i = bulk average concentration of ionic species, ion/cm^3
N = Avogadro's number
N_i = flux of species i with respect to a fixed frame
q_i = activity of species i, molar scale
R = universal gas constant
t_i = transference number of ion i
T = absolute temperature
x = distance
x_i = mole fraction of ionic species i
x_{ij} = effective mole fraction of ions i plus j
X_i = mole fraction of neutral species i
Z_i = valency of ionic species i

Greek letters

$\gamma\pm$ = mean activity coefficient of salt, molar scale
δ_i = correction for electrophoretic mobility of species i
η = viscosity of solution
κ = inverse Debye length
μ_i = chemical potential of species i
μ_i' = electrochemical potential of species i
ν_i = stoichiometric coefficient of species i
$\phi_2(\kappa d)$ = ionic concentration dependent function tabulated in Robinson and Stokes (1968b)
Δ_i = electrophoretic correction for diffusivity
ω_i = mobility of species i
$\Lambda\pm$ = mean activity coefficient of salt, molal scale

Subscripts

calc = calculated value
expt = experimental value
i = species i
j = species j
o = free solvent

Superscripts

o = infinite dilution
s = solvent-fixed frame
v = volume-fixed frame

Literature cited

Barthel, J., "Transport Properties of Electrolytes from Infinite Dilution to Saturation," *Pure Appl. Chem.*, **57**(2), 355 (1985).

Bird, R. B., W. E. Stewart, and E. N. Lightfoot, "Transport Phenomena," Wiley, New York (1960).

Chen, C. C., H. I. Britt, J. F. Boston, and L. B. Evans, "Local Composition Model for Excess Gibbs Energy of Electrolyte Systems," *AIChE J.*, **28**(4), 588 (1982).

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

Glueckauf, E., and G. P. Kitt, "A Theoretical Treatment of Cation Exchangers. III: The Hydration of Cations in Polystyrene Sulfonates," *Proc. Royal Soc. (London)*, **A228**, 32 (1955).

Graham, E. E., "Use of the Stefan-Maxwell Relations to Describe Transport in Ion-Exchange Resins," Ph.D. Thesis, Northwestern Univ., Evanston, IL (1970).

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., *Int. Encyc. Phys. Chem., Chem. Phys.*, Pergamon, New York, Topic 16, **3**, (1965).

Kim, H., G. Reinfelds, and L. J. Gosting, "Isothermal Diffusion Studies of Water-KCl-HCl and Water-NaCl-HCl Systems at 25°C," *J. Phys. Chem.*, **77**, 934 (1973).

Laity, R. W., "An Application of Irreversible Thermodynamics to the Study of Diffusion," *J. Phys. Chem.*, **63**, 80 (1959a).

Laity, R. W., "General Approach to the Study of Electrical Conductance and its Relation to Mass Transport Phenomena," *J. Chem. Phys.*, **30**, 682 (1959b).

Klemm, A., "Zur Phanomelogie der isothermen Diffusion in Elektrolyten," *Z. Naturforsch*, **17a**, 805 (1962).

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

Lightfoot, E. N., E. L. Cussler, and R. L. Retting, "Applicability of the Stefan-Maxwell Equations to Multicomponent Diffusion in Liquids," *AIChE J.*, **8**, 708 (1962).

Miller, D. G., "Application of Irreversible Thermodynamics to Electrolyte Solutions. II: Ionic Coefficients ℓ_{ij} for Isothermal Vector Transport Processes in Ternary Systems," *J. Phys. Chem.*, **71**, 616 (1967).

———, "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).

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

Newman, J. S., D. Bennion, and C. W. Tobias, "Mass Transfer in Concentrated Binary Electrolyes," *Ber. Bunsenges. Physik. Chem.*, **69**, 608 (1965)

Patterson, R., "Application of Irreversible Thermodynamics to Transport of Self-Complexing Electrolytes," *Faraday Disc. Chem. Soc.*, **64**, 304 (1977).

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

Pinto, N. G., and E. E. Graham, "Evaluation of Diffusivities in Electrolyte Solutions Using Stefan-Maxwell Equations," *AIChE J.*, **32**(2), 291 (1986).

Pinto, N. G., "Development of a Model for the Prediction of Diffusion Coefficients in Electrolyte Solutions and Ion Exchangers," Ph.D. Thesis, Penn. State Univ., University Park, PA (1985).

Robinson, R. A., and R. H. Stokes, "Electrolyte Solutions," Butterworths, London, 320–328 (1968a); 145 (1968b); 331 (1968c); 476–515 (1968d); 317 (1968e).

Schonert, H., "Evaluation of Velocity Correlation Coefficients from Experimental Transport Data in Electrolyte Systems," *J. Phys. Chem.*, **88**, 3,359 (1984).

Stokes, R. H., and R. A. Robinson, "Ionic Hydration and Activity in Electrolyte Solutions," *J. Am. Chem. Soc.*, **70**, 1,870 (1948).

Tanigaki, M., K. Kondo, M. Harada, and W. Eguchl, "Measurement of Ternary Diffusion Coefficients Using a Position-Scanning Spectrophotometer," *J. Phys. Chem.*, **87**, 586 (1983).

Woolf, L. A., and K. R. Harris, "Velocity Correlation Coefficients as an Expression of Particle-Particle Interactions in Electrolyte Solutions," *Faraday Disc. Chem. Soc.*, **64**, 933 (1977).

Manuscript received June 17, 1986, and revision received Sept. 8, 1986.