Modeling Self-diffusion in Multicomponent Aqueous Electrolyte Systems in Wide Concentration Ranges

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A comprehensive model has been developed for calculating self-diffusion coefficients in multicomponent aqueous electrolyte systems. The model combines contributions of long-range (Coulombic) and short-range interactions. The long-range interaction contribution, which manifests itself in the relaxation effect, is obtained from the dielectric continuum-based mean-spherical approximation (MSA) theory for the unrestricted primitive model. The short-range interactions are represented using the hard-sphere model. In the combined model, aqueous species are characterized by effective radii, which depend on the ionic environment. For multicomponent systems, a mixing rule has been developed on the basis of phenomenological equations of nonequilibrium thermodynamics. The effects of complexation are taken into account by combining the diffusivity model with thermodynamic speciation calculations. The model accurately reproduces self-diffusivities of ions and neutral species in aqueous solutions ranging from infinitely dilute to concentrated (up to ca. 30 mol/kg of H_2O). Also, the model makes it possible to predict diffusivities in multicomponent solutions using data for single-solute systems.

Introduction

Self-diffusion coefficients in aqueous solutions are needed to understand mass-transfer processes in a variety of industrial, primarily electrochemical, systems. Therefore, there is a need for an accurate method for predicting self-diffusivity in wide ranges of chemical composition, concentrations, and temperature. In this work, self-diffusion is defined according to Mills and Lobo (1989), who used this term to cover both intradiffusion and tracer diffusion in electrolyte solutions, primarily because the term "self-diffusion" is in general usage in the electrochemical literature.

The concentration dependence of transport coefficients, including self-diffusivity, has been one of the most important problems in the statistical mechanics of electrolyte systems. It has been extensively studied for dilute solutions. A limiting law for several transport coefficients was developed by Onsager and Fuoss (1932) using the Debye−Hückel (1924) equilibrium distribution functions. This law was later extended to self-diffusivity in ionic mixtures by Onsager and Kim (1957). More recently, Bernard et al. (1992) combined the Onsager continuity equations with equilibrium correlation functions calculated from the mean-spherical approximation (MSA) theory. The MSA theory of transport properties is valid up to the limit of the primitive model of electrolyte solutions, i.e., for concentrations ranging from infinite dilution to ca. 1 M. However, no theory is available for more concentrated electrolyte solutions. It seems evident that a diffusivity model for concentrated solutions cannot rely exclusively on the primitive model, which approximates the behavior of the solution by that of ions in a dielectric continuum.

In contrast to electrolyte solutions, the diffusivity theories for nonelectrolyte mixtures have been based mostly on hard-sphere theories (cf. reviews by Dymond, 1985; Tyrrell and Harris, 1984). The hard-sphere theories originated from the work of Enskog and Chapman (Chapman and Cowling, 1952) on transport properties of nonideal gases. The Enskog theory was extended to dense fluid mixtures by Tham and Gubbins (1971) and van Beijeren and Ernst (1973). Corrections to the Enskog theory were introduced on the basis of molecular dynamics simulations (Czworniak et al., 1975). Also, the hard-sphere theory has been extended to systems with more realistic intermolecular potentials (Ruckenstein and Liu, 1997). However, no attempt has been made to extend the hard-sphere theories to systems with Coulombic interactions.

The objective of this work is to develop an engineering-oriented model for calculating self-diffusivity in multicomponent systems that are of interest for industrial applications. We propose a model that utilizes results from the hard-sphere theory and the MSA theory for the unrestricted primitive model. The model is developed to satisfy several practical requirements:

(1) It should be applicable to systems ranging from infinitely dilute to very concentrated.

(2) It should predict the self-diffusivity of all species in multicomponent solutions using information obtained from data for single-solute systems.

(3) When combined with a realistic thermodynamic speciation model, the diffusivity model should give accurate results for systems that involve complexation, hydrolysis, and other possible reactions in solution.

After developing a model that satisfies these requirements, we apply it to several systems with different chemical characteristics.

Computation of Self-diffusion Coefficients at Infinite Dilution

Self-diffusion coefficients at infinite dilution provide a starting point for the computation of diffusivities at finite concentrations. Therefore, prior to developing a

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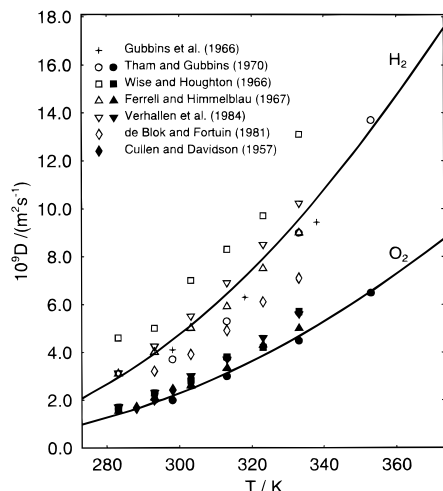
Figure 1. Diffusion coefficients of hydrogen and oxygen in pure water. The solid lines have been obtained from eq 3 with parameters listed in Table 1.
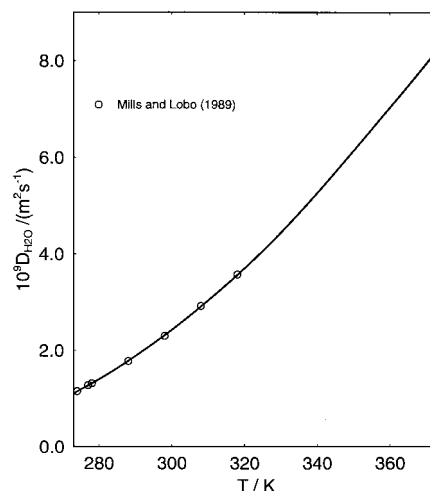

Figure 2. Self-diffusion coefficients of H_2O. The solid lines have been obtained from eq 3 with parameters listed in Table 1. The symbols are the values recommended by Mills and Lobo (1989).

model for diffusivity in wide concentration ranges, it is necessary to establish a reliable procedure for calculating infinite-dilution diffusion coefficients.

In the case of ions, self-diffusion coefficients (D^0) are related to equivalent limiting diffusivities (λ^0) by the Nernst–Einstein equation, i.e.,

$$D^0 = \frac{RT}{|z|F}\lambda^0 \tag{1}$$

where R, F, and z are the gas constant, Faraday constant, and ionic charge, respectively. The limiting ionic conductivities and, equivalently, the limiting diffusivities are strongly dependent on temperature. In the dense liquid-phase region at temperatures up to ca. 550 K, the temperature dependence of λ^0 can be accurately reproduced using Smolyakov's (1969) equation, i.e.,

$$\ln \lambda^0(T)\,\eta(T) = A + B/T \tag{2}$$

where η is the viscosity of pure water and A and B are adjustable constants. Anderko and Lencka (1997) tabulated the A and B constants for ions for which experimental data are available over wide temperature ranges. Also, Anderko and Lencka (1997) developed a correlation between parameter B (eq 2) and the structural entropy of ions, which makes it possible to predict the temperature dependence of λ^0 with good accuracy when experimental data are available only at a single temperature (e.g., at ambient conditions).

In this study, we extend the applicability of eq 2 to the diffusivity of neutral molecules in water. Combination of eqs 1 and 2 yields

$$\ln \frac{D^0(T)\,\eta(T)}{T} = C + \frac{B}{T} \tag{3}$$

In eq 3, the pure water viscosity η is calculated as a function of temperature using the equation of Watson et al. (1980). Equation 3 has been found to reproduce the temperature dependence of limiting diffusivities of neutral species within experimental uncertainty. This is illustrated in Figures 1 and 2 for H_2, O_2, and H_2O, which are the essential neutral species in aqueous systems. It should be noted that diffusivities of neutral

species are much more uncertain than those of ions and, therefore, substantial scattering of experimental data is observed in Figure 1. In the case of H_2O, no scattering is observed (cf. Figure 2) because only the values recommended by Mills and Lobo (1989) have been used. The values of the C and B parameters in eq 3 are collected in Table 1 for a number of common neutral solutes in water.

Experimental limiting diffusivity (or conductivity) data are usually available only for simple, ionic, or neutral species (cf. Anderko and Lencka, 1997, and Table 1). At the same time, complex species such as $Me(X^{m-})_n$ play an important role in aqueous systems of industrial interest. Diffusivities of such species are difficult to measure because complexes always occur together with simple species (i.e., Me^{z+} and X^{m-}) and experimental diffusion data are usually a manifestation of the diffusion of both simple and complex species. Therefore, it is necessary to establish a reasonable procedure for estimating limiting diffusivities of complex species from those of simple species. In a previous study (Anderko and Lencka, 1997), a technique was proposed for estimating the limiting conductivities of complex ions using the additivity of Stokes volumes of ions. In this work, this technique is extended to both charged and uncharged species.

The Stokes radius of a species at infinite dilution is related to its limiting diffusivity, i.e.,

$$r_{i,S} = \frac{kT}{6\pi\eta D_i^0} \tag{4}$$

It can be postulated that the volume of a hydrated complex species is, to a first approximation, equal to the sum of hydrated volumes of the constituent simple species. Since the Stokes radius is a measure of the size of a hydrated species, the cube of the Stokes radius of a complex ($r_{complex,S}$) can be approximated by the sum of the cubes of Stokes radii of the constituent simple species ($r_{i,S}$), i.e.,

$$r_{complex,S}^3 = \sum_{i=1}^{n} r_{i,S}^3 \tag{5}$$

where n is the number of simple species that make up

Table 1. Parameters of Equation 3 for the Infinite-Dilution Diffusion Coefficient of Neutral Species in Water

species	C	B	experimental data source
H_2O	−33.13	156.2	Mills and Lobo (1989)
H_2	−32.02	26.12	Gubbins et al. (1966), Tham et al. (1970), Wise and Houghton (1966), Ferrell and Himmelblau (1967), Verhallen et al. (1984), de Blok and Fortuin (1981)
O_2	−32.60	−19.88	Tham et al. (1970), Himmelblau (1964), Verhallen et al. (1984), Ferrell and Himmelblau (1967), Wise and Houghton (1966)
N_2	−32.30	−75.90	Wise and Houghton (1966), Ferrell and Himmelblau (1967), Verhallen et al. (1984)
Cl_2	−31.44	−460.5	Himmelblau (1964), Landolt−Börnstein (1969)
He	−32.28	231.2	Wise and Houghton (1966), Ferrell and Himmelblau (1962), Verhallen et al. (1984)
Ne	−32.25	37.66	Akgerman and Gainer (1972)
Ar	−29.46	−947.5	Akgerman and Gainer (1972)
Xe	−33.47	95.31	Unsworth and Gillespie (1969)
Kr	−33.10	65.07	Unsworth and Gillespie (1969)
N_2O	−33.67	270.3	Landolt−Börnstein (1969), Akgerman and Gainer (1972)
NO	−26.04	−1855	Akgerman and Gainer (1972)
NO_2	−33.24	39.03	Akgerman and Gainer (1972)
NH_3	−32.30	−121.1	Himmelblau (1964)
CH_4	−33.53	201.2	Gubbins et al. (1966)
C_2H_2	−34.95	656.7	Himmelblau (1964)
C_2H_6	−33.27	217.6	Wise and Houghton (1966)
C_3H_8	−32.85	33.14	Wise and Houghton (1966)
C_4H_{10}	−30.54	−731.7	Wise and Houghton (1966)

a complex. By substituting eq 4 into eq 5, a relationship for the limiting diffusivity of a complex is obtained:

$$D^0_{complex} = \frac{1}{\left[\sum_{i=1}^{n}\left(\frac{1}{D^0_i}\right)^3\right]^{1/3}} \qquad (6)$$

Equation 6 will be further used to estimate the limiting diffusivities of complex species.

Concentration Dependence for Single Electrolytes

In relatively dilute electrolyte solutions, the main effects that determine the deviations of transport properties from ideal behavior are the relaxation and electrophoretic effects (Robinson and Stokes, 1959). In the case of self-diffusion, the only relevant contribution is the relaxation effect, which represents the return to equilibrium after a perturbation by an external force (k_i). In general, the effect of the relaxation forces on the variation of the self-diffusion coefficient from its value at infinite dilution is given by

$$D_i = D^0_i(1 + \delta k_i/k_i) \qquad (7)$$

where $\delta k_i/k_i$ is the relaxation term. Recently, Bernard et al. (1992) developed an expression for $\delta k_i/k_i$ for the unrestricted primitive model, i.e., a system of ions with different sizes in a dielectric continuum. Bernard et al. (1992) and Chhih et al. (1995) demonstrated that eq 7 gives good agreement with experimental data for monovalent ions at concentrations up to ca. 1 M.

However, the concentrations that are of interest for industrial applications range from 0 to ca. 30 M. As the concentration is increased, representation of transport phenomena in terms of the primitive model becomes insufficient. In systems with substantial ionic concentration, the long-range interionic forces are effectively screened to short range by patterns of alternating charges. Then, interionic forces can be combined with all other interparticle forces on the same basis (Pitzer, 1980; Pitzer and Simonson, 1986). Thus, all interparticle forces in concentrated solutions can be effectively treated as short-range forces, and the solution

properties can be calculated by methods similar to those for nonelectrolytes. At the same time, the alternating charge pattern and its accompanying screening effect are lost in the dilute solution range and, therefore, the effects of long-range electrostatic interactions are significant at low concentrations. This rationale was used by Pitzer (1980) and Pitzer and Simonson (1986) to develop thermodynamic models by combining a long-range electrostatic interaction term with terms developed for nonelectrolyte solutions. Here, we use the same concept to postulate a general model for self-diffusivity in systems ranging from dilute to concentrated.

In the case of self-diffusion, the relaxation effect is a manifestation of long-range electrostatic interactions. The concentration dependence of self-diffusion in concentrated solutions can be, at the same time, represented by the hard-sphere theory, which is adequate for nonelectrolyte solutions. To combine these two effects, eq 7 can be rewritten by introducing a factor that accounts for the concentration dependence of self-diffusivity on the basis of the hard-sphere theory, i.e.,

$$D_i = D^0_i\left(\frac{D^{HS}_i}{D^0_i}\right)\left(1 + \frac{\delta k_i}{k_i}\right) \qquad (8)$$

In eq 8, the D^{HS}_i/D^0_i factor becomes significant for concentrated solutions. For relatively dilute solutions, eq 8 can be expected to reduce to eq 7.

In this study, we use the relaxation term from the work of Bernard et al. (1992) and Chhih et al. (1995) and the hard-sphere term from the extension of the Enskog theory developed by Tham and Gubbins (1971). Then, we introduce the concept of effective ionic radii in aqueous solutions to reproduce self-diffusivities over wide concentration ranges.

Relaxation Effect. To calculate the relaxation term in eq 8, we use the expressions developed by Bernard et al. (1992) and Chhih et al. (1994) for a tracer ion in an electrolyte containing one cation and one anion at finite concentrations. Specifically, we utilize the simplified form of Chhih et al. (1994), in which the average size approximation is used for the ionic sizes. According to Chhih et al. (1994), the relaxation term for a tracer ion i is given by

$$\frac{\delta k_i}{k_i} = -\frac{1}{4\pi\epsilon_0\epsilon}\frac{z_i^2 e^2(\kappa^2 - \kappa_{di}^2)}{6k_B T\sigma(1 + \Gamma\sigma)^2} \times$$
$$\frac{1 - \exp(-2\kappa_{di}\sigma)}{\kappa_{di}^2 + 2\Gamma\kappa_{di} + 2\Gamma^2[1 - \exp(-\kappa_{di}\sigma)]} \quad (9)$$

where z_i is the ionic charge, e is the charge of the electron, ϵ_0 is the permittivity of vacuum, k_B is the Boltzmann constant, and ϵ is the dielectric constant of pure water. The value of ϵ is calculated from the equation of Uematsu and Franck (1980). In eq 9, σ is the average ion diameter defined by

$$\sigma = \frac{\sum\limits_{j=1}^{2} z_j^2 \rho_j \sigma_j}{\sum\limits_{j=1}^{2} z_j^2 \rho_j} \quad (10)$$

where ρ_j and σ_j are the number density and the diameter of the jth ion, respectively. The parameters κ and κ_{di} are given by

$$\kappa^2 = \frac{e^2}{\epsilon_0\epsilon kT}\sum\limits_{j=1}^{2}\rho_j z_j^2 \quad (11)$$

$$\kappa_{di}^2 = \frac{e^2}{\epsilon_0\epsilon kT}\sum\limits_{j=1}^{2}\frac{\rho_j z_j^2 D_j^0}{D_i^0 + D_j^0} \quad (12)$$

and Γ is the MSA screening parameter, calculated in the mean diameter approximation as

$$\Gamma = \frac{\kappa}{2(1 + \Gamma\sigma)} \quad (13)$$

According to eqs 9−13, the relaxation term can be computed if the ion diameters are known. Also, the density of the solution has to be known in order to calculate the number densities of ions.

Hard-Sphere Model. In general, the diffusion coefficient in a hard-sphere system can be expressed as (Dymond, 1985; Czworniak et al., 1975; Ruckenstein and Liu, 1997)

$$D_i^{HS} = D_{i,ENS}A_iC_i(\rho,\bar{M},\bar{\sigma},\bar{x}) \quad (14)$$

where $D_{i,ENS}$ is the diffusion coefficient calculated from the Enskog theory of smooth hard spheres (Chapman and Cowling, 1952), A_i accounts for translation−rotation coupling resulting from deviations of molecular surfaces from sphericity, and $C_i(\rho,\bar{M},\bar{\sigma},\bar{x})$ is an empirical correction factor that compensates for the neglect by the Enskog theory of correlated motions in hard-sphere fluids. In eq 14, ρ is the number density and $\bar{M}$, $\bar{\sigma}$, and $\bar{x}$ are the vectors of molecular weights, diameters, and mole fractions, respectively. To utilize eq 14 for aqueous electrolyte solutions, we note that eq 14 can be constrained to match the diffusion coefficients at infinite dilution. This is advantageous because the infinite-dilution diffusivities are known with sufficient accuracy from experimental sources and do not have to be predicted from the hard-sphere theory. Therefore, we rewrite eq 14 for the diffusion coefficient of species i at infinite dilution:

$$D_i^0 = D_{i,ENS}^0 A_i C_i^0(\rho^0,\bar{M},\bar{\sigma}) \quad (15)$$

There is theoretical and experimental evidence that the parameter A_i is independent of solution composition and density (Czworniak et al., 1975). Therefore, it is the same in eqs 14 and 15 and D_i^{HS} can be expressed as

$$D_i^{HS} = D_i^0 \frac{D_{i,ENS}}{D_{i,ENS}^0}\frac{C(\rho,\bar{M},\bar{\sigma},\bar{x})}{C^0(\rho^0,\bar{M},\bar{\sigma})} \quad (16)$$

To evaluate the ratio $D_{i,ENS}/D_{i,ENS}^0$, we utilize the extension of the Enskog theory to dense fluid hard-sphere mixtures developed by Tham and Gubbins (1971). For the diffusion coefficient of a tracer ion i in a solution containing a cation j, an anion k, and a solvent s, a closed-form expression was given by Tham and Gubbins (1972):

$$D_{i,ENS} = \left[x_j\frac{g_{ij}}{d_{ij}} + x_k\frac{g_{ik}}{d_{ik}} + x_s\frac{g_{is}}{d_{is}}\right]^{-1} \quad (17)$$

where g_{ij} is the radial distribution function at contact for rigid spheres of diameters σ_i and σ_j and d_{ij} is the dilute gas diffusion coefficient for a mixture of molecules i and j. The d_{ij} coefficients in eq 17 are given by

$$d_{ij} = \frac{3}{8\sigma_{ij}^2\rho}\left[\frac{(M_i + M_j)RT}{2\pi M_i M_j}\right]^{1/2} \quad (18)$$

where ρ is the number density and the average diameter σ_{ij} is defined as

$$\sigma_{ij} = (\sigma_i + \sigma_j)/2 \quad (19)$$

The radial distribution function in eq 18 is calculated from the equation of Boublik (1970):

$$g_{ij}(\sigma_{ij}) = \frac{1}{(1 - \zeta_3)} + \frac{3\sigma_i\sigma_j}{(\sigma_i + \sigma_j)}\frac{\zeta_2}{(1 - \zeta_3)^2} +$$
$$2\left(\frac{\sigma_i\sigma_j}{\sigma_i + \sigma_j}\right)^2\frac{\zeta_2^2}{(1 - \zeta_3)^3} \quad (20)$$

where

$$\zeta_l = \frac{\pi}{6}\rho\sum\limits_{k}x_k\sigma_k^l \quad (21)$$

In contrast to the $D_{i,ENS}/D_{i,ENS}^0$ term, no analytical theory is available for the evaluation of the $C_i(\rho,\bar{M},\bar{\sigma},\bar{x})/C_i^0(\rho^0,\bar{M},\bar{\sigma})$ term in eq 16. The correction factor $C_i(\rho,\bar{M},\bar{\sigma},\bar{x})$ may be obtained from molecular dynamics simulations as a function of density for pure fluids (Ruckenstein and Liu, 1997) or two-component mixtures (Czworniak et al., 1975). However, no data are available for systems with more than two components. In the case of aqueous solutions well below the critical point, the number densities ρ and ρ_0 are reasonably close to each other. Since considerable density variations are necessary to cause a significant effect on the correction factors, it may be expected that the factors $C_i(\rho,\bar{M},\bar{\sigma},\bar{x})$ and $C_i^0(\rho^0,\bar{M},\bar{\sigma})$ in eq 16 partially cancel each other. Therefore, we make an assumption that the $C_i(\rho,\bar{M},\bar{\sigma},\bar{x})/C_i^0(\rho^0,\bar{M},\bar{\sigma})$ ratio in eq 16 can be approximated by 1. The error introduced by this assumption cannot be, at

present, reliably estimated. However, the viability of this assumption can be verified by the empirical effectiveness of the final diffusivity model.

Thus, a working equation for the hard-sphere diffusion coefficient in a solution can be obtained from eq 16 by calculating the $D_{i,\text{ENS}}$ and $D_{i,\text{ENS}}^0$ terms from eq 17 applied to the solution and pure solvent, respectively. The result is

$$\frac{D_i^{\text{HS}}}{D_i^0} = \frac{\dfrac{g_{is}^0}{d_{is}^0}}{x_j\dfrac{g_{ij}}{d_{ij}} + x_k\dfrac{g_{ik}}{d_{ik}} + x_s\dfrac{g_{is}}{d_{is}}} \qquad (22)$$

where the superscript 0 denotes pure water at the same conditions of temperature and pressure as the solution.

The final expression for the diffusion coefficient of an ion in a single-electrolyte solution is obtained by substituting eqs 9 and 22 into eq 8. In the case of a neutral species, the relaxation term (eq 9) is equal to zero and the diffusion coefficient expression (eq 8) becomes identical with eq 22.

Effective Ionic Radii. The only species-dependent parameters in the expression for the self-diffusion coefficient (eqs 8, 9, and 22) are the ionic diameters. As a first approximation, crystallographic diameters can be used to estimate the size of ions in the solution. In fact, this approximation is reasonable for relatively dilute solutions (cf. Bernard et al., 1992). However, it becomes less accurate as the concentration increases. Notably, a change in viscosity at higher concentrations entails a changing ionic mobility, which is a manifestation of altered solvation structure and short-range interactions between ions. These effects can be taken into account by assuming an effective ion size, which is a function of a changed ionic environment in a concentrated solution. Therefore, we introduce an effective diameter, which is calculated by averaging over the effects of neighboring species on the central species. Accordingly, the effective diameter of a species i is postulated to be

$$\sigma_i = 2\frac{\sum_j c_j \sigma_{i(j)}}{\sum_j c_j} \qquad (23)$$

where $\sigma_{i(j)}$ accounts for the effect of species j on the effective diameter of species i. The $\sigma_{i(j)}$ parameter has the meaning of a molecular or ionic radius (i.e., half of the diameter). For consistency, $\sigma_{i(i)}$ is equal to the crystallographic radius of species i. Also, the value of $\sigma_{i(s)}$, where s denotes the solvent, can be assumed to be equal to the crystallographic radius of i. In this way, the effective diameter becomes equivalent to the crystallographic one in dilute solutions. It may increasingly deviate from the crystallographic diameter as it becomes more affected by unlike ions in concentrated solutions.

If necessary, the parameters $\sigma_{i(j)}$ may be treated as adjustable quantities that reflect the interactions of species i and j. When it is not necessary to adjust the value of $\sigma_{i(j)}$, it remains at its default crystallographic value.

Concentration Dependence for Multicomponent Systems

The equation for the concentration dependence of self-diffusion coefficients (eq 8) can be applied only to single-solute systems because the MSA expression for the relaxation effect has been developed for systems containing only a single anion and a single cation in the solution. An analytical theory for multicomponent systems can be obtained only for very dilute solutions (Onsager and Kim, 1957). Therefore, it is necessary to develop a technique for predicting the diffusivities of multicomponent solutions in the full concentration range of industrially important systems. Specifically, we are seeking a mixing rule that will make it possible to calculate diffusivities in a multicomponent solution using the diffusivity values obtained from eqs 8, 9, and 22 for constituent single-solute solutions.

For this purpose, we consider general phenomenological equations that relate the fluxes of species in a solution to chemical potential gradients. In the Stefan–Maxwell formalism, these equations are given by

$$-x_i\nabla\mu_i = \frac{RT}{C}\sum_{j=0}^n\left(\frac{x_j J_i - x_i J_j}{a_{ij}}\right) \qquad i = 1, ..., n \quad (24)$$

where C is the total concentration in moles per unit volume and μ_i and J_i are the chemical potential and flux of species i, respectively. Graham and Dranoff (1982) and Pinto and Graham (1986) found that the phenomenological interaction coefficients of eq 24 (i.e., a_{ij}) are only weakly concentration-dependent and are independent of the other species present in the system. Thus, eq 24 provides a suitable starting point for developing a mixing rule.

Equation 24 can be simplified by considering the diffusion of a tracer species i in a mixture containing n species. Since the flux of species other than the tracer is zero, eq 24 becomes

$$J_i = -\frac{c_i}{RT}\frac{1}{\displaystyle\sum_{j=0}^n \frac{x_j}{a_{ij}}}\nabla\mu_i \qquad (25)$$

In the case of tracer diffusion, the chemical potential gradient is

$$\nabla\mu_i = \frac{RT}{c_i}\nabla c_i \qquad (26)$$

By combining eqs 25 and 26 and taking into account that $J_i = -D_i\nabla c_i$, we obtain an expression for the diffusion coefficient, i.e.,

$$D_i = \frac{1}{\displaystyle\sum_{j=0}^n \frac{x_j}{a_{ij}}} \qquad (27)$$

To derive a mixing rule from eq 27, we assume that the mixture contains N_c cations, N_a anions, and N_n neutral species. Then, the self-diffusion coefficient of tracer i can be written as

$$D_i = \frac{n_T}{\dfrac{n_s}{a_{is}} + \sum\limits_{j=1}^{N_c} \dfrac{n_j}{a_{ij}} + \sum\limits_{k=1}^{N_a} \dfrac{n_k}{a_{ik}} + \sum\limits_{l=1}^{N_n} \dfrac{n_l}{a_{il}}} \quad (28)$$

where the mole fractions from eq 27 have been replaced by mole numbers. In eq 28, n_T is the total number of moles of all components and the subscript s denotes the solvent. Without any loss of generality, the cations and anions can be formally separated into $N_c N_a$ neutral solutes containing only one cation and one anion. Then, the material balances for the jth cation and the kth anion can be written as

$$n_j = \sum_{d=1}^{N_c N_a} n_d \nu_{j(d)} \quad j = 1, ..., N_c \quad (29)$$

$$n_k = \sum_{d=1}^{N_c N_a} n_d \nu_{k(d)} \quad k = 1, ..., N_c \quad (30)$$

where the subscript d denotes the dth solute and $\nu_{j(d)}$ and $\nu_{k(d)}$ are the stoichiometric numbers of cation j in solute d and anion k in solute d, respectively. Similarly, the total number of moles of the solvent can be divided between the solutes, including the neutral species dissolved in the system:

$$n_s = \sum_{d=1}^{N_c N_a} n_{s(d)} + \sum_{l=1}^{N_n} n_{s(l)} \quad (31)$$

Thus, each of the $N_c N_a$ solutes can be envisaged, in a thought experiment, to form a solution with $n_{s(d)}$ moles of the solvent. The diffusion coefficient of tracer i in a hypothetical solution containing only solute d and $n_{s(d)}$ moles of the solvent is

$$D_{i(d)} = \frac{n_{s(d)} + n_{+(d)} + n_{-(d)}}{\dfrac{n_{s(d)}}{a_{is}} + \dfrac{n_{+(d)}}{a_{i+}} + \dfrac{n_{-(d)}}{a_{i-}}} \quad (32)$$

where $n_{+(d)}$ and $n_{-(d)}$ are the numbers of moles of the cation and anion in the solution that contain the solute d. The quantities $n_{+(d)}$ and $n_{-(d)}$ are related to the number of moles of solute d by

$$n_{+(d)} = n_d \nu_{+(d)} \quad (33)$$

and

$$n_{-(d)} = n_d \nu_{-(d)} \quad (34)$$

where $\nu_{+(d)}$ and $\nu_{-(d)}$ are the stoichiometric numbers of the cation and anion in solute d, respectively. Similarly to eq 32, we envisage a hypothetical single-solute solution containing only the neutral species l. The diffusion coefficient of tracer i in this solution is

$$D_{i(l)} = \frac{n_{s(l)} + n_l}{\dfrac{n_{s(l)}}{a_{is}} + \dfrac{n_l}{a_{il}}} \quad (35)$$

Equations 32 and 35 can be rearranged to express the coefficient D_i in a multicomponent mixture in terms of the coefficients $D_{i(d)}$ and $D_{i(l)}$. For this purpose, we calculate a sum of the denominators of eqs 32 and 35 for all $N_c N_a$ ionic solutes and N_n neutral species, i.e.,

$$SUM = \sum_{d=1}^{N_c N_a} \left(\frac{n_{s(d)}}{a_{is}} + \frac{n_{+(d)}}{a_{i+}} + \frac{n_{-(d)}}{a_{i-}} \right) + \sum_{l=1}^{N_n} \left(\frac{n_{s(l)}}{a_{is}} + \frac{n_l}{a_{il}} \right) =$$
$$\left[\sum_{d=1}^{N_c N_a} \frac{n_{s(d)}}{a_{is}} + \sum_{l=1}^{N_n} \frac{n_{s(l)}}{a_{is}} \right] + \left[\sum_{d=1}^{N_c N_a} \frac{n_{+(d)}}{a_{i+}} \right] + \left[\sum_{d=1}^{N_c N_a} \frac{n_{-(d)}}{a_{i-}} \right] + \left[\sum_{l=1}^{N_n} \frac{n_l}{a_{il}} \right] \quad (36)$$

The terms in the first set of square brackets can be simplified to n_s/a_{is} using eq 31. To evaluate the term in the second set of square brackets, we note that the subscript $(+)$ indicates any cation, which is equivalent to taking a sum over all cations, i.e.,

$$\sum_{d=1}^{N_c N_a} \frac{n_{+(d)}}{a_{i+}} = \sum_{d=1}^{N_c N_a} \frac{n_d \nu_{+(d)}}{a_{i+}} = \sum_{j=1}^{N_c} \left(\sum_{d=1}^{N_c N_a} \frac{n_d \nu_{j(d)}}{a_{ij}} \right) = \sum_{j=1}^{N_c} \frac{n_j}{a_{ij}} \quad (37)$$

The last equality in eq 37 was obtained using eq 29. Also, a relationship similar to eq 37 holds for anions (i.e., for the term in the third set of square brackets in eq 36). Therefore, eq 36 becomes

$$SUM = \frac{n_s}{a_{is}} + \sum_{j=1}^{N_c} \frac{n_j}{a_{ij}} + \sum_{k=1}^{N_a} \frac{n_k}{a_{ik}} + \sum_{l=1}^{N_n} \frac{n_l}{a_{il}} \quad (38)$$

which is identical with the denominator of eq 28. From eqs 28, 32, and 35, the quantity SUM is equal to

$$SUM = \frac{n_T}{D_i} = \sum_{d=1}^{N_c N_a} \frac{n_{s(d)} + n_{+(d)} + n_{-(d)}}{D_{i(d)}} + \sum_{l=1}^{N_n} \frac{n_{s(l)} + n_l}{D_{i(l)}} \quad (39)$$

Thus, we obtain the mixing rule for the diffusion coefficient in a multicomponent solution:

$$D_i = \frac{n_T}{\sum\limits_{d=1}^{N_c N_a} \dfrac{n_{s(d)} + n_{+(d)} + n_{-(d)}}{D_{i(d)}} + \sum\limits_{l=1}^{N_n} \dfrac{n_{s(l)} + n_l}{D_{i(l)}}} \quad (40)$$

The coefficients $D_{i(d)}$ and $D_{i(l)}$ in eq 40 can be computed from eqs 8, 9, and 22 at the same total number density as that of the multicomponent mixture. In practical calculations, the total number of moles (n_T) can be assumed to correspond to, e.g., 1 kg of solvent.

Equation 40 gives a formula for the computation of the self-diffusion coefficient in a multicomponent mixture that has been obtained by combining a number of single-solute solutions. However, it does not specify how the multicomponent solution of interest should be subdivided into hypothetical single-solute solutions. For this purpose, arbitrary assumptions have to be made. To define the quantities $n_{+(d)}$ and $n_{-(d)}$, it is reasonable to postulate that the amounts of the cation and anion in the hypothetical single-solute solution should be proportional to the concentrations of the cation and anion in the multicomponent solution. Furthermore, the hypothetical single-solute solution should be electroneutral. These conditions are satisfied when the numbers of moles of the cation and anion in the solute d are calculated as

$$n_{+(d)} = n_+ \frac{|z_-|n_-}{n_{eq}} \qquad (41)$$

$$n_{-(d)} = n_- \frac{|z_+|n_+}{n_{eq}} \qquad (42)$$

where n_{eq} is the equivalent number of moles, i.e.,

$$n_{eq} = \sum_{j=1}^{N_c} n_j |z_j| = \sum_{k=1}^{N_a} n_k |z_k| \qquad (43)$$

Finally, the number of moles of the solvent in the single-solute system is selected so that the ionic strength of the single-solute system is the same as that of the multicomponent system, i.e.,

$$n_{s(d)} = \frac{\frac{1}{2}(n_{+(d)} z_+^{\,2} + n_{-(d)} z_-^{\,2})}{V I_T} n_s \qquad (44)$$

$$n_{s(l)} = \frac{n_l}{I_T V} n_s \qquad (45)$$

where I_T is a concentration measure that generalizes the ionic strength by including the concentrations of neutral solutes, i.e.,

$$I_T = \frac{1}{2} \sum_{i=1}^{N_c+N_a} c_i z_i^2 + \sum_{l=1}^{N_n} c_l \qquad (46)$$

In contrast to eq 40, which has been derived from the phenomenological formalism of transport phenomena, eqs 41–46 are empirical and can be validated on the basis of their effectiveness for reproducing experimental data.

The final self-diffusivity model consists of eqs 8, 9, and 22 for single-solute systems and the mixing rule for multicomponent solutions (eq 40) coupled with the auxiliary relationships (41)–(46).

Results and Discussion

The performance of the self-diffusion model has been tested for a large number of single-solute and multi-component systems. First, calculations have been performed for single-solute systems with simple speciation, i.e., electrolytes that show complete dissociation and do not form complexes. For such systems, the calculations involve the use of eqs 8, 9, and 22 without invoking the mixing rule for multicomponent systems. Figures 3 and 4 show the diffusivities of aqueous species in LiCl and CaCl$_2$ solutions, respectively. In the case of these salts, relatively abundant experimental data are available over wide concentration ranges for all solution species, i.e., the cation, anion, and water. The concentration scale in Figures 3 and 4 is shown as the square root of molality to facilitate the comparison with experimental data in dilute solutions. The limiting diffusivities of ions have been calculated from eqs 1 and 2 using the A and B parameters obtained by Anderko and Lencka (1997). For water, the limiting diffusivities have been obtained from eq 3 with the parameters given in Table 1.

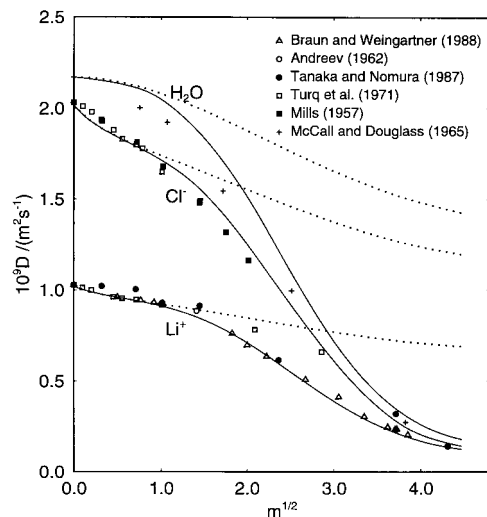The dotted lines in Figures 3 and 4 show the results obtained using only crystallographic diameters. The

Figure 3. Self-diffusion coefficients of Li$^+$ and Cl$^-$ at 298.15 K and of H$_2$O at 296.15 K in the LiCl + H$_2$O system. The solid lines have been obtained from the model using the parameters from Table 2. The dotted lines have been obtained using crystallographic ion radii for all species. The symbols denote experimental data from various authors cited by Mills and Lobo (1989), pp 97–110.
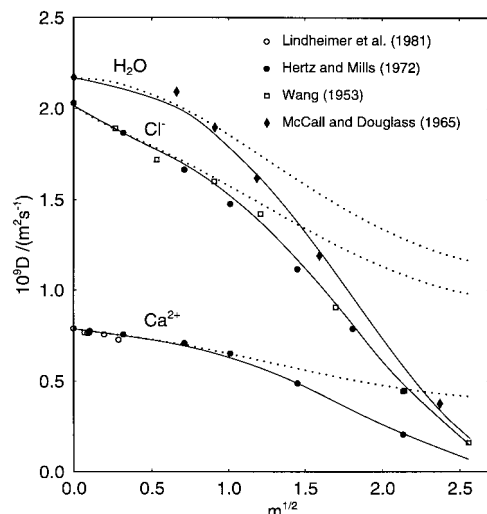

Figure 4. Self-diffusion coefficients of Ca^{2+} and Cl$^-$ at 298.15 K and of H$_2$O at 296.15 K in the CaCl$_2$ + H$_2$O system. The solid lines have been obtained from the model using the parameters from Table 2. The dotted lines have been obtained using crystallographic ion radii for all species. The symbols denote experimental data from various authors cited by Mills and Lobo (1989), pp 49–51.

values of crystallographic diameters were taken from Marcus (1985). As expected, a reasonable agreement with experimental data has been obtained only for relatively dilute solutions, i.e., for concentrations below 1 M. At higher concentrations, the model with crystallographic parameters fails to reproduce the experimentally observed rapid decrease of diffusivities with concentration. On the other hand, the model with effective ionic diameters (eq 23) reproduces the data with very good accuracy. This is shown by the solid lines in Figures 3 and 4. To reproduce the data, two empirical $\sigma_{i(j)}$ parameters (cf. eq 23) have been adjusted. These parameters represent the effects of the anion on the effective diameter of the cation (e.g., $\sigma_{Ca(Cl)}$) and vice versa (e.g., $\sigma_{Cl(Ca)}$). The parameters that are necessary for the computation of the effective diameters are collected in Table 2. All remaining $\sigma_{i(j)}$ parameters that

Table 2. Parameters $\sigma_{i(j)}$ (in Å) Used for the Computation of Effective Diameters of Species According to Equation 23

species i	species j	$\sigma_{i(j)}$
Ca^{2+}	Cl^-	3.121
Cl^-	Ca^{2+}	6.770
Li^+	Cl^-	0.001
Cl^-	Li^+	$7.646 \exp(-0.0464I)^a$
Na^+	Cl^-	0.001
Cl^-	Na^+	5.012
Mg^{2+}	Cl^-	0.292
Cl^-	Mg^{2+}	$18.813 \exp(-0.0635I)^a$
Na^+	I^-	7.367
I^-	Na^+	2.930
$CdCl^+$	H_2O	2.097
$CdCl_2^0$	H_2O	2.462
$CdCl_4^{2-}$	H_2O	3.989
CdI^+	H_2O	0.001
CdI_2^0	H_2O	0.001
CdI_3^-	H_2O	0.001
CdI_4^{2-}	H_2O	4.698
H^+	I^-	0.001
I^-	H^+	3.911
K^+	OH^-	$15.9187 \exp(-0.0958I)^a$

^{a} The ionic strength is defined as $I = (\Sigma z_i^2 c_i)/2$, where c_i is in mol/dm^3.

are needed to apply eq 23, but are not listed in Table 2, have been assumed to be equal to the crystallographic radii (e.g., those for water). Thus, only a small number of adjustable parameters is necessary to reproduce the data within essentially experimental uncertainty (as evidenced by the scattering of data from different authors in Figures 3 and 4). The adjusted $\sigma_{i(j)}$ parameters are usually independent of temperature and concentration. However, for a small number of systems for which experimental data are available over wide concentration ranges, selected $\sigma_{i(j)}$ parameters have been found to depend on the ionic strength (cf. Table 2). In such cases, a two-constant exponential function of ionic strength is used for calculating $\sigma_{i(j)}$ (cf. Table 2). For example, the $\sigma_{Cl(Li)}$ parameter depends on the ionic strength, whereas the $\sigma_{Li(Cl)}$ parameter does not. Thus, a total of three adjustable constants is necessary to reproduce the self-diffusivities of all solution species in the LiCl + H$_2$O systems over the whole concentration and temperature range of experimental data. For the CaCl$_2$ + H$_2$O system, a total of two constants is needed.

It is noteworthy that the model uses the same parameters to reproduce the concentration dependence of self-diffusion coefficients of all solution species. This indicates that the model is internally consistent. Thus, it can be used to predict the diffusivities of all species in a solution when experimental data are available for only one species.

After verifying the performance of the model for single-solute systems, calculations have been performed for mixed systems that do not show any complexation. Such calculations verify the mixing rule for multicomponent systems (eq 40). Figure 5 shows the results for the self-diffusion coefficients of H$_2$O and Na$^+$ in the NaCl + MgCl$_2$ + H$_2$O system. For this system, the $\sigma_{Na(Cl)}$ and $\sigma_{Cl(Na)}$ parameters were regressed from experimental data for the NaCl + H$_2$O system and the $\sigma_{Mg(Cl)}$ and $\sigma_{Cl(Mg)}$ parameters were obtained from data for the MgCl$_2$ + H$_2$O system. The dashed lines in Figure 5 show the diffusivities in the single-solute solutions containing NaCl and MgCl$_2$. The solid lines show the predicted diffusivities in a mixed solution with a 1:1 ratio of NaCl to MgCl$_2$. As shown in Figure 5, the
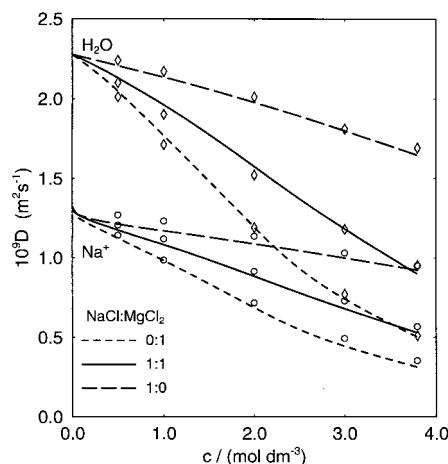

Figure 5. Self-diffusion coefficients of Na$^+$ and H$_2$O at 298.15 K in the NaCl + MgCl$_2$ + H$_2$O system. The lines have been obtained for various NaCl/MgCl$_2$ ratios using the parameters from Table 2. The hollow circles and diamonds denote the experimental data of Mills et al. for Na$^+$ and Cl$^-$, respectively. The data were taken from the compilation of Mills and Lobo (1989), pp 266−267.
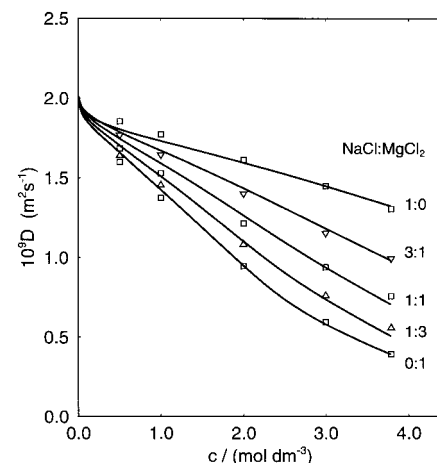

Figure 6. Self-diffusion coefficients of Cl$^-$ at 298.15 K in the NaCl + MgCl$_2$ + H$_2$O system. The lines have been obtained for various NaCl/MgCl$_2$ ratios using the parameters from Table 2. The symbols denote the experimental data of Mills et al. (taken from the compilation of Mills and Lobo, 1989, p 265).

diffusivities in the mixed solution are represented with the same accuracy as those in the single-solute solutions. It should be noted that no parameters were adjusted to match the mixed-solution data. Also, Figures 6 and 7 show the predicted diffusion coefficients of Cl$^-$ and Ca^{2+} in the same system, respectively. In this case, the results are shown for several NaCl/MgCl$_2$ molar ratios.

The results shown in Figures 5−7 demonstrate that the mixing rule (eq 40) is sufficiently accurate to predict the diffusivities in mixed-electrolyte solutions. Consistent results are obtained for all species in the solution.

For practical applications, it is particularly important to calculate the diffusivities of species in systems containing transition metals, which show appreciable complexation. For systems with aqueous complexes, the measured diffusion coefficients should usually be regarded as weighted averages of diffusion coefficients for individual (simple and complexed) species. For example, the self-diffusion coefficient of Cd in an aqueous CdCl$_2$ solution is an aggregate quantity that includes the self-diffusivities of Cd^{2+}, CdCl$^+$, CdCl$_2^0$, CdCl$_3^-$, and
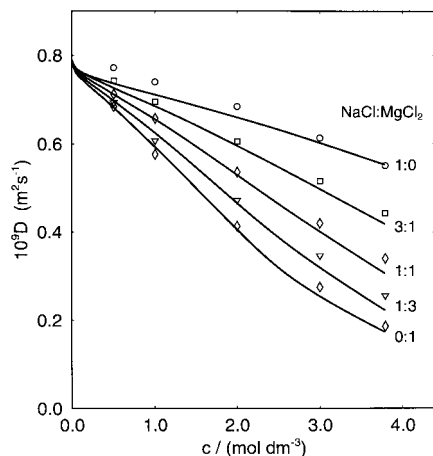
Figure 7. Self-diffusion coefficients of Ca^{2+} at 298.15 K in the $NaCl + MgCl_2 + H_2O$ system. The lines have been obtained for various $NaCl/MgCl_2$ ratios using the parameters from Table 2. The symbols denote the experimental data of Mills et al. (taken from the compilation of Mills and Lobo, 1989, p 264).

$CdCl_4{}^{2-}$. At the same time, the measured diffusivity of Cl includes the diffusivities of Cl^-, $CdCl^+$, $CdCl_2{}^0$, $CdCl_3{}^-$, and $CdCl_4{}^{2-}$. Although the diffusion coefficients of individual complexes are not measurable, they can be predicted using the proposed model. Therefore, it is necessary to express the aggregate (measurable) diffusion coefficients in terms of the diffusivities of individual species.

Dunn and Stokes (1965) derived a formula that relates the diffusion coefficient of a carboxylic acid to those of the acid monomer and dimer. Here, we generalize this formula to systems with any number of complex species. Let us denote the diffusing species by X. We assume that it can form a number of complexes with a general formula Q_iX_i where Q_i denotes any species or groups that are connected with i ions of X. The total (measurable) flux of X is related to the fluxes of individual complexes by

$$J_{X_T} = \sum_i i J_{Q_iX_i} \tag{47}$$

where the subscript T denotes the total flux of X. By inserting the Fick's law expressions into eq 47, we obtain

$$D_{X_T} \frac{\partial c_{X_T}}{\partial z} = \sum_i i D_{Q_iX_i} \frac{\partial c_{Q_iX_i}}{\partial z} \tag{48}$$

Thus, the aggregate diffusion coefficient of X becomes

$$D_{X_T} = \sum_i i D_{Q_iX_i} \frac{\partial c_{Q_iX_i}}{\partial c_{X_T}} \tag{49}$$

The derivative in eq 49 can be computed using a thermodynamic speciation model. In this study, we use the model developed by OLI Systems (Zemaitis et al., 1986; Rafal et al., 1995).

Figure 8 shows the aggregate self-diffusion coefficients for Cd and Cl in addition to the coefficient for H_2O in the $CdCl_2 + H_2O$ system. The dotted lines have been obtained by using crystallographic radii for solution species. In the case of complexes, the radii have been estimated by assuming that the volumes of the
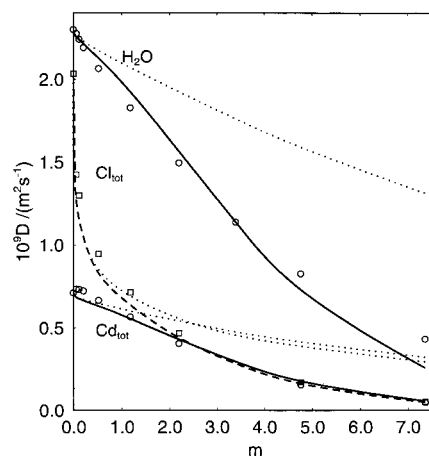

Figure 8. Aggregate self-diffusion coefficients for cadmium- and chloride-containing species (denoted by Cd_{TOT} and Cl_{TOT}, respectively) and H_2O in the system $CdCl_2 + H_2O$. The solid lines have been obtained from the model using the parameters from Table 2. The dotted lines have been obtained using crystallographic ion radii for all species. The symbols denote the experimental data of Mills and Hertz (taken from Mills and Lobo, 1989, pp 42−43).
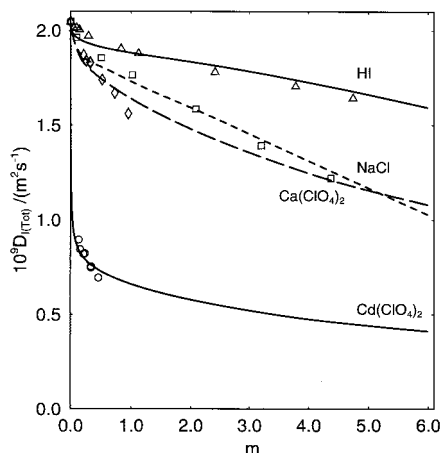

Figure 9. Aggregate self-diffusion coefficients for iodide-containing species in aqueous solutions of HI, NaCl, $Ca(ClO_4)_2$, and $Cd(ClO_4)_2$. The lines have been obtained from the model using the parameters from Table 2. Experimental data for the $Ca(ClO_4)_2$ and $Cd(ClO_4)_2$ solutions were taken from Turner and Matheson (cited in Mills and Lobo, 1989, pp 55 and 47, respectively), those for HI are from Mills and Kennedy (cited in Mills and Lobo, 1989, p 84), and those for NaCl are from Stokes et al. (cited in Mills and Lobo, 1989, p 209).

complexes are equal to the sum of the volumes of the constituent simple ions. As with uncomplexed solutes, the predictions with crystallographic radii provide reasonable estimates of diffusivities at relatively low concentrations. The solid and dashed lines in Figure 8 have been obtained by adjusting the parameters $\sigma_{CdCl^+(H_2O)}$, $\sigma_{CdCl_2{}^0(H_2O)}$, and $\sigma_{CdCl_4{}^{2-}(H_2O)}$. These parameters are listed in Table 2. As shown in Figure 8, the solid and dashed lines reproduce the experimental diffusivities with good accuracy. The effects of complexation manifest themselves in a steep decrease of the Cl diffusivity with concentration. Also, the aggregate diffusivities of both Cd and Cl tend to very low values at high concentrations.

Figure 9 shows the effects of both weak and strong complexation on the aggregate diffusivity of iodide ions in several aqueous solutions. In the case of the HI solution, the self-diffusivity of iodide ions moderately decreases with concentration. In the case of NaCl, a
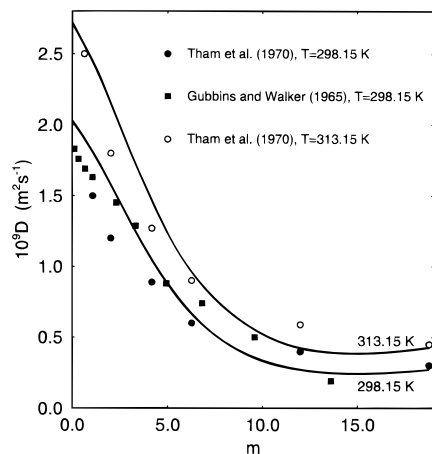
Figure 10. Diffusion coefficients of oxygen in KOH solution as a function of KOH molality. The lines have been obtained from the model using the parameters from Table 2.

weak complex NaI_{aq}^0 is formed and somewhat reduces the diffusivity at higher concentrations. In the Ca-$(ClO_4)_2$ solution, the initial decrease of D_T with concentration is stronger than that in the case of NaCl because the relaxation effect in 2:1 electrolytes (cf. eq 9) is stronger than that in 1:1 electrolytes. Finally, D_T in the $Cd(ClO_4)_2$ solution decreases very rapidly at low concentrations because of strong complexation between Cd and I. It should be noted that the experimental data for the diffusion of iodides in NaCl, $Ca(ClO_4)_2$, and Cd-$(ClO_4)_2$ were not used to adjust any model parameters. Only self-diffusion data in single-solute systems were used to determine the $\sigma_{i(j)}$ parameters that are collected in Table 2.

The proposed model is also applicable to the diffusion of neutral molecules (e.g., gases) in electrolyte solutions. To verify this, calculations have been performed for the diffusion of oxygen in KOH solutions. The results are shown in Figure 10 for two temperatures. The experimental data in Figure 10 show a significant degree of scattering, which is common for gas diffusivities. The calculated diffusivities agree with the data within experimental uncertainty.

Conclusions

The proposed model accurately reproduces self-diffusion coefficients of both ions and neutral species in multicomponent aqueous solutions over wide concentration ranges. This is made possible by four important features of the model, i.e., (1) a combination of the MSA theory of the relaxation effect in electrolyte solutions with the hard-sphere model of diffusion; (2) extension of the applicability of the model to very concentrated solutions through the introduction of effective diameters of species; (3) a mixing rule for predicting self-diffusion coefficients in multicomponent solutions using the coefficients calculated for single-solute systems; and (4) integration of the diffusivity model with a thermodynamic speciation model, which makes it possible to reproduce the effects of complexation or other reactions in solution.

The model is applicable for molalities up to ca. 30 mol/kg of H_2O. Although there are practically no self-diffusion data for concentrated solutions at high temperatures (above ca. 373 K), it can be expected that the model will provide reasonable estimates at higher temperatures because the limiting diffusivities can be predicted up to ca. 550 K and the effective ionic diameters have been found to be independent of temperature.

The primary practical applications of self-diffusion coefficients are in the area of electrochemical processes that involve the transport of electroactive species to an electrode surface through a diffusion layer. As discussed by Tyrrell and Harris (1984, and references therein), the diffusivities measured using electrochemical techniques are primarily intradiffusion coefficients. However, there are numerous applications that require the use of mutual diffusivities rather than self-diffusion (or intradiffusion) coefficients. Therefore, there is a need to develop a model that would reproduce mutual diffusivities over the same range of concentrations and temperatures that were considered here for self-diffusivities. The development of such a model will be the subject of a forthcoming study.

Literature Cited

Akgerman, A.; Gainer, J. L. Predicting Gas–Liquid Diffusivities. *J. Chem. Eng. Data* **1972**, *17*, 372.

Anderko, A.; Lencka, M. M. Computation of Electrical Conductivity of Multicomponent Aqueous Systems in Wide Concentration and Temperature Ranges. *Ind. Eng. Chem. Res.* **1997**, *36*, 1932.

Bernard, O.; Kunz, W.; Turq, P.; Blum, L. Self-Diffusion in Electrolyte Solutions Using the Mean Spherical Approximation. *J. Phys. Chem.* **1992**, *96*, 398.

Boublik, T. Hard Sphere Equation of State. *J. Chem. Phys.* **1970**, *53*, 471.

Chapman, S.; Cowling, T. G. *The Mathematical Theory of Non-Uniform Gases*; Cambridge University Press: Cambridge, U.K., 1952.

Chhih, A.; Turq, P.; Bernard, O.; Barthel, J. M.G.; Blum, L. Transport Coefficients and Apparent Charges of Concentrated Electrolyte Solutions—Equations for Practical Use. *Ber. Bunsen-Ges. Phys. Chem.* **1994**, *98*, 1516.

Cullen, E. J.; Davidson, J. F. The Determination of Diffusion Coefficients for Sparingly Soluble Gases in Liquids. *Trans. Inst. Chem. Eng.* (*London*) **1957**, *35*, 51.

Czworniak, K. J.; Andersen, H. C.; Pecora, R. Light Scattering Measurements and Theoretical Interpretation of Mutual Diffusion Coefficients in Binary Liquid Mixtures. *Chem. Phys.* **1975**, *11*, 451.

de Blok; W. J.; Fortuin, J. M. H. Method for Determining Diffusion Coefficients of Slightly Soluble Gases in Liquids. *Chem. Eng. Sci.* **1981**, *36*, 1687.

Debye, P.; Hückel, E. Theory of Electrolytes. I. Lowering of Freezing Point and Related Phenomena. *Phys. Z.* **1924**, *24*, 185.

Dunn, L. A.; Stokes, R. H. The Diffusion of Monocarboxylic Acids in Aqueous Solution at 25 °C. *Aus. J. Chem.* **1965**, *18*, 285.

Dymond, J. H. Hard-sphere Theories of Transport Properties. *Chem. Soc. Rev.* **1985**, *14*, 317.

Ferrell, R. T.; Himmelblau, D. M. Diffusion Coefficients of Nitrogen and Oxygen in Water. *J. Chem. Eng. Data* **1967**, *12*, 111.

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

Gubbins, K. E.; Bhatia, K. K.; Walker, R. D. Diffusion of Gases in Electrolytic Solutions. *AIChE J.* **1966**, *12*, 548.

Himmelblau, D. M. Diffusion of Dissolved Gases in Liquids. *Chem. Rev.* **1964**, *64*, 527.

Horvath, A. L. *Handbook of Aqueous Electrolyte Solutions*; Ellis Horwood: Chichester, U.K., 1985.

Landolt–Börnstein Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik. 5 Teil: Transportphänomene I; Springer-Verlag: Weinheim, Germany, 1969.

Marcus, Y. *Ion Solvation*; Wiley: New York, 1985.

Mills, R.; Lobo, V. M. M. *Self-Diffusion in Electrolyte Solutions*; Elsevier: Amsterdam, The Netherlands, 1989.

Onsager, L.; Fuoss, R. M. Irreversible Processes in Electrolytes. Diffusion, Conductance and Viscous Flow in Arbitrary Mixtures of Strong Electrolytes. *J. Phys. Chem.* **1932**, *36*, 2689.

Onsager, L.; Kim, S. K. The Relaxation Effect in Mixed Electrolytes. *J. Phys. Chem.* **1957**, *61*, 215.

Pinto, N. deG.; Graham, E. E. Evaluation of Diffusivities in Electrolyte Solutions Using Stefan−Maxwell Equations. *AIChE J.* **1986**, *32*, 291.

Pitzer, K. S. Electrolytes: From Dilute Solutions to Fused Salts. *J. Am. Chem. Soc.* **1980**, *102*, 2902.

Pitzer, K. S.; Simonson, J. M. Thermodynamics of Multicomponent, Miscible, Ionic Systems: Theory and Equations. *J. Phys. Chem.* **1986**, *90*, 3005.

Rafal, M.; Berthold, J. W.; Scrivner, N. C.; Grise, S. L. Models for Electrolyte Solutions. In *Models for Thermodynamic and Phase Equilibria Calculations*; Sandler, S. I., Ed.; Dekker: New York, 1995; Chapter 7, p 601.

Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*; Butterworth: London, 1959.

Ruckenstein, E.; Liu, H. Self-Diffusion in Gases and Liquids. *Ind. Eng. Chem. Res.* **1997**, *36*, 3927.

Smolyakov, B. S. Limiting Equivalent Conductivities of Ions in Water Between 25 °C and 200 °C. *VINITI* **1969**, No. 776-69 (also cited in Horvath, 1985).

Tham, M. K.; Gubbins, K. E. Kinetic Theory of Multicomponent Dense Fluid Mixtures of Rigid Spheres. *J. Chem. Phys.* **1971**, *55*, 268.

Tham, M. K.; Gubbins, K. E. Effect of Salts on the Diffusion of Dissolved Nonelectrolytes. *J. Chem. Soc., Faraday Trans. 1* **1972**, *68*, 1339.

Tham, M. K.; Walker, R. D.; Gubbins, K. E. Diffusion of Oxygen and Hydrogen in Aqueous Potassium Hydroxide Solutions. *J. Phys. Chem.* **1970**, *74*, 1747.

Tyrrell, H. J. V.; Harris, K. R. *Diffusion in Liquids*; Butterworth: London, 1984.

Uematsu, M.; Franck, E. U. Static Dielectric Constant of Water and Steam. *J. Phys. Chem. Ref. Data* **1980**, *9*, 1291.

Unsworth, J.; Gillespie, F. C. Diffusion Coefficients of Xenon and Krypton in Water from 0 °C to 80 °C and in Biological Tissues at 37 °C. In *Diffusion Processes, Proceedings of the Thomas Graham Memorial Symposium;* Gordon and Breach: London, 1969; Vol. 2, p 599.

van Beijeren, H.; Ernst, M. H. The Modified Enskog Equation for Mixtures. *Physica* **1973**, *70*, 225.

Verhallen, P. T. H. M.; Oomen, L. J. P.; v.d. Elden, A. J. J. M.; Kruger, A. J. The Diffusion Coefficients of Helium, Hydrogen, Oxygen and Nitrogen in Water Determined from the Permeability of a Stagnant Liquid Layer in the Quasi-Steady State. *Chem. Eng. Sci.* **1984**, *39*, 1535.

Watson, J. T. R.; Basu, R. S.; Sengers, J. V. An Improved Representative Equation for the Dynamic Viscosity of Water Substance. *J. Phys. Chem. Ref. Data* **1980**, *9*, 1255.

Wise, D. L.; Houghton, G. The Diffusion Coefficients of Ten Slightly Soluble Gases in Water at 10−60 °C. *Chem. Eng. Sci.* **1966**, *21*, 999.

Zemaitis, J. F., Jr.; Clark, D. M.; Rafal, M.; Scrivner, N. C. *Handbook of Aqueous Electrolyte Thermodynamics*; AIChE: New York, 1986.