Modeling Self-Diffusion in Mixed-Solvent Electrolyte Solutions

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A comprehensive model has been developed for calculating self-diffusion coefficients in mixed-solvent electrolyte solutions. The model includes methods for calculating the self-diffusion coefficients of ions and neutral species at infinite dilution and for predicting the effect of finite concentrations of electrolytes. For limiting diffusivities, a mixing rule has been developed for predicting the diffusivity in multicomponent mixed solvents using the limiting diffusivities or ion conductivities in pure solvents. The effect of finite concentrations of electrolytes is modeled by combining the contributions of long-range (Coulombic) and short-range interactions. The long-range interaction contribution is obtained from the mean spherical approximation theory of the relaxation effect, while the short-range interactions are represented using the hard-sphere model of diffusion. Aqueous species are characterized by effective species diameters, which are defined to reflect the interactions between the components of the solution. The model has been integrated with a thermodynamic speciation model, which makes it possible to take into account the effects of complexation or other reactions in the solution. The model accurately reproduces experimental self-diffusion coefficients of ions and neutral molecules in mixed solvents over wide ranges of concentrations.

Introduction

Thermodynamic and transport properties of electrolyte solutions are necessary for the design and optimization of various industrial processes, especially those involving electrochemical systems. While extensive efforts have been devoted to the development of models for predicting equilibrium properties of electrolyte solutions, much less attention has been focused on engineering-oriented models for transport properties in such systems. In particular, no attempt has been made to develop comprehensive transport property models for mixed-solvent electrolyte systems.

Traditionally, theoretical models of transport properties of electrolyte solutions have been focused on the limiting diffusivity or conductivity as a function of ion properties[1−3] and on the composition dependence of these properties in dilute solutions. In particular, limiting laws for transport properties were developed on the basis of the Debye−Huckel theory.[4,5] These laws reflect the presence of electrostatic (i.e., relaxation and electrophoretic) effects in electrolyte solutions. More recently, the limiting laws were extended to more concentrated solutions (up to ca. 1 mol/dm^3) by using the mean spherical approximation (MSA) theory.[6]

In addition to the electrostatic effects, transport properties are affected by interparticle short-range forces. It is necessary to recognize the effect of short-range forces for modeling the properties of electrolyte solutions over wide ranges of concentrations. The short-range effects can be adequately accounted for by the hard-sphere theory, which was originally developed for nonelectrolyte solutions.[7,8] In particular, Tham and Gubbins[9] utilized the hard-sphere theory for modeling self-diffusion of nonelectrolytes in aqueous electrolyte solutions. More recently, Anderko and Lencka[10] developed a comprehensive self-diffusion model by combining the MSA transport theory with the hard-sphere theory. The model of Anderko and Lencka[10] is applicable to both ionic and molecular species (such as associated ion pairs, dissolved gases, or solvent molecules) in aqueous electrolyte solutions over wide concentration ranges.

The objective of this work is to develop a comprehensive, engineering-oriented self-diffusivity model for mixed-solvent electrolyte solutions. The term "self-diffusion" is defined here according to Mill and Lobo[11] to cover diffusion in a pure liquid, tracer diffusion and intradiffusion in electrolyte solutions. In contrast to aqueous electrolyte solutions, the self-diffusion coefficient in mixed-solvent systems not only is a function of temperature and salt concentration but also varies with the composition of the solvent. The model will be compared with self-diffusion data that have been reported in the literature for numerous organic solvents, solvent mixtures, and mixed-solvent electrolyte solutions. The available data include limiting self-diffusion coefficients of ionic and molecular species in pure or mixed solvents and self-diffusion coefficients at finite electrolyte concentrations in mixed solvents.

The model is designed to be applicable to mixed-solvent electrolyte solutions over wide ranges of solvent composition and electrolyte concentration (i.e., from infinitely dilute to concentrated salt solutions). Further, the model is designed to predict the self-diffusivity of all species in multisolvent, multisolute solutions using information obtained from data for single-solute, single-solvent systems. Also, the model accounts for speciation effects, such as complexation or ion association, when combined with a speciation-based thermodynamic model. The model consists of two parts: (1) computation of limiting diffusion coefficients of ionic or molecular species in pure and mixed solvents as a function of temperature and solvent composition and (2) computation of the dependence of the self-diffusion coefficients on electrolyte concentration.

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Limiting Self-Diffusion Coefficients

Limiting diffusivities of ions have been reported in various pure solvents and in mixed-solvent systems as a function of the solvent composition. In general, diffusivity data in organic solvents are relatively few compared to those in aqueous solutions, and the majority of the available data are reported at 25 °C or over a narrow temperature range.

Limiting Diffusivity in Pure Solvents. Marcus[12] collected the transport properties of ions including the conductivity or self-diffusivity at infinite dilution in water and in a number of pure organic solvents at 25 °C. Also, Krumgalz[13] compiled limiting diffusivity data at varying temperatures for 14 ions in several organic solvents. In the case of ions, the limiting self-diffusion coefficient in a solvent s, $D_i^{0,s}$, is related to the limiting equivalent conductance, $\lambda_i^{0,s}$, by the Nernst–Einstein equation:

$$D_i^{0,s} = \frac{RT}{z_i F^2}\lambda_i^{0,s} \tag{1}$$

where R, F, and z are the ideal gas constant, Faraday constant, and ionic charge, respectively. Molecular models[1–3] have been developed to account for the temperature and pressure dependence of limiting ionic conductivity. Although these models give good results in representing limiting ion transport properties for selected electrolyte systems over a relatively wide temperature range, they require information on solvent dynamics and the dynamic structure factor of the ion, which is usually not available. In addition, these models can be applied only to aqueous solutions, whose properties are well-known compared to solutions in other solvents.

On the other hand, empirical models have shown to be success in representing the limiting ion conductivity without using any structural information for the solvent.[14–16] These empirical approaches estimate the limiting transport properties as a function of temperature and pressure on the basis of simple correlations with known properties such as the standard partial molar entropy of ions,[16] viscosity of the solvent,[14] and structural entropy of the ion.[15] In the case of aqueous solutions, Anderko and Lencka[10] used the equation of Smolyakov and Veselova[14] to reproduce the limiting self-diffusion coefficients of ions and neutral molecules. This method is also used in this study for aqueous solutions. However, for organic solvents, the transition state theory used by Oelkers and Helgeson[16] has been found to be more effective for representing the temperature dependence of the limiting conductivity or self-diffusivity of ions and neutral molecules. Thus, the ionic limiting conductivity in a pure solvent s can be reproduced by an Arrhenius-type equation of the form

$$\lambda_i^{0,s}(T) = A_{\lambda,i}^{(s)}\exp(-E_{\lambda,i}^{(s)}/RT) \tag{2a}$$

or simply by

$$\ln \lambda_i^{0,s}(T) = A_i^{(s)} + B_i^{(s)}/T \tag{2b}$$

For neutral molecules, an analogous equation can be

Table 1. Parameters of Equation 2b for the Limiting Ion Conductivities of Selected Ions in Pure Solvents

ion	solvent	$A_i^{(s)}$	$B_i^{(s)}$	temp[a] (°C)	n	AAD[b]	ref
Na$^+$	ethanol	8.5111	−1641.74	−45−25	8	0.56	17
I$^-$	ethanol	8.4973	−1552.86	−45−25	8	1.06	17
ClO$_4^-$	ethanol	8.4324	−1487.34	−45−25	8	0.88	17
I$^-$	acetone	7.6311	−862.867	−40−25	5	1.77	12, 13
Na$^+$	acetone	6.9670	−801.904	−40−25	5	2.38	12, 13

[a] The temperature range in which the experimental data are available and were used to determine the parameters. [b] AAD is the average relative deviation of the limiting ion conductivity, defined as AAD = $100(\sum_{i=1}^{n}|\lambda_{i,\exp}^0 - \lambda_{i,\mathrm{cal}}^0|/\lambda_{i,\exp}^0)/n$, where n is the number of experimental points used to determine the parameters.

Table 2. Parameters of Equation 3 for the Limiting Self-Diffusion Coefficients of Selected Pure Solvents

solvent	$C_i^{(s)}$	$B_i^{(s)}$	temp[a] (°C)	n	AAD[b]	ref
methanol	−21.1187	−1328.74	−5−55	16	1.90	18−20
ethanol	−19.7028	−1995.81	6.8−65	15	1.51	18, 19
1-propanol	−20.8343	−1790.96	15−45	5	2.28	19
benzene	−21.0790	−1374.09	6.8−65	17	4.88	18, 19, 21

[a] The temperature range in which experimental data are available and were used to determine the parameters. [b] AAD is the average relative deviation of the limiting self-diffusion coefficient, defined as AAD = $100(\sum_{i=1}^{n}|D_{i,\exp}^0 - D_{i,\mathrm{cal}}^0|/D_{i,\exp}^0)/n$, where n is the number of experimental points used to determine the parameters.

obtained by combining eqs 1 and 2b:

$$\ln \frac{D_i^{0,s}}{T} = C_i^{(s)} + \frac{B_i^{(s)}}{T} \tag{3}$$

where $A_i^{(s)}$, $B_i^{(s)}$, and $C_i^{(s)}$ are adjustable parameters specific to the ion or molecule (i) and the solvent (s). Equations 2 and 3 have been found to reproduce the temperature dependence of limiting ion conductivities and self-diffusion coefficients of neutral molecules in organic solvents within experimental uncertainty. This is shown in Tables 1 and 2 and Figures 1–3.

For complex species, the limiting self-diffusivity can be estimated using the equation previously developed by Anderko and Lencka,[10] i.e.

$$D_{\mathrm{complex}}^{0,s} = \frac{1}{[\sum_{i=1}^{n}(1/D_i^{0,s})^3]^{1/3}} \tag{4}$$

where the $D_i^{0,s}$ values are the limiting diffusivities of the simple ions that make up the complex.

Limiting Diffusivity in Mixed Solvents. The limiting ion conductivity or diffusivity data in mixed solvents are relatively few compared to those in pure solvents. Thus, it is desirable to develop a model for representing the limiting diffusivity in mixed solvents using data obtained for the constituent pure solvents. In this study, a new, general model is developed for the limiting ion conductivity or self-diffusivity in solvent mixtures that may contain any combination of components. For this purpose, a mixing rule is proposed to relate the limiting conductivity or diffusivity in the mixed solvent to those in the constituent pure solvents. Thus, the limiting conductance of an ion i in a mixed solvent is represented by

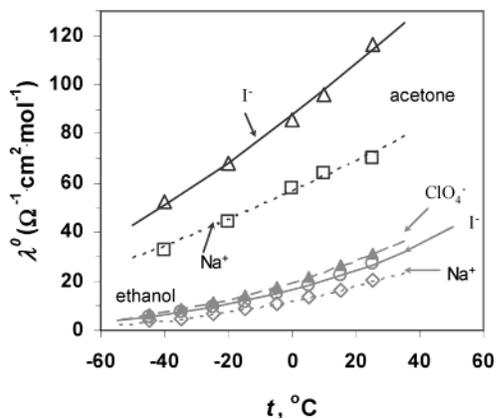$$\lambda_i^{0,m} = \sum_j \sum_k Y_j Y_k \lambda_{ijk} \tag{5}$$

Figure 1. Limiting conductance of ions in acetone (Na$^+$, □; I$^-$, △) and in ethanol (Na$^+$, ◇; I$^-$, ○; ClO$_4^-$, ▲) as a function of temperature. The lines are calculated from eq 2b with parameters listed in Table 1. The symbols are the experimental data of Marcus,[12] Krumgalz,[13] and Barthel et al.[17]
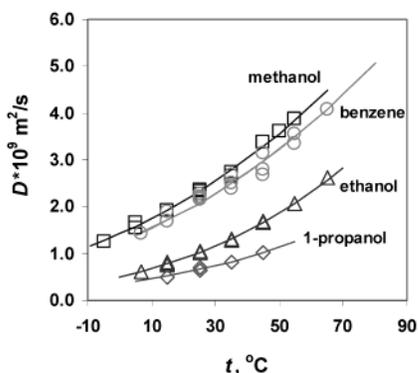

Figure 2. Self-diffusion coefficients of several pure organic liquids. The solid lines are obtained from eq 3 with parameters listed in Table 2. The symbols are the experimental data of Ruthbun and Babb,[18] Johnson and Babb,[19] and Falcone et al.[21]

where j and k are solvents and λ_{ijk} is a modified arithmetic average of limiting ion conductivities as defined by

$$\lambda_{ijk} = \frac{1}{2}(\lambda_i^{0,j} + \lambda_i^{0,k})(1 + k_{ijk}) \qquad (6)$$

Y_j is a modified volume fraction of the solvent j:

$$Y_j = \frac{v_{ij}^* x_j}{\displaystyle\sum_l (v_{il}^* x_l)} \qquad (7)$$

v_{ij}^* is an adjusted molar volume of the solvent j in the presence of ion i and other solvents denoted by k:

$$v_{ij}^* = v_j^0 + \sum_{k \neq j} x_k^{1/4} v_k^0 g_{ijk} \qquad (8)$$

In eqs 5–8, $\lambda_i^{0,m}$ is the limiting conductivity of ion i in the mixed solvent, $\lambda_i^{0,j}$ and $\lambda_i^{0,k}$ are the limiting conductivities of ion i in pure solvents j and k, respectively, x_j is the mole fraction of the constituent solvent j, v_j^0 is the liquid molar volume of the pure solvent j, and g_{ijk} and k_{ijk} are adjustable parameters determined from experimental limiting conductivity data. The g_{ijk} parameter accounts for the effect of solvent molar volumes on the variation of the limiting ion conductivity with

composition. It has been found that the limiting ion conductivity versus composition curve strongly depends on the redefined molar volumes (v_{ij}^*) of the components. The selection of the formula for v_{ij}^* is primarily based on its effectiveness for representing experimental data. Equation 8 with a $1/4$ power on x is found to give the best accuracy and, therefore, it is used to calculate v_{ij}^*. The quantity v_{ij}^* may be interpreted as an effective molar volume of the solvent j, which is affected by the presence of other solvents and the ion i in the mixture. This effect can be represented by eq 8, where the pure liquid molar volume (v_j^0) is corrected for the presence of other solvent components, k ($k \neq j$) and the ion i. It should be noted that when $g_{ijk} = 0$ for all solvents j and k, v_{ij}^* reduces to v_j^0, and when all $k_{ijk} = 0$, eq 5 becomes a simple volume fraction-averaged ideal mixing equation. For neutral species (including solvent molecules), a similar equation can be derived for the limiting diffusivity based on eq 1:

$$D_n^{0,m} = \sum_j \sum_k Y_j Y_k D_{njk} \qquad (9)$$

In eq 9, D_{njk} is a modified arithmetic average of limiting diffusivities as defined by

$$D_{njk} = \frac{1}{2}(D_n^{0,j} + D_n^{0,k})(1 + k_{njk}) \qquad (10)$$

The modified volume fraction of the solvent component Y_j is given by expressions similar to eqs 7 and 8:

$$Y_j = \frac{v_{nj}^* x_j}{\displaystyle\sum_l (v_{nl}^* x_l)} \qquad (11)$$

and

$$v_{nj}^* = v_j^0 + \sum_{k \neq j} x_k^{1/4} v_k^0 g_{njk} \qquad (12)$$

Similarly, the parameters g_{njk} and k_{njk} are adjustable constants determined from experimental limiting diffusivity data. The model uses only pure liquid molar volumes and limiting ion conductivities or diffusivities in pure solvents. It can be applied to solvent mixtures of any composition. In this study, the term "limiting self-diffusion coefficient" pertains to solutions in which the concentration of any solute species is zero or at infinite
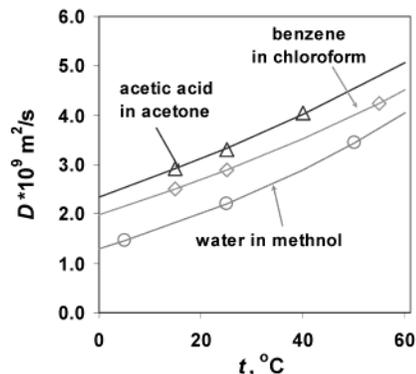
Figure 3. Limiting self-diffusion coefficients of neutral species in pure solvents. The solid lines are obtained from eq 3. The symbols are taken from Weast and Lide[22] and Woolf.[20]

dilution. Thus, the model described by eqs 9–12 is also applicable to self-diffusion coefficients of solvent components in a solvent mixture of any composition.

Self-Diffusion Coefficients in Concentrated Single-Electrolyte Solutions

The method developed by Anderko and Lencka[10] for modeling the concentration dependence of self-diffusivity in aqueous solutions is extended in the present work to mixed-solvent electrolyte systems. In electrolyte solutions, the concentration dependence of the self-diffusion coefficient of a tracer species i can be accounted for by the combination of two effects. In relatively dilute electrolyte solutions, the *relaxation effect* plays a dominant role. As the electrolyte concentration increases, *short-range forces* due to interparticle interactions become increasingly significant. The effect of short-range interactions can be represented by the hard-sphere theory, which was originally developed for nonelectrolyte solutions. Thus, the self-diffusion coefficient of a tracer i in a single-solvent, single-electrolyte solution can be expressed as[10]

$$D_i = D_i^0 \left(\frac{D_i^{HS}}{D_i^0} \right) \left(1 + \frac{\delta k_i}{k_i} \right) \quad (13)$$

where D_i^0 is the limiting self-diffusion coefficient of the tracer i in a given solvent, $\delta k_i/k_i$ is a contribution resulting from the relaxation effect, and D_i^{HS}/D_i^0 represents the effects of short-range forces, which are calculated from the hard-sphere model. It should be noted that eq 13 and the equations that define the $\delta k_i/k_i$ and D_i^{HS}/D_i^0 terms (eqs 14–23) pertain to a single-solvent electrolyte solution containing one cation and one anion.

Relaxation Effect. The relaxation factor is calculated from an expression developed by Bernard et al.[6] and Chhih et al.[23] for systems containing ions of different sizes in a dielectric continuum. This expression was derived by combining the Onsager continuity equations with equilibrium correlation functions calculated from the MSA theory. For a tracer i, the relaxation term is given by

$$\frac{\delta k_i}{k_i} = -\frac{1}{4\pi\epsilon_0\epsilon} \frac{z_i^2 e^2 (\kappa^2 - \kappa_{di}^2)}{6 k_B T \sigma (1 + \Gamma\sigma)^2} \times$$
$$\frac{1 - \exp(-2\kappa_{di}\sigma)}{\kappa_{di}^2 + 2\Gamma\kappa_{di} + 2\Gamma^2 [1 - \exp(-\kappa_{di}\sigma)]} \quad (14)$$

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 the solvent. In eq 14, σ is the average ion diameter defined by

$$\sigma = \frac{\displaystyle\sum_{l=1}^{2} z_l^2 \rho_l \sigma_l}{\displaystyle\sum_{l=1}^{2} z_l^2 \rho_l} \quad (15)$$

where ρ_l is the number density and σ_l is the diameter

of the lth ion. The parameters κ and κ_{di} are given by

$$\kappa^2 = \frac{e^2}{\epsilon_0\epsilon k_B T} \sum_{l=1}^{2} \rho_l z_l^2 \quad (16)$$

$$\kappa_{di}^2 = \frac{e^2}{\epsilon_0\epsilon k_B T} \sum_{l=1}^{2} \frac{\rho_l z_l^2 D_l^0}{D_i^0 + D_l^0} \quad (17)$$

and Γ is the MSA screening parameter, calculated in the MSA as

$$\Gamma = \frac{\kappa}{2(1 + \Gamma\sigma)} \quad (18)$$

In eqs 15–17, the sums are over the two distinct ions (i.e., the cation and the anion).

Hard-Sphere Model. As described in a previous paper,[10] the hard-sphere contribution to the concentration dependence of the diffusion coefficient of a tracer ion i in a solution containing a cation c, an anion a, and a solvent j can be expressed as

$$\frac{D_i^{HS}}{D_i^{0,j}} = \frac{\dfrac{g_{ij}^0}{d_{ij}^0}}{x_c \dfrac{g_{ic}}{d_{ic}} + x_a \dfrac{g_{ia}}{d_{ia}} + x_j \dfrac{g_{ij}}{d_{ij}}} \quad (19)$$

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 superscript 0 denotes the pure solvent j at the same conditions as the solution. The d_{ij} coefficient is given by

$$d_{ij} = \frac{3}{8\sigma_{ij}^2 \rho} \left[\frac{(M_i + M_j) RT}{2\pi M_i M_j} \right]^{1/2} \quad (20)$$

where M_i is the molecular weight of species i, ρ is the total number density, and σ_{ij} is the average diameter σ_{ij} defined as

$$\sigma_{ij} = (\sigma_i + \sigma_j)/2 \quad (21)$$

The radial distribution function g_{ij} in eq 19 is calculated from

$$g_{ij}(\sigma_{ij}) = \frac{1}{1 - \zeta_3} + \frac{3\sigma_i\sigma_j}{\sigma_i + \sigma_j} \frac{\zeta_2}{(1 - \zeta_3)^2} +$$
$$2 \left(\frac{\sigma_i\sigma_j}{\sigma_i + \sigma_j} \right)^2 \frac{\zeta_2^2}{(1 - \zeta_3)^3} \quad (22)$$

where

$$\zeta_l = \frac{\pi}{6} \rho \sum_k x_k \sigma_k^l \quad (23)$$

Relaxation and Hard-Sphere Effects in a Mixed-Solvent Solution. To apply the expressions for the relaxation and hard-sphere terms, it is necessary to calculate the relevant solvent properties, i.e., the di-

electric constant (in the relaxation term), molecular weight (in the hard-sphere term), and density (in both terms). To extend the applicability of the relaxation and hard-sphere terms to mixed-solvent systems, the solvent properties need to be redefined as averaged values. Thus, the molecular weight of the solvent is calculated as a weighted average:

$$M_s = \sum_{j=1}^{N_S} x'_j M_j \qquad (24)$$

where x'_j and M_j are the salt-free mole fraction and the molecular weight, respectively, of solvent j and N_S is the number of solvent components in the solvent mixture. The density of the solvent mixture is calculated by assuming ideal mixing, i.e.

$$\rho_s = \frac{1}{\sum_{j=1}^{N_S} x'_j v_j^0} \qquad (25)$$

Although the use of excess volume data is desirable for the calculation of densities of solvent mixtures, especially for those mixtures in which the excess volumes are significant, the neglect of excess volumes can be compensated for by the adjustable parameters in the model, as will be described below. The dielectric constant of the mixed solvent, ϵ_s, is calculated using a general model described in a previous paper.[24]

The only species-dependent parameters in the model (eqs 13, 14, and 19) are the diameters, σ_i. As a first approximation, crystallographic diameters can be used to estimate σ_i. This approximation is reasonable for relatively dilute solutions. However, it becomes less accurate as the ionic concentration increases because of changes in the ionic environment. For example, a change in the viscosity at higher concentrations entails a changing ionic mobility, which results from altered solvation structure and short-range interactions between ions. Therefore, to reproduce experimental diffusivities over wide composition ranges, Anderko and Lencka[10] introduced an effective diameter. The effective diameter σ_i reflects the effect of other species on the diameter of species i and is defined as

$$\sigma_i = \frac{\sum_l c_l \sigma_{i(l)}}{\sum_l c_l} \qquad (26)$$

where c_l is the molar concentration of species l (i.e., ions or neutral species or solvent molecules). The parameter $\sigma_{i(l)}$ has the meaning of a species diameter and is treated as an adjustable parameter to reflect the interactions between species i and l. In mixed-solvent electrolyte solutions, the parameters that represent the interactions of species with the mixed solvent, $\sigma_{i(s)}$ and $\sigma_{s(i)}$, are defined as averages, i.e.

$$\sigma_{i(s)} = \sum_{j=1}^{N_S} x'_j \sigma_{i(j)} \qquad (27)$$

and

$$\sigma_{s(i)} = \sum_{j=1}^{N_S} x'_j \sigma_{j(i)} \qquad (28)$$

where i denotes a cation, an anion, or a neutral species including solvent molecules and s denotes the mixed solvent. Crystallographic diameters have been assumed for all of the $\sigma_{i(l)}$ parameters. It should be noted that when eq 13 is applied to mixed-solvent electrolyte systems, the D_i^0 value is the limiting self-diffusion coefficient of tracer i in the mixed solvent, as calculated from eqs 1 and 5 or eq 9.

Self-Diffusion Coefficients in Systems with Multiple Solutes and Solvents

The equations for the relaxation and hard-sphere terms (eqs 13, 14, and 19) are limited to systems containing only a single electrolyte. For the treatment of multicomponent aqueous electrolyte solutions, Anderko and Lencka[10] formulated a mixing rule on the basis of the Stefan–Maxwell formalism for multicomponent diffusion. Derivation of this mixing rule was described in a previous paper[10] and will not be repeated here. This formalism gives an accurate representation of the concentration dependence of self-diffusion coefficients in complex aqueous electrolyte solutions. By treating a mixed solvent as a single solvent with averaged properties, we extend this mixing rule to represent self-diffusion coefficients in systems with multiple solutes.

First, a multicomponent system that contains N_c cations, N_a anions, and N_n neutral species (excluding the solvent molecules) is divided into a number of hypothetical single-solute systems. These systems contain either one cation and one anion in the averaged single solvent or one neutral species in the averaged solvent. The self-diffusion coefficient of tracer i in each of the hypothetical single-solute systems can be calculated using the models described by eqs 13, 14, and 19 with the redefined solvent properties and effective species diameters. Then, the mixing rule is applied to calculate the self-diffusion coefficient in the multicomponent system:

$$D_i = \frac{n_T}{\sum_{d=1}^{N_c N_a} \left[\frac{n_{s(d)} + n_{c(d)} + n_{a(d)}}{D_{i(d)}} \right] + \sum_{l=1}^{N_n} \left[\frac{n_{n(l)} + n_{s(l)}}{D_{i(l)}} \right]} \qquad (29)$$

where $n_{c(d)}$, $n_{a(d)}$, and $n_{s(d)}$ are the numbers of moles of cation (c), anion (a), and solvent (s) in the hypothetical single-solute system d ($\{c,a\}-s$) and $D_{i(d)}$ is the self-diffusion coefficient of tracer i in this system as calculated from eqs 13, 14, and 19. Similarly, $n_{n(l)}$ and $n_{s(l)}$ are the numbers of moles of the neutral species (n) and the solvent in the hypothetical single-solute system l ($n-s$), and $D_{i(l)}$ is the self-diffusion coefficient of tracer i in this system. The quantity n_T is the total number of moles of all components in the mixed-solvent electrolyte solution with N_S solvent components

$$n_T = \sum_{i=1}^{N_c + N_a} n_i^0 + \sum_{n=1}^{N_n} n_n^0 + \sum_{j=1}^{N_S} n_s^0 \qquad (30)$$

where the superscript 0 denotes the total number of

moles of each species in the multicomponent system. The definition of the number of moles of each species in a hypothetical single-solute system (i.e., $n_{c(d)}$, $n_{a(d)}$, $n_{s(d)}$, $n_{n(l)}$, and $n_{s(l)}$) is not given by the theory and has to be defined using empirical rules. However, it must satisfy the electroneutrality conditions, and the total amount of a given species in all of the hypothetical single-solute solutions must be equal to its amount in the multicomponent system. The material balance for the kth cation and the mth anion can be written as

$$n_k^0 = \sum_{d=1}^{N_c N_a} n_{k(d)} \nu_{k(d)} \qquad k = 1, \ldots, N_c \qquad (31)$$

$$n_m^0 = \sum_{d=1}^{N_c N_a} n_{m(d)} \nu_{m(d)} \qquad m = 1, \ldots, N_a \qquad (32)$$

where $\nu_{k(d)}$ and $\nu_{m(d)}$ are the stoichiometric numbers of cation k and anion m, respectively, in the electrolyte that forms the single-solute system d. The total number of moles of the solvent is

$$n_s^0 = \sum_{j=1}^{N_S} n_j = \sum_{d=1}^{N_c N_a} n_{s(d)} + \sum_{l=1}^{N_n} n_{s(l)} \qquad (33)$$

The electroneutrality conditions are satisfied when the numbers of moles of cation c and anion a in the subsystem d ({c,a}$-s$) are defined as

$$n_{c(d)} = n_c^0 \frac{|z_a| n_a^0}{n_{eq}} \qquad (34)$$

$$n_{a(d)} = n_a^0 \frac{|z_c| n_c^0}{n_{eq}} \qquad (35)$$

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

$$n_{eq} = \sum_{k=1}^{N_c} n_k^0 |z_k| = \sum_{m=1}^{N_a} n_m^0 |z_m| \qquad (36)$$

For a neutral species n, only one single-solute system is formed with the solvent, i.e.

$$n_{n(l)} = n_n^0 \qquad (37)$$

The numbers of moles of the solvent in each of the hypothetical single-solute solutions are defined so that the ionic strength of the single-solute solution is the same as that of the multicomponent system. For this purpose, the ionic strength has been generalized[10] to include the neutral solute species, i.e.,

$$I_T = \frac{1}{2} \sum_{i=1}^{N_c+N_a} n_i^0 z_i^2 + \sum_{l=1}^{N_n} n_l^0 \qquad (38)$$

Thus, in a solution d ({c,a}$-s$), the number of moles of the solvent is

$$n_{s(d)} = n_s^0 \frac{\frac{1}{2}(n_{c(d)} z_c^2 + n_{a(d)} z_a^2)}{I_T} \qquad (39)$$

In a solution l ($n-s$), the corresponding number is

$$n_{s(l)} = n_s^0 \frac{n_{n(l)}}{I_T} \qquad (40)$$

When the relaxation and hard-sphere models are applied to the hypothetical single-solute systems, the values of $D_{i(d)}$ and $D_{i(l)}$ in eq 29 must be computed at the same total number densities as those of the multicomponent mixture. Thus, the final self-diffusivity model for a mixed-solvent electrolyte solution consists of eqs 13, 14, and 19 for single-solute systems and the mixing rule for multisolute systems (eq 29) coupled with the auxiliary equations (33)−(40). The model requires the density of the solution in order to calculate the number densities of ions in the relaxation term (eq 14) and the total number density in the hard-sphere contribution (eq 19). The densities are calculated using a model described in a previous paper.[25] When water is the only solvent in a solution, the number of solvent components (N_S) becomes 1 and the mixed-solvent model reduces to the aqueous model originally developed by Anderko and Lencka.[10]

Results and Discussion

The performance of the self-diffusivity model described above has been verified using experimental data for a number of mixed-solvent electrolyte systems. First, tests have been performed for the limiting ion conductivities and self-diffusion coefficients of ions or molecules in mixed solvents. For such tests, the calculations involve the use of eqs 5 and 9 without introducing the terms that represent the effects of finite electrolyte concentrations (eqs 14 and 19). Tables 3 and 4 give some representative k_{ijk} and g_{ijk} (eqs 5−8) or k_{njk} and g_{njk} (eqs 9−12) parameters obtained from limiting conductivity or limiting self-diffusivity data. It has been found that, in many cases, a single set of parameters (i.e., g_{ijk} and k_{ijk}) can represent all ions or a group of ions (such as alkali-metal cations or tetraalkylammonium ions) in a given mixed solvent (cf. Table 3). This feature is of great importance for predicting the limiting transport properties of ions in mixed solvents when experimental data are not available.

Figure 4 shows the obtained results for the limiting ion conductivities of the tetrabutylammonium ion (Bu$_4$N$^+$), Na$^+$, and Br$^-$ in ethanol−water mixtures at 25 °C as a function of the mole fraction of ethanol. The results for self-diffusion coefficients of water, n-propanol, Na$^+$, and I$^-$ at infinite dilution of NaI in the n-propanol−water−NaI system at 25 °C are shown in Figure 5. Figure 6 shows the self-diffusion coefficients of water and methanol in methanol−water mixtures at 5 and 25 °C.

The temperature dependence of the limiting self-diffusion coefficient or ion conductivity can be represented by introducing a temperature-dependent function for the g_{ijk} and k_{ijk} (or k_{njk} and g_{njk}) parameters:

$$k_{ijk} = k_{ijk}^{(0)} + k_{ijk}^{(1)}/T \qquad (41)$$

$$g_{ijk} = g_{ijk}^{(0)} + g_{ijk}^{(1)}/T \qquad (42)$$

Because the majority of self-diffusivity or ion conductivity data in mixed solvents is reported at a single temperature at or in the vicinity of 25 °C, the temper-

Table 3. Parameters of Equations 5−8 for Selected Ions in Mixed Solvents^a

ion (i)	solvent (j)	solvent (k)	$k_{ijk}^{(0)}$	$k_{ijk}^{(1)}$	$g_{ijk}^{(0)}$	$g_{ijk}^{(1)}$	AAD^b	ref
Li$^+$	ethanol	water	−4.096	984.54	4.213	−1307.68	7.92	26−28
Na$^+$	ethanol	water	−4.096	984.54	4.213	−1307.68	2.38	26−28
K$^+$	ethanol	water	−4.096	984.54	4.213	−1307.68	2.57	26−29
Me$_4$N$^+$	ethanol	water	−1.087	0	0.1193	0	5.67	26
Et$_4$N$^+$	ethanol	water	−1.087	0	0.1193	0	6.26	26
Pr$_4$N$^+$	ethanol	water	−1.087	0	0.1193	0	5.50	26
Bu$_4$N$^+$	ethanol	water	−1.087	0	0.1193	0	4.61	26
Cl$^-$	ethanol	water	0.460	−297.51	1.00	−402.349	4.20	26, 27, 29
Br$^-$	ethanol	water	0.460	−297.51	1.00	−402.349	3.11	26
I$^-$	ethanol	water	0.460	−297.51	1.00	−402.349	2.82	26

^{a} The temperature dependence of k_{ijk} and g_{ijk} is expressed as $k_{ijk} = k_{ijk}^{(0)} + k_{ijk}^{(1)}/T$ and $g_{ijk} = g_{ijk}^{(0)} + g_{ijk}^{(1)}/T$. ^{b} AAD is the average absolute deviation of the limiting ion conductivity, defined as AAD $= \sum_{i=1}^{n}|\lambda_{i,exp}^0 - \lambda_{i,cal}^0|/n$, where n is the number of data points used to determine the parameters.

Table 4. Parameters of Equations 9−12 for Selected Neutral Molecules in Mixed Solvents^a

neutral species (n)	solvent (j)	solvent (k)	$k_{njk}^{(0)}$	$k_{njk}^{(1)}$	$g_{njk}^{(0)}$	$g_{njk}^{(1)}$	m	AAD^b	ref
1-propanol	1-propanol	water	−0.904	0	−0.0959	0	17	5.28	30
water	1-propanol	water	−0.639	0	0	0	13	8.84	30
methanol	methanol	water	2.378	−974.43	0.183	0	44	4.29	19, 20, 31
water	methanol	water	2.238	−932.97	0.189	0	24	3.29	20

^{a} The temperature dependence of k_{njk} and g_{njk} is expressed as $k_{njk} = k_{njk}^{(0)} + k_{njk}^{(1)}/T$ and $g_{njk} = g_{njk}^{(0)} + g_{njk}^{(1)}/T$. ^{b} AAD is the average relative deviation of the limiting self-diffusion coefficient, defined as AAD $= 100(\sum_{i=1}^{m}|D_{i,exp}^0 - D_{i,cal}^0|/D_{i,exp}^0)/m$, where m is the number of data points used to determine the parameters.

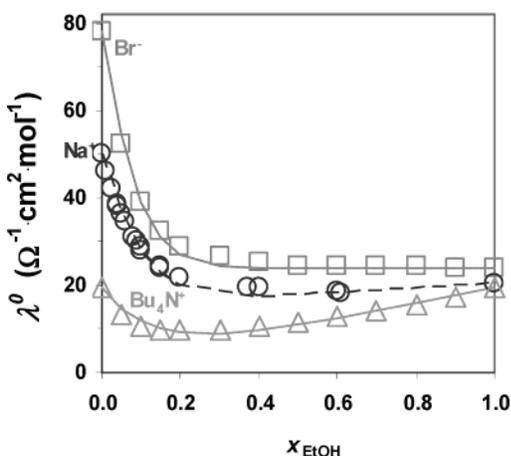**Figure 4.** Limiting conductance of Bu$_4$N$^+$ (tetrabutylammonium ion), Na$^+$, and Br$^-$ in ethanol−water mixtures at 25 °C as a function of the mole fraction of ethanol. The lines are obtained from eq 5 with parameters listed in Table 3. The symbols are the experimental data of Kay and Broadwater,[26] Spivey and Shedlovsky,[27] and Sanchez et al.[28]

Figure 5. Self-diffusion coefficients of water, n-propanol, I$^-$, and Na$^+$ in the n-propanol−water−NaI system at infinite dilution of NaI at 25 °C. The lines are obtained using eqs 5 and 9. The symbols are the experimental data from Hawlicka and Grabowski.[30,32]

ature dependence of these parameters can only be determined for a limited number of species in systems for which data are available over a substantial range of temperatures.

It should be noted that, although a significant amount of limiting ion conductivity data was determined using the direct method (i.e., by the measurement of transference numbers in electrolyte solutions), indirect methods have also been employed to determine the limiting ion conductivity through the separation of the conductivity of the electrolyte, Λ^0, into individual ionic components. This approach is necessary in the absence of experimental transference numbers. A wide variety of assumptions have been used in the attempt to split the limiting conductivity of an electrolyte. These indirect methods have been reviewed by Krumgalz.[13] Thus, to ensure the internal consistency of ionic limiting conductivities taken from different sources, the data determined using indirect methods have been recalculated
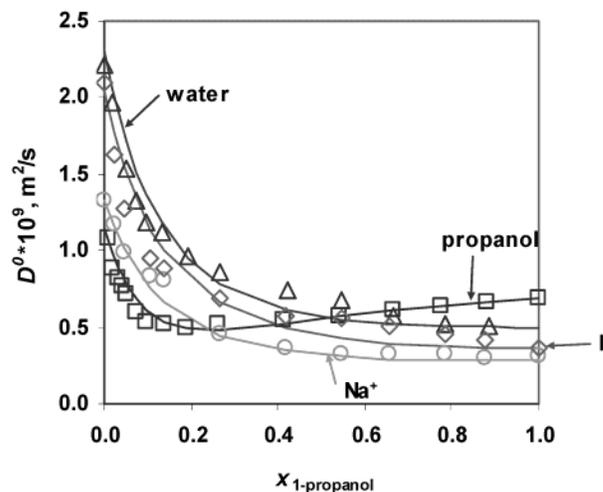
in this study based on the recommendation of Marcus,[12] i.e., by using $\lambda_{Bu_4N^+}^0 \eta^0 = 0.2131$, where $\lambda_{Bu_4N^+}^0$ is the limiting conductivity of the Bu$_4$N$^+$ ion and η^0 is the solvent viscosity. This product can be regarded as independent of temperature.[13]

After verification of the limiting diffusivity, the terms that define the effect of the electrolyte concentration (i.e., eqs 13, 14, 19, and 29) were tested using experimental data. Because the model reduces to the previously developed model for aqueous solutions[10] when water is the only solvent, the calculations have been focused on mixed-solvent systems. The interactions between species are accounted for by the $\sigma_{i(j)}$ parameters, which define the effective diameters in eqs 26−28. In general, the parameters reflecting the interactions between a cation and an anion, e.g., $\sigma_{c(a)}$ and $\sigma_{a(c)}$, are determined using self-diffusivity data in aqueous electrolyte solutions because such data are usually more extensive than those in other solvents. The parameters
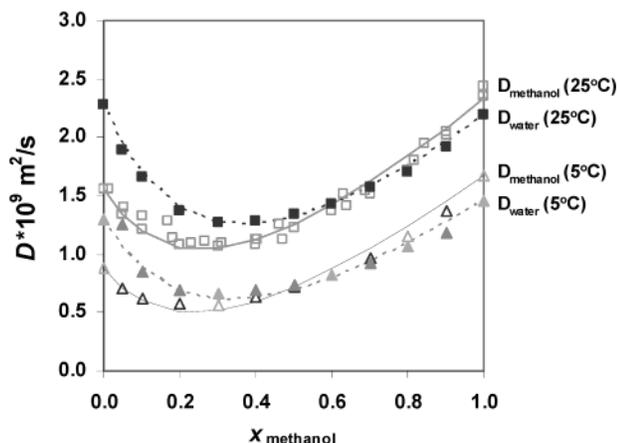
Figure 6. Self-diffusion coefficients of water (25 °C, ■; 5 °C, ▲) and methanol (25 °C, □; 5 °C, △) in methanol−water mixtures as a function of $x_{methanol}$. The lines are obtained from eq 9 with parameters listed in Table 4. The symbols are the literature data of Johnson and Babb,[19] Woolf,[20] and Hawlicka.[31]

Table 5. Parameters $\sigma_{i(j)}$ (in Å) Used for the Computation of Effective Diameters of Selected Species (Equation 26)

species i	species j	$\sigma_{i(j)}$	species i	species j	$\sigma_{i(j)}$
methanol	Na$^+$	0.001	Cl$^-$	methanol	4.302
Na$^+$	methanol	0.001	Li$^+$	methanol	1.550
methanol	Cl$^-$	16.894	methanol	Li$^+$	0.001

for the interactions between a solute ion or a neutral species and a solvent molecule, i.e., $\sigma_{s(i)}$ and $\sigma_{i(s)}$, are then adjusted to give the best fit to experimental self-diffusivity data in mixed-solvent systems. Table 5 lists selected parameters that were determined in this study. In some cases, the calculated self-diffusivities in mixed solvents are not sensitive to the binary parameters. In such cases, $\sigma_{s(i)}$ or $\sigma_{i(s)}$ is set equal to a value of 0.001. Anderko and Lencka[10] found that the $\sigma_{i(j)}$ parameters may be dependent on the ionic strength for a small number of systems for which experimental data are available over wide concentration ranges. However, for the mixed-solvent systems studied in this work, the ionic strength dependence of the $\sigma_{i(j)}$ parameters is not necessary because the electrolyte concentrations usually extend over a relatively small range, which is frequently because of solubility limits. The ionic strength dependent function for the parameters pertaining to aqueous electrolyte systems remains to be the same as that used by Anderko and Lencka.[10] These parameters, once determined from aqueous data, are fixed in the calculations, and only the $\sigma_{i(j)}$ parameters that are pertinent to mixed-solvent systems are adjusted.

Figure 7 shows the calculated self-diffusion coefficients of methanol in methanol−water−LiCl mixtures at 25 °C at various LiCl concentrations. The results for methanol and the Na$^+$ ion in the methanol−water−NaCl system at 25 °C are illustrated in Figures 8 and 9 as a function of the methanol mole fraction recalculated on a salt-free basis ($x_{methanol}$). As shown in the figures, the effect of finite salt concentrations on self-diffusion coefficients is accurately reproduced. This is further demonstrated in Figure 10, in which the self-diffusion coefficients of water, methanol, Cl$^-$, and Na$^+$ are shown in the methanol−water−NaCl system as a function of NaCl molality at a fixed solvent composition [$x_{methanol}$ = 0.4 (salt-free)]. Because only limiting self-diffusion coefficients for the Cl$^-$ ion are available, the dashed line in Figure 10 for D_{Cl^-} represents predicted
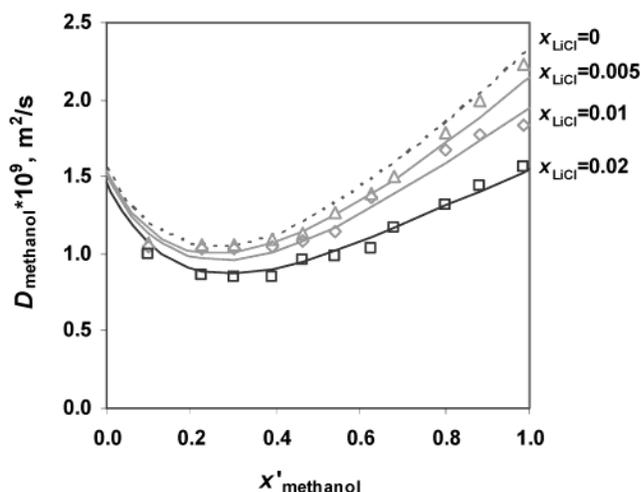

Figure 7. Self-diffusion coefficients of methanol in the methanol−water−LiCl system at 25 °C at various LiCl concentrations. The dashed line denotes the results for salt-free mixtures. The solid lines are obtained from the model as described by eqs 13, 14, 19, and 29. The symbols are the experimental results of Hawlicka.[33]
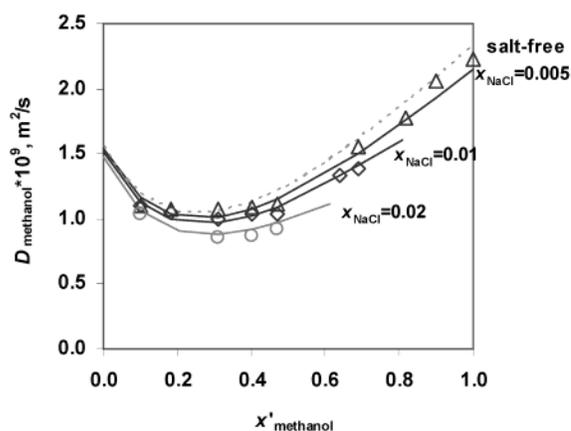

Figure 8. Self-diffusion coefficients of methanol in the methanol−water−NaCl system at 25 °C at various NaCl concentrations. The dashed line denotes the results for salt-free mixtures. The solid lines are obtained from the model as described by eqs 13, 14, 19, and 29. The symbols are the experimental results of Hawlicka.[33]

results. The effect of the salt concentration on self-diffusion coefficients is also shown in Figure 11, in which $D_{propanol}$ in the n-propanol−water−NaI system at 25 °C is plotted as a function of $x_{propanol}$ with and without 2 mol of NaI per 100 mol of the mixed solvent. Finally, calculated self-diffusion coefficients of methanol, acetonitrile, Na$^+$, and I$^-$ in the methanol−acetonitrile−NaI mixture at 25 °C are shown in Figure 12. This figure compares the results at infinite dilution and at a fixed NaI concentration of 0.5 mol per 100 mol of the mixed solvent. These results demonstrate that the model developed in this study is capable of accurately representing the self-diffusion coefficients of ions and neutral molecules at finite concentrations of electrolytes as well as at infinite dilution.

Conclusions

A model has been developed for the computation of self-diffusion coefficients in mixed-solvent electrolyte solutions. The model consists of two distinct parts, i.e., (1) a correlation for calculating the self-diffusion coefficients of ions and neutral species at infinite dilution
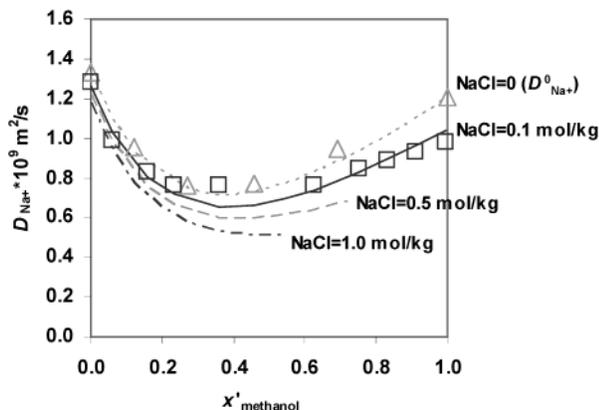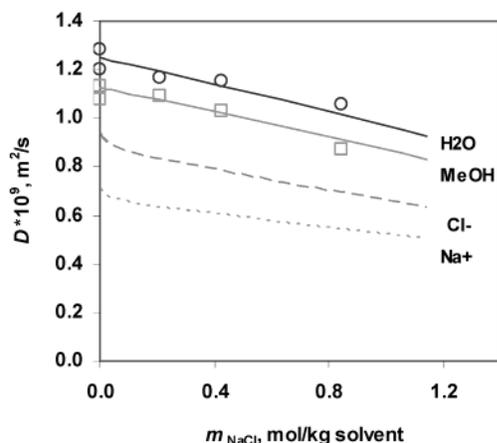
Figure 9. Self-diffusion coefficients of the Na$^+$ ion in the methanol−water−NaCl system at 25 °C at various NaCl concentrations. The dashed lines at 0.5 and 1.0 mol of NaCl/kg of solvent denote the predicted results. The dotted line and the symbols ($\triangle$)[34] represent the limiting self-diffusion coefficients of Na$^+$, $D^0_{Na^+}$. The solid line is obtained from the model as described by eqs 13, 14, 19, and 29. The symbols ($\square$) are the experimental results of Marcinkowsky et al.[35]

Figure 10. Self-diffusion coefficients of water, methanol, Cl$^-$, and Na$^+$ in the methanol−water−NaCl system as a function of the NaCl concentration at 25 °C and at $x'_{methanol}$ = 0.4 (salt-free). All lines are obtained from the model as described by eqs 13, 14, 19, and 29. The symbols are the experimental data of Johnson and Babb,[19] Woolf,[20] and Hawlicka.[31,33]

Figure 11. Self-diffusion coefficients of n-propanol in the n-propanol−water−NaI system at 25 °C. The dashed line and hollow symbols are the results for salt-free mixtures. The solid line represents the result for 2 mol of NaI/100 mol of solvent and is obtained using eqs 13, 14, 19, and 29. The symbols are the experimental data from Hawlicka and Grabowski.[30,32]
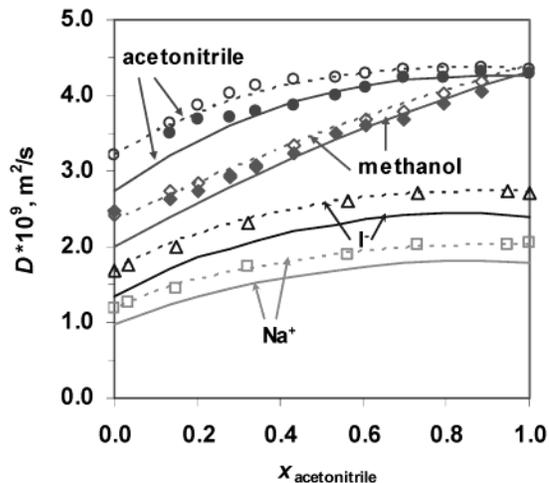
Figure 12. Self-diffusion coefficients of methanol, acetonitrile, Na$^+$, and I$^-$ in methanol−acetonitrile−NaI mixtures at 25 °C. The dashed lines and hollow symbols represent self-diffusion coefficients at infinite dilution of NaI; the solid lines and solid symbols denote those for a system containing 0.5 mol of NaI/100 mol of solvent. All lines are obtained using the model described by eqs 13, 14, 19, and 29; the symbols are experimental data from Hawlicka and Grabowski.[36] The solid lines for D_{Na^+} and D_{I^-} for 0.5 mol of NaI/100 mol of solvent are predicted.

as a function of temperature and solvent composition and (2) a model for the effect of finite electrolyte concentrations on the diffusion coefficients. For the limiting diffusivity in mixed solvents, a mixing rule has been developed using pure-solvent molar volumes and limiting ion conductivities or self-diffusivities in pure solvents as input information. For finite concentrations of electrolyte components, the model treats the mixed solvent as a hypothetical single solvent with averaged properties and combines the MSA theory of the relaxation effect with the hard-sphere model of diffusion. Because closed-form expressions for the relaxation and hard-sphere terms are available only for single-solute systems, the model utilizes a mixing rule for predicting self-diffusion coefficients in multicomponent solutions using the coefficients calculated for single-solute systems. The diffusion model has been integrated with a thermodynamic speciation model, which has been recently developed for mixed-solvent electrolyte solutions.[25] This makes it possible to reproduce the effects of complexation or other reactions in the solution. In all cases in which experimental data are available, the
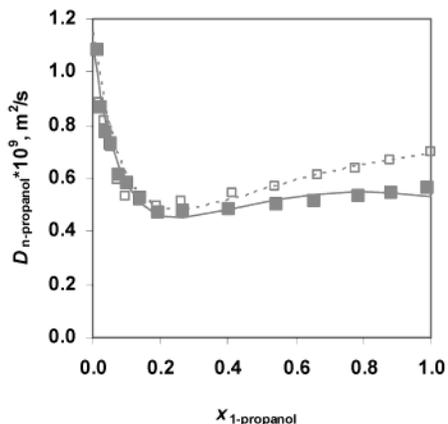
model has been shown to be accurate for reproducing self-diffusion coefficients over wide ranges of composition with respect to both solvents and electrolytes. The model has been implemented in software for simulating both thermodynamic and transport properties of electrolyte systems.

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