GENERAL RESEARCH

Modeling Electrical Conductivity in Concentrated and Mixed-Solvent Electrolyte Solutions

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A comprehensive model has been developed for calculating electrical conductivities of aqueous or mixed-solvent electrolyte systems ranging from dilute solutions to fused salts. The model consists of a correlation for calculating ionic conductivities at infinite dilution as a function of solvent composition and a method for predicting the effect of finite electrolyte concentration. The effect of electrolyte concentration is calculated using an extended form of the mean-spherical-approximation (MSA) theory coupled with a mixing rule for predicting the conductivities of multicomponent systems on the basis of the conductivities of constituent binary cation–anion subsystems. The MSA theory has been extended to very concentrated and mixed-solvent systems by introducing effective ionic radii that take into account various interactions between ions, solvent molecules, and ion pairs. The model has been coupled with thermodynamic equilibrium computations to provide the necessary concentrations of individual ions in complex, multicomponent systems. The model accurately reproduces experimental conductivity data over wide ranges of composition with respect to both solvents and electrolytes. In particular, the model is shown to be accurate for aqueous acids (e.g., H_2SO_4, HNO_3, and H_3PO_4) up to the pure acid limit, various nitrates ranging from dilute solutions to fused salts, salts in water + alcohol mixtures, and $LiPF_6$ solutions in propylene and diethyl carbonate.

Introduction

The electrical conductivity of liquid solutions and its dependence on concentration, chemical nature of the solvent, and temperature are of both theoretical and technological interest. In engineering applications, knowledge of the electrical conductivity is important for the design and optimization of various processes and devices, especially those involving electrochemical systems such as electrolysis instruments and high-performance batteries. Also, electrical conductivity can be used to gain insight into the properties of electrolyte solutions and to evaluate characteristic physical quantities such as dissociation constants. The practical importance of the electrical conductivity of electrolyte solutions has attracted increasing interest of researchers as reflected by the large quantity of experimental results published in recent years. However, little attention has been paid to the development of engineering-oriented models for calculating the electrical conductivity in such systems. In particular, to the best of our knowledge, no attempt has been made to develop a comprehensive electrical conductivity model for mixed-solvent electrolyte systems.

Most of the existing electrical conductivity models are focused on the limiting conductivity or the concentration dependence of conductivity in dilute solutions with a single solvent. In general, the computation of electrical conductivity requires the knowledge of the limiting conductivities of ions and the concentration dependence of the conductivity at finite electrolyte concentrations. Recently, an engineering-oriented electrical conductivity model was developed by Anderko and Lencka[1] for aqueous solutions. This model utilized and extended the mean-spherical-approximation (MSA) conductivity equations derived by Bernard et al.,[2] which combine Onsager's theory[3] and the MSA expressions for the equilibrium and structural properties of electrolyte solutions. The Anderko–Lencka model extended the practical applicability of the MSA theory to relatively high electrolyte concentrations (30 *m*) by introducing effective ionic radii, which are determined by ionic-strength-dependent cation–anion interactions. This model was shown to be effective for representing electrical conductivities of concentrated aqueous electrolyte solutions over wide temperature ranges.[1]

In contrast to aqueous electrolyte solutions, the electrical conductivity of a mixed-solvent solution is not only a function of temperature and salt concentration but also varies with the composition of the solvent. Modeling of the electrical conductivity of such systems requires that the effects not only of cation–anion interactions but also of interactions involving solvent molecules and other neutral species be taken into account. This is especially the case when the predominant species are ion pairs, e.g., in fully miscible acids when the water content approaches zero. In addition, in a mixed-solvent electrolyte solution, the solvent

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composition also contributes to the interactions between species through changes in viscosity and solvation structure.

The objective of this work is to develop a comprehensive, engineering-oriented model for electrical conductivity in concentrated aqueous and mixed-solvent electrolyte solutions. The model is designed to be applicable over wide ranges of solvent composition and electrolyte concentration (i.e., from infinitely dilute to saturated salt solutions). Further, the model is designed to predict the electrical conductivities in multisolvent, multisolute solutions using information obtained from data on single-solute, single-solvent systems. Also, the model is intended to account for speciation effects, such as complexation or ion association, when combined with a speciation-based thermodynamic model. The model consists of two parts: (1) one part is used to compute the limiting conductivities of ions in pure and mixed solvents as a function of temperature and solvent composition, and (2) and the other is for the computation of the dependence of electrical conductivity on electrolyte concentration.

Limiting Electrical Conductivities

Experimentally determined limiting conductivities of ions have been extensively reported in various pure solvents and in mixed-solvent systems as a function of solvent composition. In general, electrical conductivity data in organic solvents are less abundant than those in aqueous solutions, and the majority of the available data are reported at 25 °C or over a narrow temperature range. Models for the calculation of the limiting conductivity of ions in pure and mixed solvents were described in a previous paper.[4] A brief summary is provided in this section.

In a pure solvent s, the ionic limiting conductivity can be reproduced by an empirical, Arrhenius-type equation

$$\lambda_i^{0,s}(T) = A_{\lambda,i}^{(s)} \exp\left(-\frac{E_{\lambda,i}^{(s)}}{RT}\right) \tag{1a}$$

or simply by

$$\ln \lambda_i^{0,s}(T) = A_i^{(s)} + \frac{B_i^{(s)}}{T} \tag{1b}$$

This equation has been shown to be quite effective for representing limiting conductivities in pure nonaqueous solvents as a function of temperature.[4] For complex species, the limiting conductivity can be estimated using an equation previously developed by Anderko and Lencka,[1] i.e.

$$\lambda_{\text{complex}}^{0,s} = \frac{|z_{\text{complex}}|}{\left[\sum_{i=1}^{n}\left(\frac{|z_i|}{\lambda_i^{0,s}}\right)^3\right]^{1/3}} \tag{2}$$

where the $\lambda_i^{0,s}$ values are the limiting conductivities of the simple ions i that make up the complex.

For a mixed solvent, a mixing rule was introduced to relate the limiting ionic conductivity of the mixed solvent to those of the constituent pure solvents. Thus, the limiting conductivity of an ion i in a mixed solvent is represented by

$$\lambda_i^{0,\text{m}} = \sum_j \sum_k Y_j Y_k \lambda_{ijk} \tag{3}$$

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

$$\lambda_{ijk} = \frac{1}{2}(\lambda_i^{0,j} + \lambda_i^{0,k})(1 + k_{ijk}) \tag{4}$$

Y_j is a modified volume fraction of solvent j

$$Y_j = \frac{v_{ij}^* x_j}{\sum_l (v_{il}^* x_l)} \tag{5}$$

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

$$v_{ij}^* = v_j^0 + \sum_{k \neq j} x_k^{1/4} v_k^0 g_{ijk} \tag{6}$$

In eqs 3–6, $\lambda_i^{0,\text{m}}$ 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. The quantity v_{ij}^* can be interpreted as an effective molar volume of solvent j, which is affected by the presence of other solvents and the ion i in the mixture. 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 3 becomes a simple volume-fraction-averaged ideal mixing equation. The model uses only pure-liquid molar volumes and limiting ion conductivities in pure solvents. It can be applied to solvent mixtures of any composition.

Concentration Dependence of Electrical Conductivity

The MSA expressions derived by Bernard et al.[2] for the concentration dependence of electrical conductivity in electrolyte solutions are utilized in this work. The methodology developed by Anderko and Lencka[1] for treating higher electrolyte concentrations in aqueous solutions is also adopted, and an extension to mixed-solvent solutions is developed.

In the MSA expression, the electrical conductivity of an ion in a finite-concentration solution (λ_i) is related to the limiting conductivity of this ion (λ_i^0) by

$$\lambda_i = \lambda_i^0\left(1 + \frac{\delta v_i^{\text{el}}}{v_i^0}\right)\left(1 + \frac{\delta X}{X}\right) \tag{7}$$

where $\delta X/X$ is the relaxation effect, which describes the return to equilibrium after a perturbation by an external force, and $\delta v_i^{\text{el}}/v_i^0$ is the electrophoretic correction, which is due to the hydrodynamic interactions between the ions and solvent molecules. Detailed expressions for the relaxation and electrophoretic terms can be found

in Bernard et al.[2] and Anderko and Lencka.[1] Calculation of the conductivity of an electrolyte solution containing a cation i and an anion j using eq 7 requires (1) the limiting conductivities of both ions, λ_i^0 and λ_j^0; (2) the ionic radii, σ_i and σ_j; (3) the ionic charges, z_i and z_j; and (4) the dielectric constant and viscosity of the solvent. In a mixed-solvent electrolyte solution, the limiting ionic conductivities and the solvent properties (dielectric constant and viscosity) must pertain to those in the solvent mixture. These properties can be independently calculated. Specifically, the limiting ionic conductivities can be calculated using eqs 1−6, the dielectric constant can be computed as a function of temperature and solvent composition using a model described previously,[5] and the viscosity of the solvent mixture can be evaluated using a new model described in a separate paper.[6]

Because the expressions for $\delta X/X$ and $\delta v_i^{\text{el}}/v_i^0$ in the MSA conductivity model were obtained only for systems containing a single cation and a single anion, a technique for extending the model to multicomponent solutions was developed by Anderko and Lencka.[1] Anderko and Lencka[1] derived a mixing rule for predicting the electrical conductivities of multicomponent systems on the basis of the conductivities of the individual ions belonging to binary cation−anion pairs. Accordingly, the specific conductivity of a multicomponent electrolyte solution can be expressed as

$$\kappa = \sum_{k}^{N_{\text{T}}} c_k |z_k| \lambda_k \tag{8}$$

where N_{T} is the total number of ions and λ_k is the conductivity of the kth ion in a multicomponent solution. From the MSA theory, the conductivity of a cation i in the presence of an anion j and the conductivity of an anion j in the presence of a cation i can be calculated. These quantities can be denoted by $\lambda_{i(j)}$ and $\lambda_{j(i)}$, respectively. It was postulated[1] that λ_k in eq 8 can be approximated by an average value $\bar{\lambda}_k$, i.e.

$$\lambda_k \approx \bar{\lambda}_k \quad (k = i \text{ for a cation}, k = j \text{ for an anion}) \tag{9}$$

The average conductivity of the ith cation ($\bar{\lambda}_i$) is obtained by averaging over all anions that exist in the mixture, i.e.

$$\bar{\lambda}_i = \sum_{j}^{N_{\text{A}}} f_j \lambda_{i(j)}(I) \tag{10}$$

where N_{A} is the total number of anions, f_j is a fraction of the jth anion, and $\lambda_{i(j)}$ (i.e., the conductivity of cation i in the presence of anion j) is calculated at the ionic strength of the multicomponent mixture (I). Similarly, the average conductivity of the jth anion is obtained by averaging over all cations, i.e.

$$\bar{\lambda}_j = \sum_{i}^{N_{\text{C}}} f_i \lambda_{j(i)}(I) \tag{11}$$

where N_{C} is the number of cations, f_i is a fraction of the ith cation, and $\lambda_{j(i)}$ (i.e., the conductivity of anion j in the presence of cation i) is calculated at the same ionic strength I. To calculate the quantities $\lambda_{i(j)}$ and $\lambda_{j(i)}$ at the ionic strength of the mixture, eq 7 is applied at the

following concentrations of the ions in a binary pair $i−j$

$$c_i = \frac{2I}{|z_i|(|z_i| + |z_j|)} \qquad c_j = \frac{2I}{|z_j|(|z_i| + |z_j|)} \tag{12}$$

where I is the ionic strength, defined by

$$I = \frac{1}{2} \sum_i c_i z_i^2 \tag{13}$$

Equations 12 were derived to satisfy the condition of constant ionic strength. The definition of the fraction of the ith ion (f_i) in eqs 10 and 11 is given by

$$f_i = \frac{|z_i| c_i}{c_{\text{eq}}} \tag{14}$$

where the equivalent concentration c_{eq} is defined as

$$c_{\text{eq}} = \sum_i^{N_{\text{C}}} c_i |z_i| = \sum_j^{N_{\text{A}}} c_j |z_j| \tag{15}$$

Equations 9−15 make it possible to predict the conductivity of a multicomponent mixture from the conductivities of ions computed for binary subsystems containing a single cation and a single anion.

Effective Ionic Radii

For accurate modeling of electrical conductivity using the MSA model, the essential quantities are the ionic radii σ_i and σ_j. When these radii are approximated by crystallographic values,[2] the MSA model yields reasonable predictions for electrolyte concentrations up to ca. 1 mol·dm^{-3}. In general, a change in viscosity at higher concentrations entails a change in ionic mobility, which is a manifestation of the altered solvation structure around the ions and the short-range interactions between them. Therefore, the change in ionic environment necessitates the introduction of effective radii. Such radii are defined as a function of the ionic strength[1] and reflect the interactions between cations and anions. The use of effective radii makes it possible to reproduce experimental conductivity data for electrolyte concentrations up to 30 m in aqueous solutions. In a mixed-solvent electrolyte solution, the change in solvent composition must also be taken into account when the effective radius is defined because the changes in solvent properties such as viscosity and dielectric constant due to changing solvent composition can significantly alter the ion solvation and interactions. Additionally, when the electrolyte concentration approaches the limit of pure solute (e.g., at zero or low water contents in fully miscible acids), ion pairs become the predominant species. Consequently, interactions between ions and neutral species can significantly affect electrical conductivities.

An expression for the effective radii is necessarily empirical as there is no a priori relationship that would guide its functional form. Therefore, an expression is proposed in this study that is guided by the following assumptions:

(1) The effect of a single species k on the effective radius of ion i (i.e., $\sigma_{i,\text{eff}}$) can be reproduced by a binary interaction parameter σ_{ik}. If $i = k$, the binary parameter reduces to the crystallographic radius σ_i because self-interactions are not expected to affect the effective

Table 1. Model Parameters That Were Regressed to Reproduce Electrical Conductivities in Selected Systems[a]

parameter[b]	value	parameter[b]	value
	H_2SO_4 + Water		
	$T = 5-155$ °C, $x_{H_2SO_4} = 0.0009-0.948$		
$\sigma^{(00)}_{H_2O,H^+/HSO_4^-}$	$-0.581\,388$	$\sigma^{(00)}_{H_2SO_4,H^+/HSO_4^-}$	$7.283\,67$
$d^{(10)}_{H_2O,H^+/HSO_4^-}$	$0.734\,188$	$d^{(10)}_{H_2SO_4,H^+/HSO_4^-}$	$-3.856\,97$
$d^{(20)}_{H_2O,H^+/HSO_4^-}$	$-0.461\,635$	$d^{(20)}_{H_2SO_4,H^+/HSO_4^-}$	$-0.362\,234$
$d^{(30)}_{H_2O,H^+/HSO_4^-}$	$0.575\,414 \times 10^{-1}$	$d^{(30)}_{H_2SO_4,H^+/HSO_4^-}$	$0.519\,627 \times 10^{-1}$
$\sigma^{(01)}_{H_2O,H^+/HSO_4^-}$	$=0.214\,687 \times 10^{-2}$	$\sigma^{(01)}_{H_2SO_4,H^+/HSO_4^-}$	$-0.141\,873 \times 10^{-1}$
$d^{(11)}_{H_2O,H^+/HSO_4^-}$	$0.175\,727 \times 10^{-2}$	$d^{(11)}_{H_2SO_4,H^+/HSO_4^-}$	$-0.141\,982 \times 10^{-1}$
$d^{(21)}_{H_2O,H^+/HSO_4^-}$	$-0.343\,691 \times 10^{-3}$	$d^{(21)}_{H_2SO_4,H^+/HSO_4^-}$	$0.205\,181 \times 10^{-1}$
$d^{(31)}_{H_2O,H^+/HSO_4^-}$	$0.129\,864 \times 10^{-4}$	$d^{(31)}_{H_2SO_4,H^+/HSO_4^-}$	$-0.245\,287 \times 10^{-2}$
$\sigma^{(02)}_{H_2O,H^+/HSO_4^-}$	464.279	$\sigma^{(02)}_{H_2SO_4,H^+/HSO_4^-}$	-1724.49
$d^{(12)}_{H_2O,H^+/HSO_4^-}$	-160.763	$d^{(12)}_{H_2SO_4,H^+/HSO_4^-}$	1080.95
	H_3PO_4 + Water		
	$T = 0-60$ °C, $x_{H_3PO_4} = 0.000\,018\,1-0.859$		
$\sigma^{(00)}_{H_2O,H^+/H_2PO_4^-}$	$5.754\,38$	$\sigma^{(00)}_{H_2O,H^+/H_3PO_4}$	33.2661
$d^{(10)}_{H_2O,H^+/H_2PO_4^-}$	$-2.206\,13$	$d^{(10)}_{H_2O,H^+/H_3PO_4}$	$-6.359\,76$
$d^{(20)}_{H_2O,H^+/H_2PO_4^-}$	$-0.106\,620$	$d^{(20)}_{H_2O,H^+/H_3PO_4}$	$-2.276\,88$
$d^{(30)}_{H_2O,H^+/H_2PO_4^-}$	$0.170\,240 \times 10^{-1}$	$d^{(30)}_{H_2O,H^+/H_3PO_4}$	$0.733\,000$
$\sigma^{(01)}_{H_2O,H^+/H_2PO_4^-}$	$0.697\,842 \times 10^{-1}$	$\sigma^{(01)}_{H_2O,H^+/H_3PO_4}$	$0.601\,763$
$d^{(11)}_{H_2O,H^+/H_2PO_4^-}$	$0.938\,585 \times 10^{-2}$	$d^{(11)}_{H_2O,H^+/H_3PO_4}$	$0.142\,591$
$d^{(21)}_{H_2O,H^+/H_2PO_4^-}$	$-0.109\,473 \times 10^{-1}$	$d^{(21)}_{H_2O,H^+/H_3PO_4}$	$-0.761\,586 \times 10^{-1}$
$d^{(31)}_{H_2O,H^+/H_2PO_4^-}$	$0.366\,264 \times 10^{-5}$	$d^{(31)}_{H_2O,H^+/H_3PO_4}$	$0.469\,473 \times 10^{-2}$
$\sigma^{(00)}_{H_2O,H^+/H_2PO_4^+}$	$0.475\,721$	$\sigma^{(01)}_{H_2O,H_3PO_4/H^+}$	$0.101\,041 \times 10^{-1}$
$d^{(10)}_{H_2O,H^+/H_2PO_4^+}$	$4.269\,05$	$d^{(11)}_{H_2O,H_3PO_4/H^+}$	$0.203\,226 \times 10^{-1}$
$d^{(20)}_{H_2O,H^+/H_2PO_4^+}$	$-0.426\,664$	$d^{(21)}_{H_2O,H_3PO_4/H^+}$	$-0.648\,802 \times 10^{-2}$
$d^{(30)}_{H_2O,H^+/H_2PO_4^+}$	$-0.156\,167$	$d^{(31)}_{H_2O,H_3PO_4/H^+}$	$-0.433\,764 \times 10^{-3}$
	HNO_3 + Water		
	$T = 0-50$ °C, $x_{HNO_3} = 0.009-0.982$		
$\sigma^{(00)}_{H_2O,H^+/NO_3^-}$	$1.285\,55$	$\sigma^{(00)}_{HNO_3,H^+/NO_3^-}$	$0.901\,991$
$d^{(10)}_{H_2O,H^+/NO_3^-}$	$-0.334\,609$	$d^{(10)}_{HNO_3,H^+/NO_3^-}$	$2.621\,42$
$d^{(20)}_{H_2O,H^+/NO_3^-}$	$-0.288\,606$	$d^{(30)}_{HNO_3,H^+/NO_3^-}$	$-1.522\,47$
$d^{(30)}_{H_2O,H^+/NO_3^-}$	$0.420\,231 \times 10^{-1}$	$d^{(30)}_{HNO_3,H^+/NO_3^-}$	$0.515\,359 \times 10^{-1}$
$\sigma^{(01)}_{H_2O,H^+/NO_3^-}$	$0.196\,941 \times 10^{-3}$	$\sigma^{(01)}_{HNO_3,H^+/NO_3^-}$	$-0.953\,599 \times 10^{-2}$
$d^{(11)}_{H_2O,H^+/NO_3^-}$	$-0.219\,318 \times 10^{-2}$	$d^{(11)}_{HNO_3,H^+/NO_3^-}$	$-0.313\,053 \times 10^{-1}$
$d^{(21)}_{H_2O,H^+/NO_3^-}$	$0.127\,321 \times 10^{-2}$	$d^{(21)}_{HNO_3,H^+/NO_3^-}$	$0.264\,257 \times 10^{-1}$
$d^{(31)}_{H_2O,H^+/NO_3^-}$	$-0.212\,897 \times 10^{-4}$	$d^{(31)}_{HNO_3,H^+/NO_3^-}$	-0.388565×10^{-2}
	$LiPF_6$ + Propylene Carbonate (PC) + Diethyl Carbonate (DEC)		
	$T = 0-59$ °C, $m_{LiPF_6} = 0.01-3.44$ mol·kg^{-1}, $x_{DEC} = 0-0.9$ (salt-free)		
$\sigma^{(00)}_{PC,Li^+/PF_6^-}$	$0.209\,263$	$\sigma^{(00)}_{PC,Li^+/PF_6^-}$	$4.099\,32$
$d^{(10)}_{PC,Li^+/PF_6^-}$	$0.208\,384$	$d^{(10)}_{PC,Li^+/PF_6^-}$	$1.182\,55$
$d^{(20)}_{PC,Li^+/PF_6^-}$	$0.133\,393$	$d^{(20)}_{PC,PF_6^-/Li^+}$	$-0.182\,351$
$d^{(30)}_{PC,Li^+/PF_6^-}$	$0.267\,370$	$d^{(30)}_{PC,PF_6^-/Li^+}$	$0.609\,729 \times 10^{-1}$
$\sigma^{(01)}_{PC,Li^+/PF_6^-}$	$-0.172\,421 \times 10^{-2}$	$\sigma^{(01)}_{PC,PF_6^-/Li^+}$	$-0.475\,358 \times 10^{-1}$
$d^{(11)}_{PC,Li^+/PF_6^-}$	$0.658\,696 \times 10^{-2}$	$d^{(11)}_{PC,PF_6^-/Li^+}$	$-0.239\,846 \times 10^{-1}$
$d^{(21)}_{PC,Li^+/PF_6^-}$	$-0.215\,887 \times 10^{-2}$	$d^{(21)}_{PC,PF_6^-/Li^+}$	$0.253\,925 \times 10^{-1}$
$d^{(31)}_{PC,Li^+/PF_6^-}$	$-0.202\,905 \times 10^{-2}$	$d^{(31)}_{PC,PF_6^-/Li^+}$	$-0.574\,336 \times 10^{-2}$
$\sigma^{(00)}_{DEC,Li^+/PF_6^-}$	$0.838\,953 \times 10^{-1}$	$\sigma^{(00)}_{DEC,PF_6^-/Li^+}$	$0.239\,880$
$d^{(10)}_{DEC,Li^+/PF_6^-}$	$3.972\,52$	$d^{(10)}_{DEC,PF_6^-/Li^+}$	$6.977\,89$
$d^{(20)}_{DEC,Li^+/PF_6^-}$	$0.336\,317$	$d^{(20)}_{DEC,PF_6^-/Li^+}$	$-4.165\,68$
$d^{(30)}_{DEC,,Li^+/PF_6^-}$	$-0.903\,422$	$d^{(30)}_{DEC,PF_6^-/Li^+}$	$-0.477\,459 \times 10^{-1}$
$\sigma^{(01)}_{DEC,Li^+/PF_6^-}$	$-0.559\,836 \times 10^{-3}$	$\sigma^{(01)}_{DEC,PF_6^-/Li^+}$	$-0.600\,351 \times 10^{-2}$
$d^{(11)}_{DEC,Li^+/PF_6^-}$	$0.348\,269 \times 10^{-1}$	$d^{(11)}_{DEC,PF_6^-/Li^+}$	$0.650\,491 \times 10^{-1}$
$d^{(21)}_{DEC,Li^+/PF_6^-}$	$-0.599\,332 \times 10^{-1}$	$d^{(21)}_{DEC,Li^+/PF_6^-}$	$-0.962\,292 \times 10^{-1}$
$d^{(31)}_{DEC,Li^+/PF_6^-}$	$0.206\,427 \times 10^{-1}$	$d^{(31)}_{DEC,Li^+/PF_6^-}$	$0.28\,919 \times 10^{-1}$

Table 1 (Continued)

parameter[b]	value	parameter[b]	value
$AgNO_3 + TlNO_3 + Water$ $T = 75-113\ °C, x_w = 0.0-0.98$			
$\sigma^{(00)}_{H_2O,Ag^+/NO_3^-}$	0.448 650	$\sigma^{(00)}_{H_2O,Tl^+/NO_3^-}$	0.442 757
$d^{(10)}_{H_2O,Ag^+/NO_3^-}$	0.063 861 8	$d^{(10)}_{H_2O,Tl^+/NO_3^-}$	0.102 618
$d^{(20)}_{H_2O,Ag^+/NO_3^-}$	$0.131\ 682 \times 10^{-1}$	$d^{(20)}_{H_2O,Tl^+/NO_3^-}$	$-0.123\ 221 \times 10^{-1}$
$d^{(30)}_{H_2O,Ag^+/NO_3^-}$	$-0.120\ 046 \times 10^{-2}$	$d^{(30)}_{H_2O,Tl^+/NO_3^-}$	$0.330\ 937 \times 10^{-2}$
$\sigma^{(01)}_{H_2O,Ag^+/NO_3^-}$	$-0.657\ 300 \times 10^{-5}$	$\sigma^{(01)}_{H_2O,Tl^+/NO_3^-}$	$0.717\ 602 \times 10^{-3}$
$d^{(11)}_{H_2O,Ag^+/NO_3^-}$	$0.929\ 198 \times 10^{-3}$	$d^{(11)}_{H_2O,Tl^+/NO_3^-}$	$-0.637\ 745 \times 10^{-3}$
$d^{(21)}_{H_2O,Ag^+/NO_3^-}$	$0.148\ 270 \times 10^{-5}$	$d^{(21)}_{H_2O,Tl^+/NO_3^-}$	$0.182\ 157 \times 10^{-3}$
$\sigma^{(00)}_{H_2O,Ag^+/Tl^+}$	0.892 065	$\sigma^{(01)}_{H_2O,Ag^+/Tl^+}$	$0.188\ 269 \times 10^{-2}$
$d^{(10)}_{H_2O,Ag^+/Tl^+}$	$-0.117\ 887$	$d^{(11)}_{H_2O,Ag^+/Tl^+}$	$-0.474\ 483 \times 10^{-2}$
$d^{(20)}_{H_2O,Ag^+/Tl^+}$	$0.389\ 065 \times 10^{-1}$	$d^{(21)}_{H_2O,Ag^+/Tl^+}$	$0.916\ 788 \times 10^{-3}$
$d^{(30)}_{H_2O,Ag^+/Tl^+}$	$0.354\ 742 \times 10^{-2}$		

[a] Experimental conductivity data under the indicated conditions were used to determine the parameters. [b] Units for the parameters are as follows: $\sigma^{(00)}$ in Å, $\sigma^{(01)}$ in Å·K^{-1}, $\sigma^{(02)}$ in Å·K; $d^{(10)}$ in (mol·L^{-1})$^{-0.2}$, $d^{(20)}$ in (mol·L^{-1})$^{-0.6}$, $d^{(30)}$ in (mol·L^{-1})$^{-1.2}$; $d^{(11)}$ in (mol·L^{-1})$^{-0.2}$·K^{-1}, $d^{(21)}$ in (mol·L^{-1})$^{-0.6}$·K^{-1}, $d^{(31)}$ in (mol·L^{-1})$^{-1.2}$·K^{-1}; $d^{(12)}$ in (mol·L^{-1})$^{-0.2}$·K, $d^{(22)}$ in (mol·L^{-1})$^{-0.6}$·K, $d^{(32)}$ in (mol·L^{-1})$^{-1.2}$·K.

radius. Similarly, the binary interaction parameter between an ion and a solvent molecule (e.g., σ_{ion,H_2O}) ordinarily reduces to the crystallographic radius because this interaction corresponds to an ion placed in a dilute solution environment. This assumption is justified by the fact that ionic radii are appropriate in dilute solutions (up to ca. 1 M) although some exceptions can be made if warranted by the chemistry. On the other hand, the binary interaction parameters between ions (e.g., $\sigma_{cation,anion}$) are expected to deviate from the crystallographic radii because they reflect interactions in concentrated solutions between solvated ions.

(2) The binary interaction parameters between unlike ions might not be symmetrical (i.e., $\sigma_{cation,anion}$ is not necessarily equal to $\sigma_{anion,cation}$). This is due to the fact that the effect of a given anion on a given central cation is expected to be different from the effect of the same cation on a central anion.

(3) The effective radius should be obtained as a weighted average of the interaction parameters. The weighting should be performed according to the concentrations of the ions and neutral molecules in a system.

Thus, taking into consideration all short-range interactions, i.e., ion/ion, ion/ion pair, and ion/solvent, we define the effective radii for each cation (i)−anion (j) pair as

$$\sigma_{i,\text{eff}} = \sigma_{i,j}\frac{\sum_k c_k\sigma_{k,i}}{\sum_k c_k\sigma_{i,k}} \quad (16)$$

$$\sigma_{j,\text{eff}} = \sigma_{i,j}\frac{\sum_k c_k\sigma_{k,j}}{\sum_k c_k\sigma_{j,k}} \quad (17)$$

where the sum over k covers all species in the solution (i.e., ions, ion pairs, and solvent molecules) and c_k is the concentration (in mol·dm^{-3}) of species k. The parameter $\sigma_{i,j}$ (and similarly $\sigma_{i,k}$, $\sigma_{k,i}$, $\sigma_{j,k}$, and $\sigma_{k,j}$) can be interpreted as the effective radius of species i in the presence of species j, reflecting the short-range interactions between the two species. Compared with the previously devel-
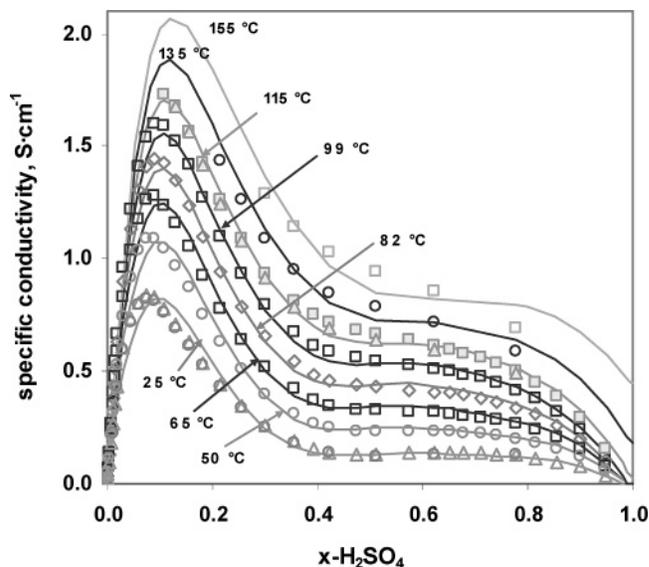

Figure 1. Results of modeling conductivities of aqueous H_2SO_4 at various temperatures. Experimental data were taken from Lobo.[8] The lines were calculated using the new model.

oped model for electrical conductivities of aqueous solutions,[1] the ionic radii defined in eqs 16 and 17 introduce additional binary parameters involving ion pairs and solvent molecules. The binary parameter between ions i and j is then defined as a function of the ionic strength, I

$$\sigma_{i,j} = \sigma^0_{i,j}\exp\lfloor I^{0.2}(d_{1,ij} + d_{2,ij}I^{0.4} + d_{3,ij}I)\rfloor \quad (18)$$

The values of $\sigma^0_{i,j}$, $d_{1,ij}$, $d_{2,ij}$, and $d_{3,ij}$ are linearly dependent on solvent composition and are calculated as

$$\sigma^0_{i,j} = \sum_L^{N_S} x_L\sigma^{(0)}_{L,ij} \quad (19)$$

and

$$d_{m,ij} = \sum_L^{N_S} x_L d^{(m)}_{L,ij} \quad (m = 1-3) \quad (20)$$

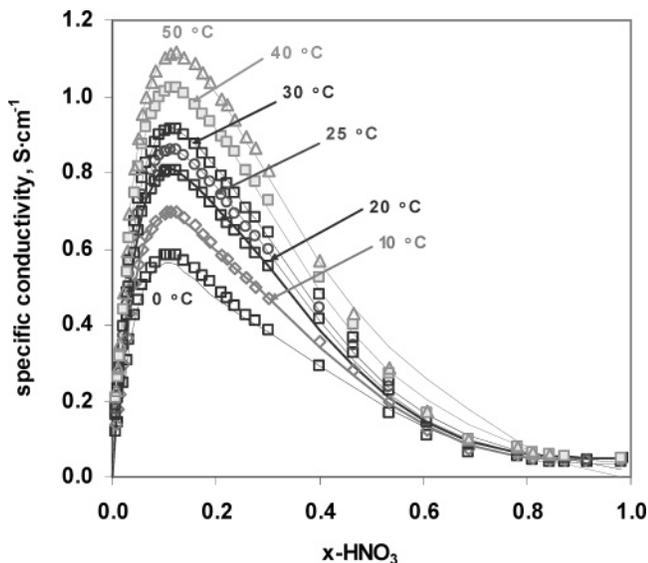where x_L is the mole fraction of solvent L on a solute-

Figure 2. Results of modeling conductivities of aqueous HNO_3 at various temperatures. Experimental data were taken from Lobo.[8] The lines were calculated using the model.
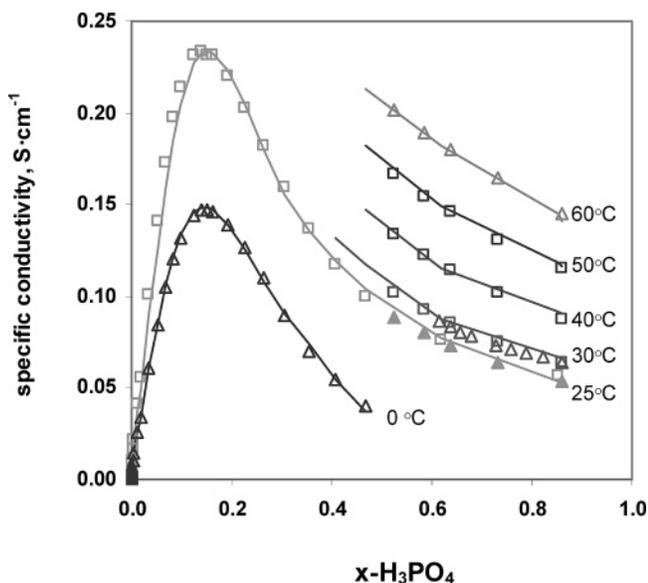

Figure 3. Results of modeling conductivities of aqueous H_3PO_4 at various temperatures. Experimental data were taken from Lobo[8] and Wydeven.[11] The lines were calculated using the model.

Table 2. Model Parameters That Were Regressed to Reproduce Electrical Conductivities in Weakly Ionized Systems: Acetic Acid and Formic Acid[a]

parameter(s)[b]	value
Acetic Acid + Water	
$T = 15-55$ °C, $x_{HAc} = (5.1 \times 10^{-7})-0.992$	
$k^{(0)}_{H^+,H_2O,HAc} = k^{(0)}_{Ac^-,H_2O,HAc}$	-1.99755
$k^{(1)}_{H^+,H_2O,HAc} = k^{(1)}_{Ac^-,H_2O,HAc}$	289.776
$g^{(0)}_{H^+,H_2O,HAc} = g^{(0)}_{Ac^-,H_2O,HAc}$	1.25577
$g^{(1)}_{H^+,H_2O,HAc} = g^{(1)}_{Ac^-,H_2O,HAc}$	-411.249
Formic Acid + Water	
$T = 15-55$ °C, $x_{HCOOH} = (1.94 \times 10^{-5})-0.783$	
$k^{(0)}_{H^+,H_2O,HCOOH} = k^{(0)}_{HCOO^-,H_2O,HCOOH}$	1.63125
$k^{(1)}_{H^+,H_2O,HCOOH} = k^{(1)}_{HCOO^-,H_2O,HCOOH}$	-427.902
$g^{(0)}_{H^+,H_2O,HCOOH} = g^{(0)}_{HCOO^-,H_2O,HCOOH}$	-0.517401×10^{-1}
$g^{(1)}_{H^+,H_2O,HCOOH} = g^{(1)}_{HCOO^-,H_2O,HCOOH}$	-86.1264
$\sigma^{(00)}_{H_2O,H^+/HCOO^-}$	2.65134

[a] Experimental conductivity data under the indicated conditions were used to determine the parameters. [b] Units for the parameters are as follows: $k^{(0)}$ and $g^{(0)}$, dimensionless; $k^{(1)}$ and $g^{(1)}$, K; $\sigma^{(00)}$, Å.
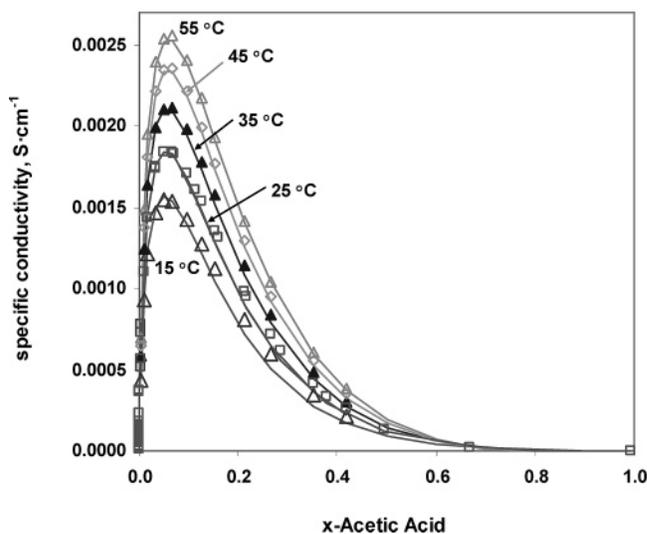

Figure 4. Results of modeling conductivities of the acetic acid + H_2O system at various temperatures. Experimental data were taken from Lobo,[8] and the lines were calculated using the model.

free basis and the sums are over all solvent components. In eqs 19 and 20, $\sigma^{(0)}_{L,ij}$ and $d^{(m)}_{L,ij}$ are adjustable parameters that can be determined from experimental conductivity data. The selection of a linear solvent composition dependence in $\sigma^0_{i,j}$, $d_{1,ij}$, $d_{2,ij}$, and $d_{3,ij}$ was a simplification for calculating the effective radii in a mixed-solvent environment. The default values for $\sigma_{i,k}$ and $\sigma_{k,i}$ are the crystallographic radii (in Å) of i and k (the first species in the subscripts, i.e., i for i,k and k for k,i), respectively, if i and k are ions and are set equal to 1 Å if the first subscript species is neutral (ion pairs or solvent molecules).

Results and Discussion

The performance of the model described above was tested using experimental data for a number of aqueous, nonaqueous, and mixed-solvent electrolyte systems over wide ranges of temperature and concentration. The limiting conductivity model for mixed solvents was previously shown to give results that are in excellent agreement with experimental values.[4] Thus, the validation of the new electrical conductivity model was focused on the conductivities at finite electrolyte concentrations. Speciation data required by the conductivity model are calculated from the recently developed thermodynamic model for mixed-solvent electrolyte solutions.[7] Experimental data for the following types of systems have been used to test the model: (i) aqueous fully miscible acids with strong dissociation/association effects, such as HNO_3 + water, H_2SO_4 + water, and H_3PO_4 + water; (ii) fully miscible acids that show weak ionization, such as acetic acid + water and formic acid + water; (iii) aqueous electrolytes ranging from dilute solutions to the fused salt limit, such as the $AgNO_3$ + $TlNO_3$ + water system; and (iv) electrolytes in organic or mixed solvents, such as $MgCl_2$ (or $MgSO_4$) + ethanol + H_2O and $LiPF_6$ (or $LiClO_4$) + propylene carbonate + diethyl carbonate.
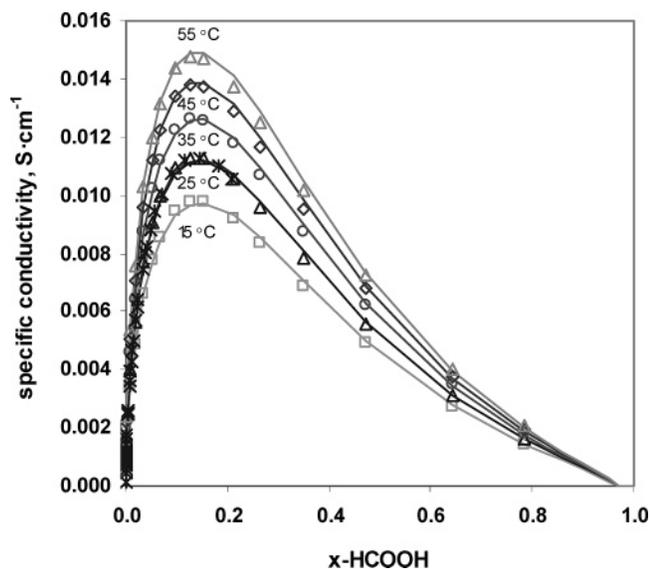
Figure 5. Results of modeling conductivities of the formic acid + H_2O system at various temperatures. Experimental data were taken from Lobo,[8] and the lines were calculated using the model.
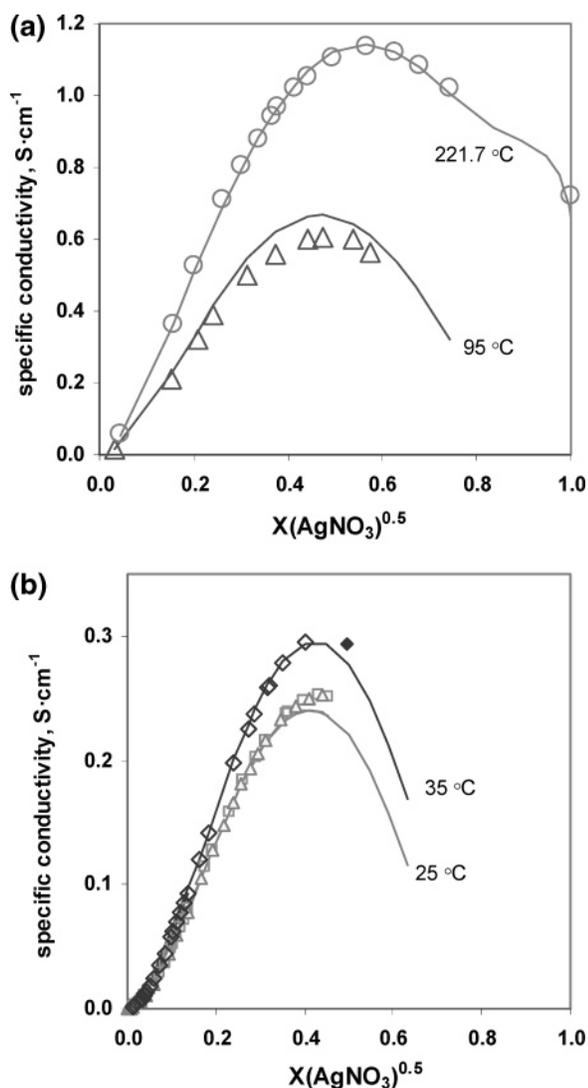

Figure 6. Conductivity results for the $AgNO_3$ + H_2O system at various temperatures. Experimental data were taken from Lobo.[8] The lines were calculated using the model.

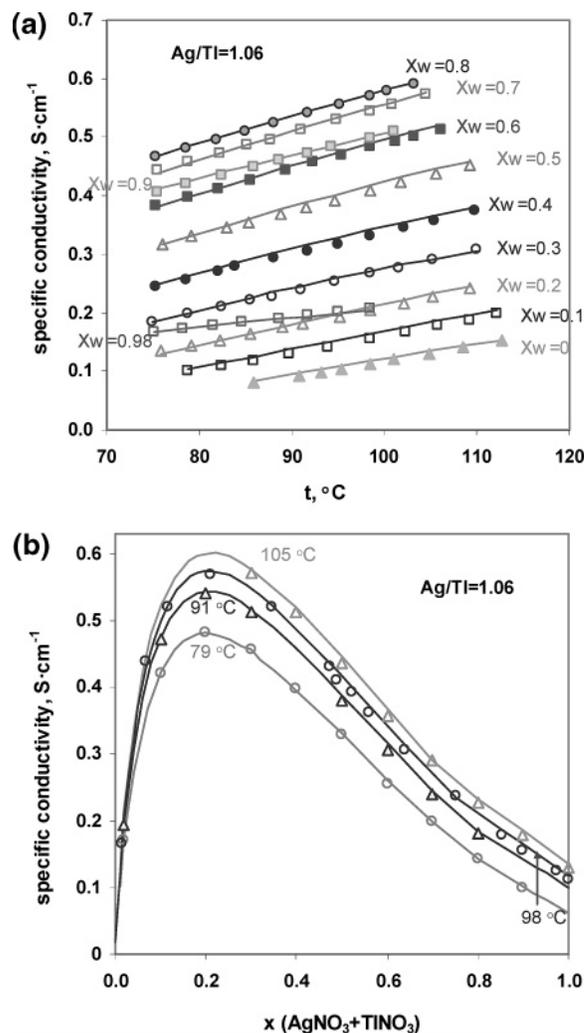When experimental conductivity data cover a wide range of temperatures, it was found that they can be

Figure 7. Conductivity results for the $AgNO_3$ + $TlNO_3$ + H_2O system (Ag/Tl = 1.06) as a function of (a) temperature at various water contents and (b) total mole fraction of $AgNO_3$ + $TlNO_3$ at various temperatures. Experimental data were taken from Abraham and Abraham.[9,10] The lines were calculated using the model.

best represented if $\sigma_{L,ij}^{(0)}$ and $d_{L,ij}^{(m)}$ in eqs 19 and 20 are expressed as

$$\sigma_{L,ij}^{(0)} = \sigma_{L,ij}^{(00)} + \sigma_{L,ij}^{(01)}(T - 298.15) + \sigma_{L,ij}^{(02)}/T \quad (21a)$$

and

$$d_{L,ij}^{(m)} = d_{L,ij}^{(m0)} + d_{L,ij}^{(m1)}(T - 298.15) + d_{L,ij}^{(m2)}/T$$
$$(m = 1-3) \quad (21b)$$

In most cases, only the first two terms (i.e., up to linear temperature dependence) are necessary. Table 1 lists parameters obtained by regressing experimental data for selected systems.

Aqueous Fully Miscible Acids with Strong Dissociation/Association Effects. When modeling systems of this type, both water and the undissociated acid (e.g., $H_2SO_4^0$, $H_3PO_4^0$, or HNO_3^0) are treated as solvent components. In such systems, speciation can change dramatically as acid concentration increases, and a significant amount of neutral acid molecules might exist as the acid concentration approaches a mole fraction of 1. Details of speciation for modeling systems such as H_2SO_4 + H_2O and H_3PO_4 + H_2O are given elsewhere.[7] Although several species have been taken into account
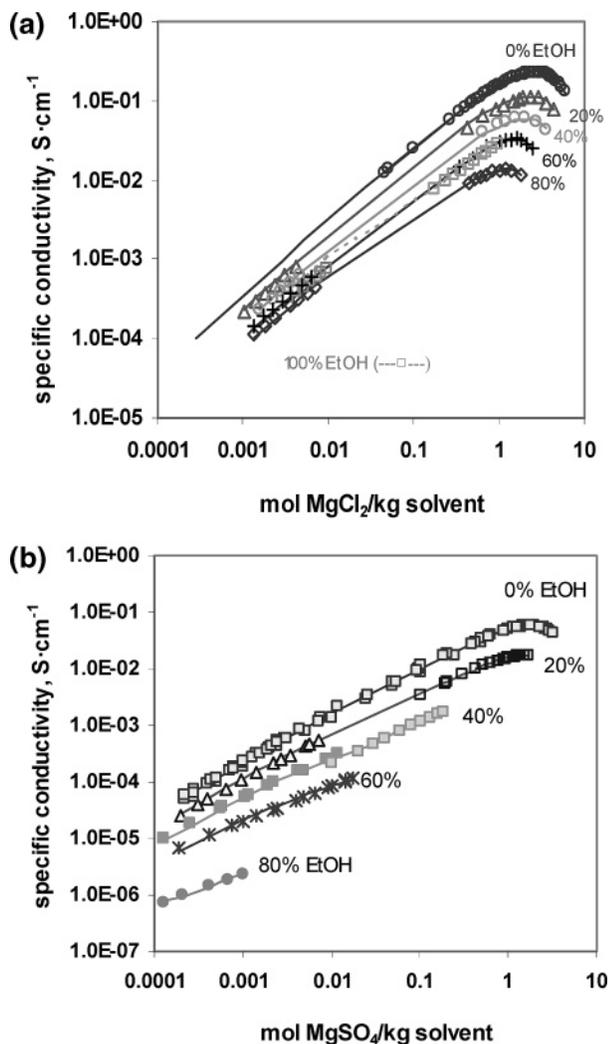
Figure 8. Specific conductivities of (a) the $MgCl_2$ + ethanol + H_2O system at 45 °C[12,14,15] and (b) the $MgSO_4$ + ethanol + H_2O system at 25 °C.[13,14] The lines were calculated using the model.

in speciation calculations, only interactions between the predominant ions or neutral species are necessary in modeling electrical conductivities. Specifically, only interactions between H^+ and $H_2PO_4^-$ and between H^+ and $H_3PO_4^0$ are introduced for modeling conductivities in the H_3PO_4 + H_2O system, although other species resulting from stepwise dissociation, HPO_4^{2-} and PO_4^{3-}, are also included in the thermodynamic model.[7b] Similarly, the relevant binary parameters are for H^+ and HSO_4^- in the H_2SO_4 + H_2O system and for H^+ and NO_3^- in the HNO_3 + H_2O system. For example, the parameters introduced for modeling electrical conductivity in the H_2SO_4 + H_2O system are $\sigma_{H_2O,H^+/HSO_4^-}^{(0)}$, $d_{H_2O,H^+/HSO_4^-}^{(m)}$ and $\sigma_{H_2SO_4,H^+/HSO_4^-}^{(0)}$, $d_{H_2SO_4,H^+/HSO_4^-}^{(m)}$ (including their temperature dependence). Figures 1–3 show the results of modeling conductivities in the systems H_2SO_4 + H_2O, HNO_3 + H_2O, and H_3PO_4 + H_2O using the parameters given in Table 1. It should be noted that, once the thermodynamic model is revised to include more detailed information on speciation (e.g., to include the dimeric species $H_2P_2O_7^{2-}$, $HP_2O_7^{3-}$, $P_2O_7^{4-}$ and $H_5P_2O_8^-$ in the H_3PO_4 + H_2O system or NO_2^+ from the dissociation/self-dehydration of nitric acid in the HNO_3 + H_2O system) or to update thermochemical data associated with the species, the conductivity model parameters must be updated to reflect such changes.
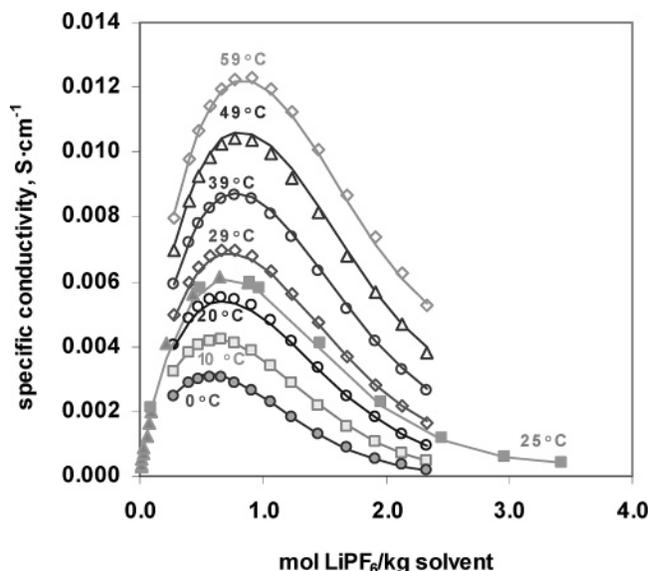

Figure 9. Specific conductivities of the $LiPF_6$ + propylene carbonate system at various temperatures. Experimental data were taken from Ding et al.,[16] Kondo et al.,[17] and Christie and Vincent.[18] The lines were calculated using the model.

Weakly Ionized, Fully Miscible Acids. Acids of this type weakly dissociate, and the concentrations of ions are small over the entire concentration range from pure water to pure acid. Because of the low ionic strength in such systems, the total electrical conductivity is primarily determined by the limiting conductivities of ions in solvent mixtures containing water and an undissociated acid. For example, in the acetic acid + water system, the maximum ionic strength over the entire composition range ($x_{acid} = 0–1$) is only 6×10^{-4} in mole fraction units or 1×10^{-2} mol·dm^{-3} at 25 °C, based on the speciation analysis obtained from a recently developed thermodynamic model.[7] At the same temperature, the maximum ionic strength of the formic acid + water system is 2.5×10^{-3} in mole fraction units or 6.5×10^{-2} mol·dm^{-3}. Thus, only the limiting ionic conductivity model (eqs 3–6) with appropriate mixing rule parameters (g_{ijk} and k_{ijk}) is necessary in practice for modeling conductivity in the acetic acid + water system. For the formic acid + water system, only a single temperature-independent parameter, $\sigma_{H_2O,H^+/COOH^-}^{(00)}$ was adjusted, in addition to the limiting conductivity mixing rule parameters. The parameters obtained for the acidic acid + water and formic acid + water systems are listed in Table 2. The results of modeling these two systems are shown in Figures 4 and 5 and demonstrate excellent agreement between the experimental and calculated values.

Aqueous Electrolytes from Dilute Solutions to the Fused Salt Limit. For aqueous electrolyte solutions, the only difference between the present model and the model previously developed for aqueous-only solutions[1] is the use of different expressions for the effective ionic radii. The effectiveness of using the new expressions (eqs 16–18) was verified by excellent fits obtained for a number of aqueous electrolyte systems. These results are identical to or better than those obtained using the Anderko–Lencka[1] expression for aqueous electrolyte solutions with concentrations up to 30 m. Thus, we are focusing here on systems for which experimental data cover concentration ranges well beyond the 30 m limit. Experimental measurements of
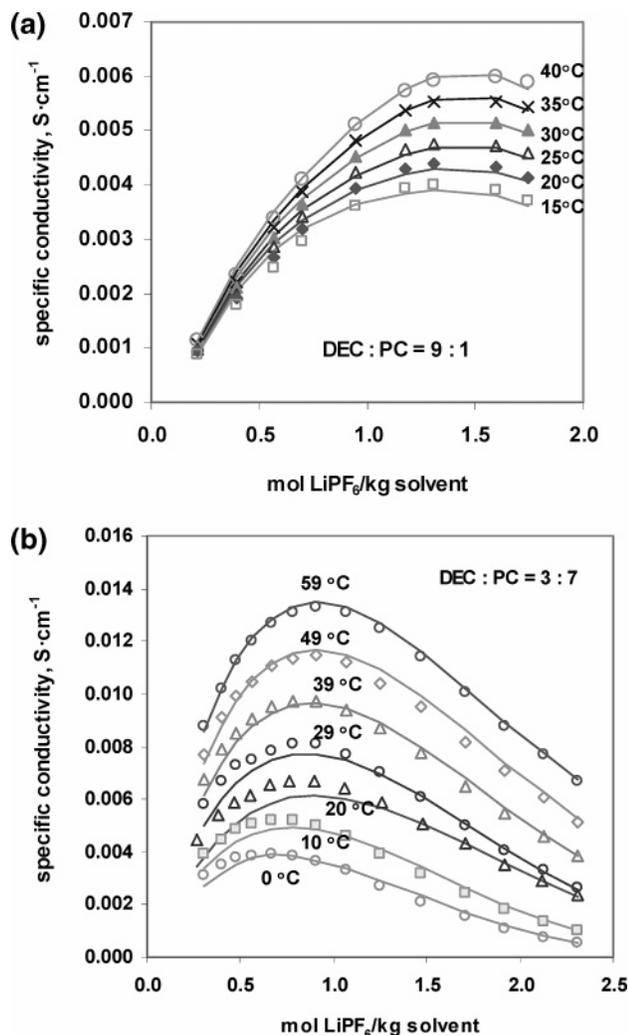
Figure 10. Specific conductivities of the $LiPF_6$ + diethyl carbonate (DEC) + propylene carbonate (PC) system at various temperatures and two solvent compositions: (a) x(DEC) = 0.9[19] and (b) x(DEC) = 0.3.[16] The lines were calculated using the model.

Abraham and Abraham[9,10] for the $AgNO_3$ + $TlNO_3$ + H_2O system and the results for the $AgNO_3$ + H_2O binary system from Lobo's compilation[8] provide excellent sources of data for this purpose. Figures 6 and 7 show an excellent agreement between these data and the modeling results for these two systems over the entire range of electrolyte concentration at various temperatures.

Electrolytes in Organic or Mixed Solvents. Several systems of this type were selected for the verification of the new model. Data for these systems cover extended ranges of temperature, electrolyte concentration, and solvent composition. Figure 8 shows a comparison between experimental data and calculated results for the $MgCl_2$ + ethanol + H_2O and $MgSO_4$ + ethanol + H_2O systems at various solvent compositions as a function of salt concentration. Figure 9 shows the results for the system $LiPF_6$ + propylene carbonate. Predictions for the system $LiPF_6$ + propylene carbonate + diethyl carbonate are shown in Figure 10 at two different solvent compositions. Finally, Figure 11 shows the results of calculations for the $LiClO_4$ + diethyl carbonate + propylene carbonate system at a fixed $LiClO_4$ concentration of 1.7 m and at various solvent compositions. All of these results indicate that the new model is capable of accurately reproducing experimental
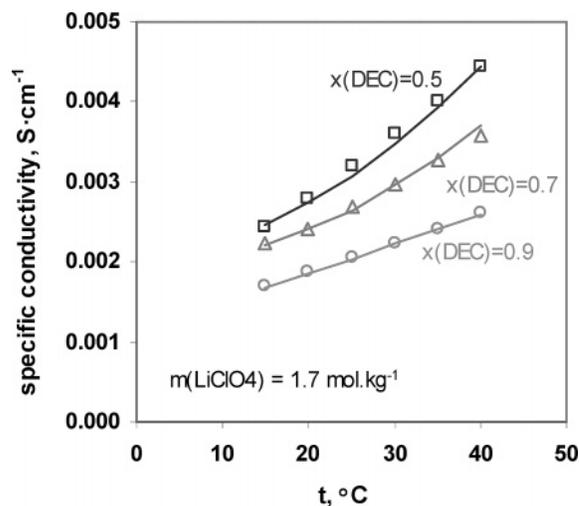

Figure 11. Specific conductivity of the $LiClO_4$ + diethyl carbonate (DEC) + propylene carbonate (PC) system as a function of temperature at a fixed $LiClO_4$ concentration of 1.7 $mol \cdot kg^{-1}$ and at various solvent compositions. Experimental data were taken from Moumouzias et al.[19] The lines were calculated using the model.

electrical conductivities over wide ranges of solvent composition and electrolyte concentration.

Conclusions

A comprehensive model has been developed for the computation of electrical conductivities in aqueous or mixed-solvent, dilute or concentrated electrolyte solutions. The model consists of two distinct parts, i.e., a correlation for calculating ionic conductivities at infinite dilution as a function of temperature and solvent composition and a model for the effect of finite electrolyte concentrations. To capture the effect of electrolyte concentration on electrical conductivity in mixed-solvent environments, the model utilizes the MSA expressions derived by Bernard et al.[2] and the methodology of Anderko and Lencka[1] for predicting the conductivities of multicomponent system on the basis of the conductivities of binary cation−anion subsystems. An extension of this methodology to mixed-solvent systems has been developed by introducing additional ionic interaction parameters involving solvent molecules and ion pairs. These parameters determine the effective ionic radii and, subsequently, shape the concentration dependence of the conductivity. The conductivity model was coupled with a previously developed thermodynamic equilibrium model[7] to provide the concentratiosn of free ions that are necessary for conductivity calculations. In all cases in which experimental data are available, the new conductivity model was shown to be accurate for reproducing electrical conductivities over wide ranges of composition with respect to both solvents and electrolytes. The model was implemented in software for simulating both thermodynamic and transport properties of electrolyte systems.

Acknowledgment

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