Modeling Thermal Conductivity of Concentrated and Mixed-Solvent Electrolyte Systems

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A comprehensive model has been developed for calculating the thermal conductivity of aqueous, nonaqueous, and mixed-solvent electrolyte systems ranging from dilute solutions to fused salts or pure solutes. The model consists of a correlation for calculating the thermal conductivity of solvent mixtures and a method for predicting the effect of electrolyte components. The thermal conductivity of multicomponent solvent mixtures can be represented using surface area parameters and thermal conductivities of pure solvents in conjunction with a single binary parameter per solvent pair. The effect of electrolytes is modeled by accounting for a contribution of individual ions, which is quantified by the Riedel coefficients, and a contribution of specific interactions between ions or neutral species. Formulations have been developed for the contributions of individual ions and species−species interactions to represent the effect of multiple solvents. In addition to solvent composition, the species−species interaction term is also a function of ionic strength. The model accurately reproduces experimental thermal conductivity data over a wide range of electrolyte concentrations in aqueous and nonaqueous systems. In particular, the model has been shown to be accurate for aqueous acids and bases (e.g., H_2SO_4, HNO_3, H_3PO_4, NaOH, and KOH) up to the limit of a pure acid or base, various nitrates ranging from dilute solutions to fused salts, and other salts in water and various organic solvents. The model has been coupled with thermodynamic equilibrium calculations to reproduce the effects of complexation or other ionic reactions on thermal conductivity.

Introduction

The thermal conductivity of electrolyte solutions plays a significant role in the chemical process industry and various geological and engineering applications because of the importance of heat transfer in a multitude of processes. The design and optimization of various processes and devices such as those used in refrigeration, in geothermal power generation, and in chemical plants utilizing seawater as a cooling medium require a detailed knowledge of thermal conductivity in electrolyte solutions.[1] Increasing attention has been focused on detailed studies of thermal conductivity of electrolyte solutions, as reflected by the large number of experimental results published in recent years. Therefore, accurate models for representing thermal conductivities of electrolyte solutions are highly desirable. However, analysis of experimental data has been commonly performed only on a case-by-case basis and no attempt has been made so far to develop a comprehensive thermal conductivity model for mixed-solvent electrolyte systems.

The existing models for the thermal conductivity of electrolyte solutions have been designed mainly for salt + solvent binary systems and are applicable only up to moderate concentrations. A theoretical equation for the contribution of interionic forces to the thermal conductivity of dilute electrolyte solutions was derived by Bearman[2,3] based on the Debye−Hückel−Onsager−Falkenhagen model. This equation predicts that the contribution of long-range electrostatic forces to thermal conductivity is a function of κ_D^3 (where κ_D is the inverse Debye length) or, equivalently, $c^{3/2}$. However, Bearman[2] noted that even in the concentration range where the Debye−Hückel model is valid this ion−ion interaction contribution does not have a "measurable" effect on the overall thermal conductivity due to the fact that the contribu-

tions of other effects are much greater and vary as a function of κ_D^2 (or c). Such behavior is quite different from that found for the viscosity and, especially, electrical conductivity of dilute electrolyte solutions. Thus, in practice, the thermal conductivity of electrolyte solutions has been reproduced by empirical or semiempirical correlations. The published correlation methods have been reviewed by Horvath[1] and Corti et al.[4]

The most widely used expression is that of Riedel,[5] which is a simple linear expansion in terms of molar concentrations:

$$\lambda = \lambda_{H_2O}^0 + \sum_i \alpha_i c_i \tag{1}$$

where $\lambda_{H_2O}^0$ is the thermal conductivity of pure water, c_i is the molar concentration of ion i, and α_i is the contribution of ion i. This equation is a statement of the additivity of individual ionic contributions in dilute solutions and is analogous to the Jones−Dole[6] equation for viscosity. Although the Riedel equation is applicable to multicomponent systems and can be used for dilute and moderately concentrated electrolyte solutions with good accuracy, it fails to represent experimental data over extended concentration ranges such as those commonly encountered for concentrated acids or alkaline solutions of NaOH or KOH. Also, it is not accurate for systems that show more complicated trends with changing concentrations, such as the aqueous solutions of NaF where the thermal conductivity increases first with concentration and then decreases. For the cases of NaOH and KOH, Riedel[7] extended his equation to include an extra term $\varphi(c)$ and evaluated this term at various concentrations of the bases.

Alternative approaches to modeling thermal conductivity include the use of the concept of "apparent molar thermal conductivity" in analogy to apparent molar thermodynamic quantities (e.g., volumes and heat capacities). This quantity was related to $c^{1/2}$ through a linear equation.[8,9] Also, Vargaftik and Os'minin[10] developed a method that relates the thermal

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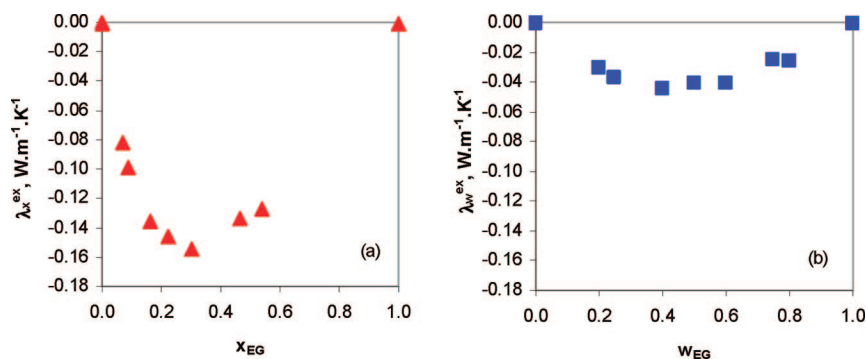
Figure 1. Excess thermal conductivity of the water + ethylene glycol system at 50 °C as a function of (a) mole fraction and (b) weight fraction of ethylene glycol. The excess thermal conductivities, λ_x^{ex} and λ_w^{ex}, are defined as $\lambda_x^{ex} = \lambda_m - \sum_k x_k \lambda_k$ and $\lambda_w^{ex} = \lambda_m - \sum_k w_k \lambda_k$. Symbols are from experimental data of Vanderkooi et al.[50]

Table 1. α Coefficients in Equations 18 for Selected Aqueous Ions

cations	α_{1,H_2O}	α_{2,H_2O}	anions	α_{1,H_2O}	α_{2,H_2O}
H_3O^+	−0.716 880	0.289 719	Cl^-	−0.360 439	0.006 076
Li^+	−0.207 041	0.057 691	NO_3^-	−0.422 374	0.033 717
Na^+	0.0	0.0	SO_4^{2-}	−0.029 457	0.044 903
K^+	−0.382 485	0.044 932	HSO_4^-	−1.235 53	0.120 45
Mg^{2+}	−0.496 250	0.052 652	OH^-	0.492 307 6	−0.018 014
Ca^{2+}	−0.052 799	0.126 519	F^-	0.059 371	−0.108 86
Ba^{2+}	−0.651 055	0.065 461	HCO_3^-	−0.215 690	−0.167 037
NH_4^+	0.045 80	−0.358 17	CO_3^{2-}	0.341 711	0.0
Fe^{3+}	−1.141 49	−0.536 22	PO_4^{3-}	−0.168 58	−1.140 83
Fe^{2+}	−1.524 35	0.771 68	HPO_4^{2-}	0.217 76	−0.271 54
Ni^{2+}	−0.281 946	0.007 328	$H_2PO_4^-$	−0.541 15	0.319 69
Cu^{2+}	−0.975 205	−0.098 87			
Zn^{2+}	−0.971 744	0.055 408			
Cr^{3+}	−1.139483	−0.536 249			

conductivity to other properties of the solution and of the solvent such as the heat capacities and densities. These methods, however, are applicable only to binary electrolyte solutions, and their accuracy deteriorates with rising concentration.[1] More recently, a generalized corresponding-states correlation has been proposed by Qureshi et al.[11] Using two system-dependent parameters for each binary solution and 10 universal parameters, their model has been shown to reproduce the experimental data for over 20 aqueous electrolyte systems within 4% over wide ranges of concentration, pressure, and temperature. Although

the model of Qureshi et al.[11] is accurate for the solutions studied, it is applicable only to aqueous binary systems.

In mixed-solvent electrolyte solutions, thermal conductivity is determined not only by the concentration of electrolytes, but also by the composition of the solvent. The thermal conductivity of solvent mixtures alone may change significantly with composition. In addition, in systems with strong ion association effect (e.g., in fully miscible acids or bases), thermal conductivity is influenced by concentrations of both ions and associated ion pairs. Thus, a comprehensive treatment of thermal conductivity of mixed-solvent electrolyte systems requires taking into account not only the ion−solvent and ion−ion interactions that predominate in aqueous solutions, but also the solvent−solvent and ion pair−solvent interactions.

The objective of this work is to develop a comprehensive, engineering-oriented model for predicting thermal conductivity of mixed-solvent electrolyte solutions. In this study, the term "mixed-solvent electrolytes" is used in the broadest possible sense to include (1) aqueous electrolyte solutions from the dilute region to the molten salt limit, (2) fully miscible acids or bases in water, and (3) electrolytes in pure organic or mixed organic−water solvents. Further, the model is designed to account for speciation effects, such as complexation or ion association, when combined with a speciation-based thermodynamic model. The model developed in this study consists of two parts: (1) computation of thermal conductivity of pure and

**Table 2. Parameters of Equations 10 and 16 for Selected Solvent Pairs**

solvent pairs		parameters					
i	j	$k_{ij}^{(0)}$	$k_{ij}^{(1)}$	T (°C)	relevant systems	no. of points	AAD	references
methanol	H_2O	0.006 428 7	0.000 863 5	0−70	methanol + H_2O	143	1.55	42−44
				40	2-propanol + methanol + H_2O	8	1.74	
ethanol	H_2O	0.141 844	0.000 761 6	0−80	ethanol + H_2O	37	1.28	43, 45−47
				−40−70	ethanol + ethylene glycol + H_2O	26	1.13	
ethylene glycol	H_2O	0.350 350	−0.000 510 2	−20−198	ethylene glycol+H_2O	162	1.39	14, 43, 46−53
				−40−70	ethanol + ethylene glycol + H_2O	26	1.13	
ethylene glycol	ethanol	6.308 36	−0.027 643	−40−70	ethanol + ethylene glycol + H_2O	26	1.13	46, 47
diethylene glycol	H_2O	0.345 126	−0.000 362 1	−10−200	diethylene glycol + H_2O	124	1.11	14, 48, 54, 55
1-propanol	H_2O	0.148537	0.0009413	0−80	1-propanol + H_2O	36	0.98	14, 43
2-propanol	H_2O	0.325 503	0.000 414 6	0−80	2-propanol + H_2O	36	1.72	14, 43, 44
				40	2-propanol + methanol + H_2O	8	1.74	
2-propanol	methanol	−0.023 849	0.0	40	2-propanol + methanol	8	0.73	
				40	2-propanol + methanol + ethylene glycol	8	0.61	44
				40	2-propanol + methanol + H_2O	8	1.74	
acetic acid	H_2O	0.238 284	0.0	23−139	acetic acid + H_2O	24	0.90	56
acetone	H_2O	0.074 507	0.001 244 3	0−60	acetone + H_2O	30	1.58	43
acetone	CCl_4	0.047 927	0.0	0−50	acetone + CCl_4	15	1.42	14, 57
toluene	CCl_4	−0.646 339	0.002 474	0−40	toluene + CCl_4	7	0.88	14, 17, 58
				25, 40	toluene + CCl_4 + cyclohexane	26	1.12	
cyclohexane	CCl_4	0.106 991	0.0	25−50	cyclohexane + CCl_4	10	1.48	
				25, 40	toluene + CCl_4 + cyclohexane	26	1.12	17, 57, 58
				25, 40	benzene + CCl_4 + cyclohexane	26	1.24	
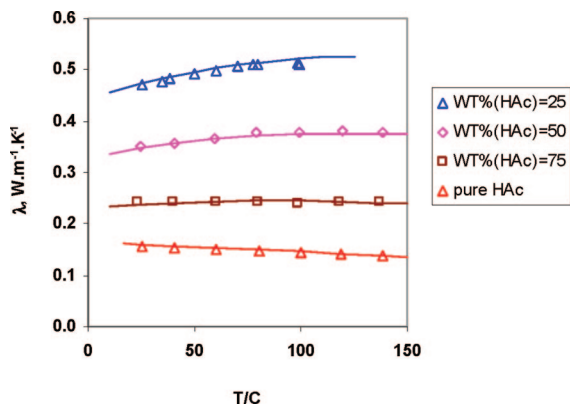
Figure 2. Thermal conductivity of the water + acetic acid system as a function of temperature at various fixed compositions (in mass percent) of acetic acid. Experimental data are from Bleazard et al.,[56] and the lines are calculated from eqs 2, 8, 10, and 16 using parameters listed in Table 2.
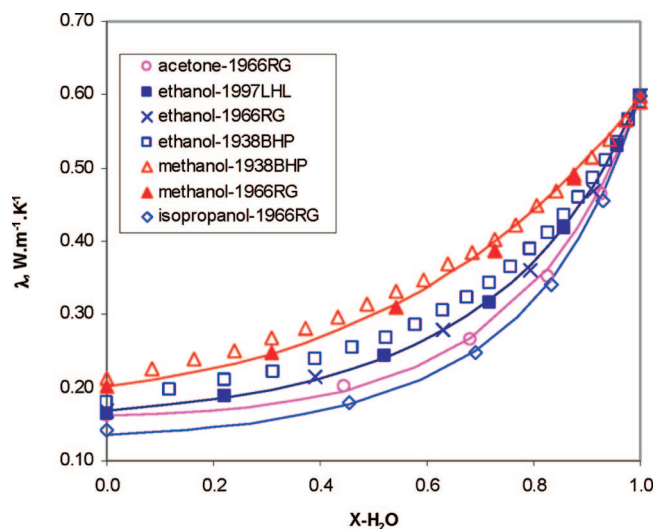
Figure 3. Thermal conductivity of organic + water mixtures as a function of the mole fraction of water at 20 °C. The symbols are experimental data from Rastorgu and Ganiev,[43] Lei et al.,[45] and Bates et al.,[42] and the lines are calculated from eqs 2, 8, 10, and 16 using the parameters listed in Table 2.
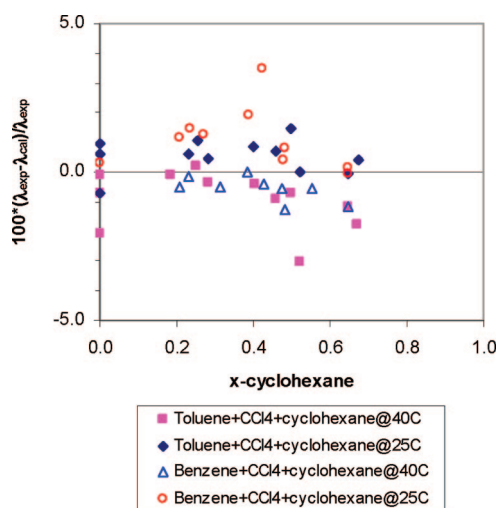
Figure 4. Percentage deviations for the prediction of thermal conductivities as a function of the mole fraction of cyclohexane for ternary systems cyclohexane + CCl$_4$ + benzene and cyclohexane + CCl$_4$ + toluene. Experimental data are from Rowley et al.[17] and Rowley and Gubler.[58]

mixed solvents as a function of temperature and solvent composition and (2) computation of the dependence of thermal conductivity on electrolyte concentration.

Thermal Conductivity of Solvent Mixtures

It has been observed in the literature that thermal conductivities of liquid mixtures are usually lower than either a mole or weight fraction average of pure-component conductivities.[12] Various models for representing the thermal conductivity of liquid mixtures have been described in the literature. Some notable models that are applicable to multicomponent systems include the power law method,[13] the harmonic mean method of Li[14] and its modification,[15] and models based on the local composition concept such as those of Rowley,[16,17] Cao et al.,[18] and Huang.[19] Although the power law method has been successfully used for a number of liquid mixtures, it is limited to nonaqueous mixtures and the ratio of thermal conductivities of any two pure components can not exceed 2.[12] The harmonic method of Li fails to predict the thermal conductivity behavior of azeotropic liquid mixtures.[14] Correlations based on the corresponding-states principle[20–23] have also been proposed for calculating the thermal conductivity of liquids and liquid mixtures. The results obtained from these methods depend on the selection of reference fluids, which may have a substantial influence on the calculated values for liquid mixtures, especially when the system goes beyond binary. Several hard-sphere theory-based models have been developed for organic mixtures.[24–26] However, these models are focused on mixtures containing components with similar chemical structures. A number of other correlation methods have been limited only to binary systems.[12]

In this section, we develop a new correlation that relates the thermal conductivity of solvent mixtures to those of pure components. This correlation is targeted primarily at mixtures containing dissimilar components such as water and organics because of the preeminence of such solvents in electrolyte systems. The local composition concept embodied in the UNIQUAC model of Abrams and Prausnitz[27] has been used to derive the correlation. This approach relies on the use of local area fractions to represent the local compositions, which appears to be a more appropriate choice than using the mole fractions for modeling energy transport in liquid mixtures.[14] The structural parameters used in this approach are readily available in the literature.[12]

It has been previously noted[16] that the weight fraction average of thermal conductivity ($\sum_k w_k \lambda_k^0$), rather than the mole fraction average ($\sum_k x_k \lambda_k^0$), leads to a more symmetrical "excess thermal conductivity", λ^{ex} (defined as $\lambda^{ex} = \lambda_m - \sum_k y_k \lambda_k^0$, with λ_m and λ_k^0 being the thermal conductivities of the mixture and of the pure component k, respectively, and y_k is the weight or mole fraction of k). In addition, it can be observed that the value of this "excess thermal conductivity" is generally much smaller when weight fractions rather than mole fractions are used, indicating that a much smaller and more symmetrical correction is needed when modeling the thermal conductivity of a mixture using weight fractions. These observations are demonstrated in Figure 1 for the ethylene glycol + water system. Thus, the thermal conductivity of an n-component mixture is assumed to be a modified weight fraction (w_i) average of the thermal conductivities of the n components using local area fractions, θ_{ji}:

$$\lambda_m = \sum_i^n w_i \sum_j^n \theta_{ji} \lambda_{ji} \qquad (2)$$

where λ_{ji} ($\lambda_{ji} = \lambda_{ij}$) should be an appropriately defined average of thermal conductivities of pure components i and j and it should also reflect interactions between the two solution species i and j. In the UNIQUAC model,[27] the local area fraction, θ_{ji},

is the fraction of external sites around molecule i that are occupied by molecule j. It can be related to the excess free energy of a liquid mixture through binary interaction parameters (a_{ji}), which can be, in principle, determined from phase equilibrium data:

$$\theta_{ji} = \frac{\theta_j \tau_{ji}}{\sum\limits_{k}^{n} \theta_k \tau_{ki}}, \quad \sum\limits_{j}^{n} \theta_{ji} = 1 \quad (i = 1, 2, \ldots, n) \quad (3)$$

where

$$\tau_{ji} = \exp\left(-\frac{a_{ji}}{RT}\right) \quad (4)$$

and θ_j is the average area fraction defined by

$$\theta_j = \frac{x_j q_j}{\sum\limits_{k}^{n} x_k q_k} \quad (5)$$

q_j is the surface area parameter for molecule j and x_j is the overall mole fraction of j in the mixture. When the parameters a_{ji} and $a_{ij}(a_{ji} \neq a_{ij})$ are determined, the local compositions, expressed in terms of average local area fractions, can be calculated from eqs 3–5.

The scheme for evaluating λ_{ji} is similar to Rowley's[16] derivation using the NRTL model. By substituting eq 3 into eq 2, an expression for the mixture thermal conductivity can be obtained:

$$\lambda_{m} = \sum\limits_{i}^{n} w_i \sum\limits_{j}^{n} \frac{q_j x_j \tau_{ji}}{\sum\limits_{k}^{n} q_k x_k \tau_{ki}} \lambda_{ji} \quad (6)$$

In the limit of a pure component i, it can be easily determined from eq 6 that

$$\lambda_{ii} = \lambda_i^0 \quad (7)$$

In order to evaluate λ_{ji} for $i \neq j$, only a binary mixture of i and j needs to be considered. We now assume that the binary interaction parameter λ_{ji} is the thermal conductivity of the binary mixture when the local area fractions θ_{ji} and θ_{ij} are equal. This condition can be satisfied only at a single composition, which can be solved using eqs 3 and 5 and expressed as weight fractions

$$w_i^* = \frac{q_j M_i \sqrt{\tau_{ji}}}{q_j M_i \sqrt{\tau_{ji}} + q_i M_j \sqrt{\tau_{ij}}}, \quad w_j^* = 1 - w_i^* \quad (8)$$

where M_i and M_j are the molecular weights of i and j, respectively. At the composition given by eq 8 (i.e., for $\theta_{ji} = \theta_{ij}$), when the binary mixture thermal conductivity, λ_m, is set equal to the interaction parameter λ_{ji}, eq 2 leads to a simple expression for λ_{ji}:

$$\lambda_{ji} = w_i^* \lambda_i^0 + w_j^* \lambda_j^0 \quad (9)$$

which has been derived using eq 7 and the condition $\sum\limits_{j}^{n} \theta_{ji} = 1$ for the binary system i–j.

Table 3. Interaction Parameters (Equations 14, 16, and 19) Used for Modeling Thermal Conductivities of Selected Systems

system and conditions	parameters	
HNO$_3$ + water[a] $T = 0$–100 °C $x_{HNO_3} = 0$–0.93	$\beta^{(10)}_{H_3O^+,NO_3^-/H_2O,H_2O} = -0.001\,907\,3$ $\beta^{(11)}_{H_3O^+,NO_3^-/H_2O,H_2O} = -0.009\,765\,1$ $\beta^{(20)}_{H_3O^+,NO_3^-/H_2O,H_2O} = 13.717\,3$ $\beta^{(21)}_{H_3O^+,NO_3^-/H_2O,H_2O} = 0.004\,103\,3$	$k^{(0)}_{H_2O,HNO_3} = -0.322\,39$ $k^{(1)}_{H_2O,HNO_3} = 0.0$
KNO$_3$ + water[a] $T = 20$–338 °C $x_{KNO_3} = 0$–1	$\beta^{(10)}_{K^+,NO_3^-/H_2O,H_2O} = -0.013\,43\,77$ $\beta^{(11)}_{K^+,NO_3^-/H_2O,H_2O} = -0.018\,694\,6$	$\beta^{(20)}_{K^+,NO_3^-/H_2O,H_2O} = 6.509\,9$ $\beta^{(21)}_{K^+,NO_3^-/H_2O,H_2O} = 0.0$
NaOH + water[a] $T = 1.5$–80 °C $x_{NaOH} = 0$–0.4	$\beta^{(10)}_{Na^+,OH^-/H_2O,H_2O} = -4.952\,38$ $\beta^{(11)}_{Na^+,OH^-/H_2O,H_2O} = -0.000\,254\,09$	$\beta^{(20)}_{Na^+,OH^-/H_2O,H_2O} = 0.0$ $\beta^{(21)}_{Na^+,OH^-/H_2O,H_2O} = -0.0$
H$_3$PO$_4$ + water[b] $T = 0$–150 °C $x_{P_2O_5} = 0$–0.387 (wt % H$_3$PO$_3$ = 0–115%)	$k^{(0)}_{H_2O,H_3PO_4} = 0.24156$ $k^{(1)}_{H_2O,H_3PO_4} = -0.00048$	$k_{P_2O_5,H_3PO_4} = 0.273\,76$ $k_{P_2O_5,H_3PO_4} = 0.000\,30$
FeCl$_3$ + water $T = 0$–100 °C $x_{FeCl_3} = 0$–0.1	$\beta^{(10)}_{FeCl^{2+},Cl^-/H_2O,H_2O} = 0.129\,606$ $\beta^{(11)}_{FeCl^{2+},Cl^-/H_2O,H_2O} = -0.027\,527\,8$ $\beta^{(20)}_{FeCl^{2+},Cl^-/H_2O,H_2O} = 10.683\,6$ $\beta^{(21)}_{FeCl^{2+},Cl^-/H_2O,H_2O} = -0.001\,376\,0$	$\beta^{(30)}_{FeCl^{2+},Cl^-/H_2O,H_2O} = -0.093\,325\,1$ $\beta^{(31)}_{FeCl^{2+},Cl^-/H_2O,H_2O} = 0.0$ $\beta^{0}_{FeCl^{2+},Cl^-/H_2O,H_2O} = -8.213\,58$
ZnCl$_2$ + ethanol $T = 25$–73 °C $x_{ZnCl_2} = 0.0$–0.19	$\beta^{(10)}_{Zn^{2+},Cl^-/EtOH,EtOH} = -0.073\,803\,5$ $\beta^{(11)}_{Zn^{2+},Cl^-/EtOH,EtOH} = 0.0$ $\beta^{(20)}_{Zn^{2+},Cl^-/EtOH,EtOH} = -1.940\,44$ $\beta^{(21)}_{Zn^{2+},Cl^-/EtOH,EtOH} = -0.002\,811\,86$ $\beta^{(30)}_{Zn^{2+},Cl^-/EtOH,EtOH} = 0.068\,676\,1$ $\beta^{(31)}_{Zn^{2+},Cl^-/EtOH,EtOH} = 0.000\,864\,161$ $\beta^{0}_{Zn^{2+},Cl^-/EtOH,EtOH} = 3.67978$	$\beta^{(10)}_{Zn^{2+},ZnCl_4^{2-}/EtOH,EtOH} = 0.084\,862\,3$ $\beta^{(11)}_{Zn^{2+},ZnCl_4^{2-}/EtOH,EtOH} = 0.0$ $\beta^{(20)}_{Zn^{2+},ZnCl_4^{2-}/EtOH,EtOH} = 0.019\,775\,3$ $\beta^{(21)}_{Zn^{2+},ZnCl_4^{2-}/EtOH,EtOH} = 0.028\,468\,8$ $\beta^{(30)}_{Zn^{2+},ZnCl_4^{2-}/EtOH,EtOH} = -0.070\,617\,4$ $\beta^{(31)}_{Zn^{2+},ZnCl_4^{2-}/EtOH,EtOH} = 0.002\,515\,39$ $\beta^{0}_{Zn^{2+},ZnCl_4^{2-}/EtOH,EtOH} = 0.878\,862$
SbCl$_3$ + acetone[a] $T = 25$–70 °C $x_{SbCl_3} = 0.0$–0.29	$\beta^{(10)}_{Sb^{3+},SbCl_3/acetone,acetone} = 0.0$ $\beta^{(11)}_{Sb^{3+},SbCl_3/acetone,acetone} = 0.0$ $\beta^{(20)}_{Sb^{3+},SbCl_3/acetone,acetone} = 7.751\,83$ $\beta^{(21)}_{Sb^{3+},SbCl_3/acetone,acetone} = 0.0$	$\beta^{(10)}_{Cl^-,SbCl_3/acetone,acetone} = 0.0$ $\beta^{(11)}_{Cl^-,SbCl_3/acetone,acetone} = 0.0$ $\beta^{(20)}_{Cl^-,SbCl_3/acetone,acetone} = 0.925\,531$ $\beta^{(21)}_{Cl^-,SbCl_3/acetone,acetone} = 0.0$

[a] $\beta^{(30)}$, $\beta^{(31)}$, and β^0 for the indicated species pairs are set equal to 0. [b] No interaction β parameters for this system were introduced.
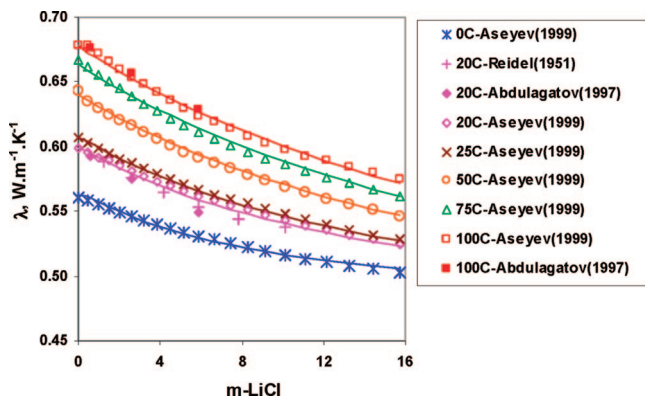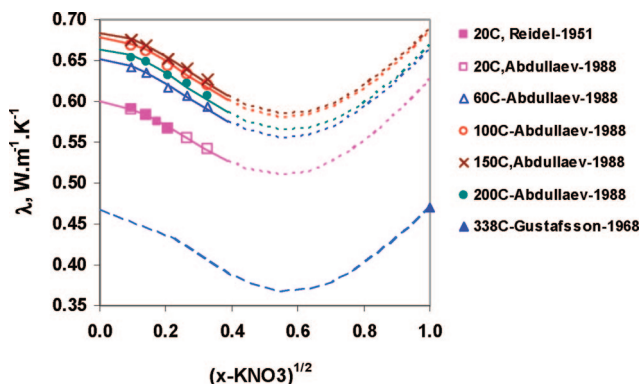
Figure 5. Thermal conductivities of aqueous LiCl solutions as a function of LiCl molality at various temperatures. The experimental data are from Aseyev,[32] Abdulagatov and Magomedov,[59] and Riedel,[5] and the lines are calculated using the model. The average percentage deviation of the fit is 0.34.
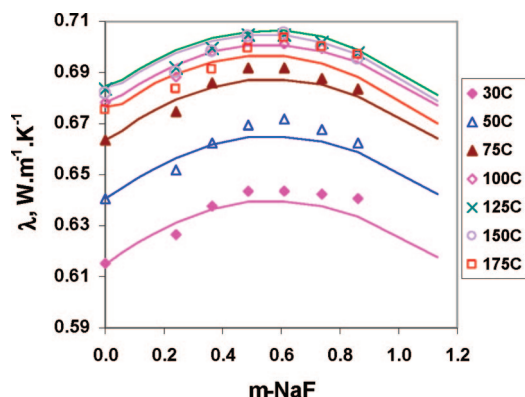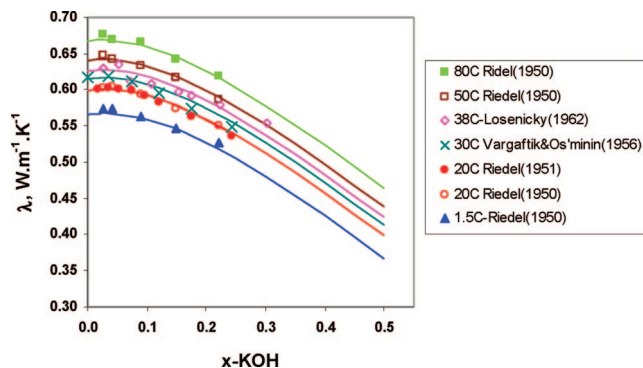

Figure 6. Thermal conductivities of aqueous NaF solutions as a function of NaF molality at various temperatures. The experimental data are from Aseyev,[32] and the lines are calculated using the model. The average percentage deviation of the fit is 0.48.

Figure 7. Thermal conductivities of the KNO_3 + water system as a function of $x_{KNO_3}{}^{1/2}$ at various temperatures. The experimental data are from Abdullaev and El'darov,[37] Riedel,[5] and Gustafsson et al.,[38] and the lines are calculated using the model. The average percentage deviation of the fit is 0.32.

In a similar approach, Rowley[16,17] noted that the thermal conductivities predicted using a correlation derived from the local-composition NRTL model were not sensitive to the choice of NRTL interaction parameters although the final results agreed well with experimental data. At the same time, a reverse procedure of calculating vapor–liquid equilibria (VLE) from thermal conductivity data has failed. Also, in our preliminary studies, it has been determined that the practical advantage of using UNIQUAC energetic interaction parameters derived from

Figure 8. Thermal conductivities of the KOH + water system as a function of x_{KOH} at various temperatures. The experimental data are from Vargaftik and Os'minin,[10] Riedel,[5,7] and Losenicky,[60] and the lines are calculated using the model. The average percentage deviation of the fit is 0.71.

phase equilibrium data is minimal in calculating thermal conductivity using eqs 6–9. Therefore, it is convenient to simplify the proposed thermal conductivity model (eqs 2, 8, and 9) by setting all of the interaction parameters, a_{ji}, and a_{ij} equal to 0 and introducing an empirical correction factor into the parameter λ_{ji} in eq 9. Thus

$$\lambda_{ji} = (w_i^* \lambda_i^0 + w_j^* \lambda_j^0)(1 - k_{ji}) \qquad (10)$$

where the values of w_i^* and w_j^* are determined from eq 8 by setting all τ_{ji} and τ_{ij} equal to 1. The use of a single correction factor k_{ji} is more efficient than regressing two UNIQUAC interaction parameters on the basis of thermal conductivity data. After this simplification, all of the binary terms can be defined using pure component thermal conductivities, the surface area parameters, q_i and q_j, molecular weights of the pure components, and a single correction factor, k_{ji}. The values of pure liquid thermal conductivities, λ_i^0, are available from the compilation of Daubert and Danner[28] for organic solvents, and from Sengers and Watson[29] for water. The surface area parameters are well established[27] and are available from Poling et al.[12] The binary parameter k_{ji} can be determined from experimental thermal conductivity data for the binary mixture of i and j.

It can be shown using algebraic manipulations that when the correction factors k_{ji} are 0 for all component pairs, eq 2 reduces to a simple weight average of the thermal conductivities of pure components:

$$\lambda_m = \sum_i^n w_i \lambda_i^0 \qquad (11)$$

Dependence of Thermal Conductivity on Electrolyte Concentration

In modeling the concentration dependence of several transport properties (e.g., viscosity, electrical conductivity, and self-diffusivity) in electrolyte solutions, a long-range electrostatic interaction term is generally introduced to represent a limiting-law slope in dilute solutions. This contribution is usually calculated using a primitive model of electrostatic interactions in a dielectric continuum.[4] However, this contribution is negligible for thermal conductivity as derived by Bearman from the Debye–Hückel–Onsager–Falkenhagen model.[2,3] Indeed, thermal conductivities of very dilute electrolyte solutions (i.e., 0–0.002 molal) are not much different from those of pure solvents. Hence, a practical thermal conductivity model does not need to explicitly include this contribution.
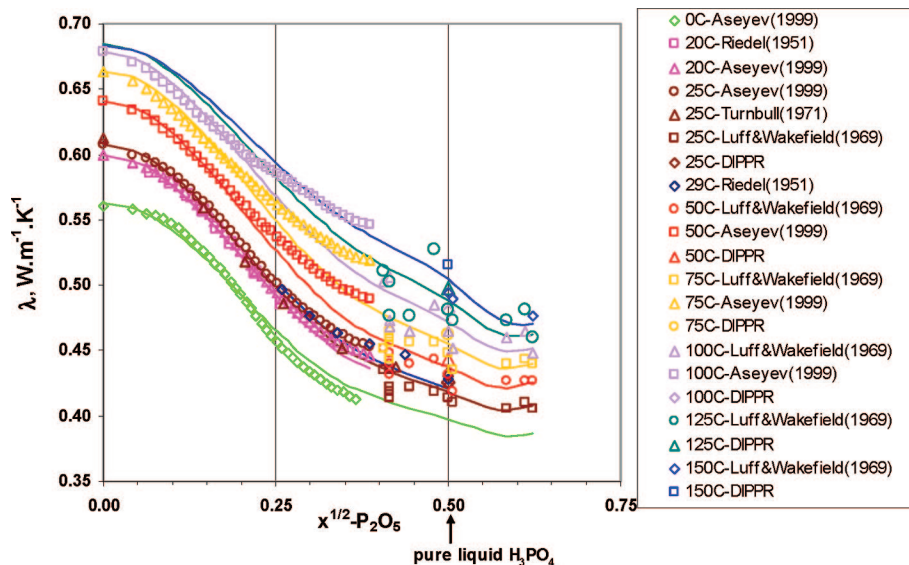
Figure 9. Thermal conductivities of the P_2O_5 + water system as a function of $x_{P_2O_5}^{1/2}$ at various temperatures. The experimental data are from Aseyev,[32] Riedel,[5] Luff and Wakefield,[41] Turnbull,[61] and Daubert and Danner.[28] The lines are calculated using the model. The average percentage deviation of the fit is 1.75.
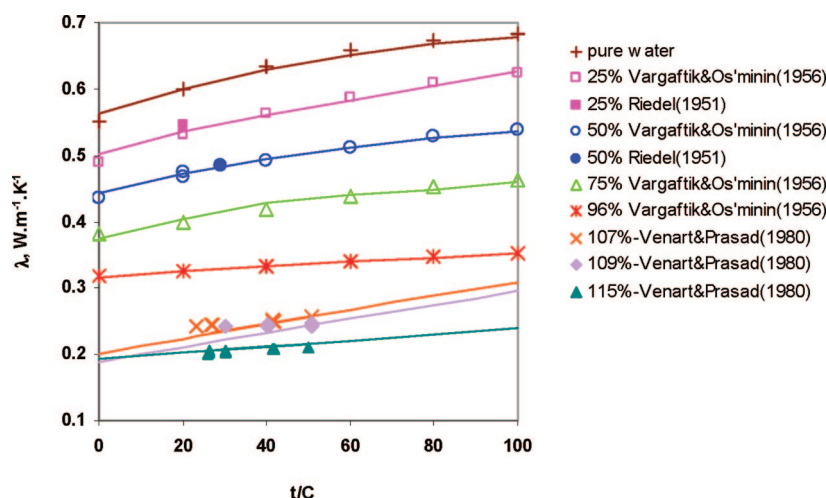
Figure 10. Thermal conductivities of the H_2SO_4 + water system as a function of temperature at various weight percents of H_2SO_4. The experimental data are from Vargaftik and Os'minin,[10] Riedel,[5] and Venart and Prasad.[62] The lines are calculated using the model. The average percentage deviation of the fit is 1.22.

Thus, a general model for the thermal conductivity of electrolyte solutions can be postulated to include the following two contributions: (1) a contribution of individual ions ($\Delta\lambda^s$), which is characterized by ion-specific coefficients and can be interpreted as the effect of ion−solvent interactions; this contribution is a generalized version of Riedel's[5] additivity rule (eq 1); (2) a contribution of interactions between ions or neutral species ($\Delta\lambda^{s-s}$). These two contributions are analogous to those used in a previously developed model for calculating viscosities of electrolyte systems.[30] Accordingly, the difference between the thermal conductivity of an electrolyte solution (λ) and that of a solvent mixture (λ_m^0) can be expressed as

$$\lambda - \lambda_m^0 = \Delta\lambda^s + \Delta\lambda^{s-s} \qquad (12)$$

As with the viscosity and electrical conductivity models developed previously,[30,31] the effect of solvent composition on the contributions of individual ions and on the interactions between species must be taken into account in the thermal conductivity model. In eq 12, λ_m^0 can be evaluated using eqs 2, 8, and 10 as described in the previous section.

An expression based on the Riedel equation[5] is used to represent the contribution of individual ions, $\Delta\lambda^s$. However, mole fractions rather than molar concentrations have been selected as more convenient composition variables. For aqueous electrolyte solutions, the use of either molar concentrations or mole fractions with rescaled ionic coefficients α_i has been found to yield similar deviations between the calculated and experimental values. However, a mole fraction based conductivity model does not necessitate the use of a separate density model in order to calculate molar concentrations, which eliminates the possibility of error propagation when other composition variables are converted to molar concentrations. In fact, most thermal conductivity data in the literature are reported as a function of either mass percent or molal concentration, which can be easily converted to mole fractions. Thus, in a mixed-solvent electrolyte solution, the individual ion contribution can be expressed as

$$\Delta\lambda^s = \sum_j \sum_i x_j' x_i \alpha_{i,j} \qquad (13)$$
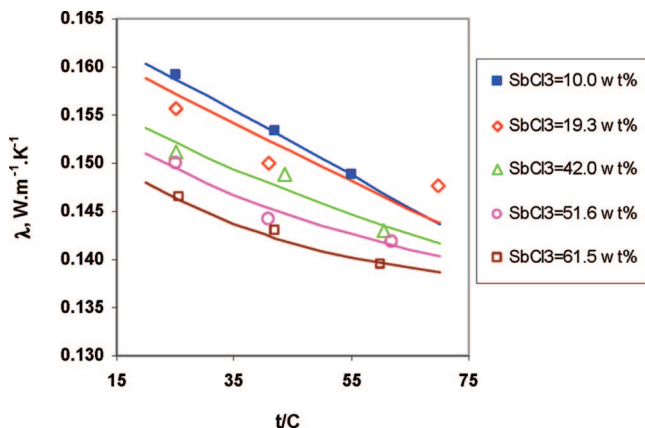
Figure 11. Thermal conductivities of the $SbCl_3$ + acetone system as a function of temperature at various weight percents of $SbCl_3$. The experimental data are from El'darov,[63] and the lines are calculated using the model. The average percentage deviation of the fit is 0.54.
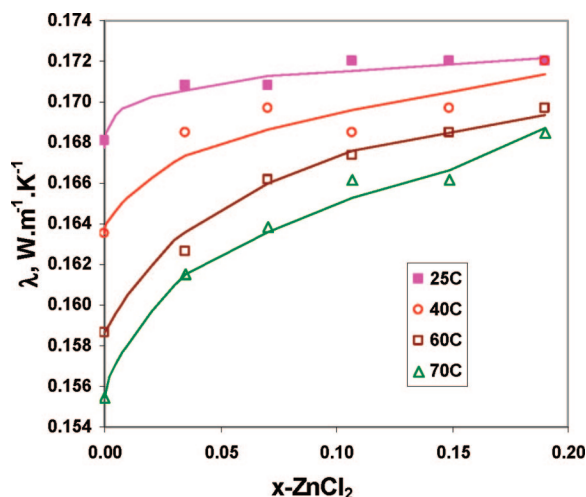
Figure 12. Thermal conductivities of the $ZnCl_2$ + ethanol system as a function of the mole fraction of $ZnCl_2$ at various temperatures. The experimental data are from El'darov,[63] and the lines are calculated using the model. The average percentage deviation of the fit is 0.24.

where the subscript j denotes the solvent components, i pertains to the solutes (ions and neutral species), x_i is the mole fraction of the ith species, $\alpha_{i,j}$ is the α-coefficient of the ith species in a pure solvent j, and x_j' is the mole fraction of solvent j on a salt-free basis. For an electrolyte solution with a single solvent, eq 13 reduces to

$$\Delta\lambda^s = \sum_i x_i \alpha_i \qquad (13a)$$

which is a mole fraction based version of the original Riedel[5] term.

For the $\Delta\lambda^{s-s}$ term, contributions of interactions between all species pairs must be included. Also, in mixed-solvent electrolyte solutions, the effects of different solvents and their composition on the species–species interactions must be recognized. To include these effects, the $\Delta\lambda^{s-s}$ term is expressed as

$$\Delta\lambda^{s-s} = \sum_j \sum_l \sum_i \sum_k x_j' x_l' f_i f_k \beta_{ik,jl} \qquad (14)$$

where the first and second sums (j and l) are over all solvent components, the sums over i and k are over all solutes, x_j' and x_l' are the mole fractions of solvents j and l on a salt-free basis,
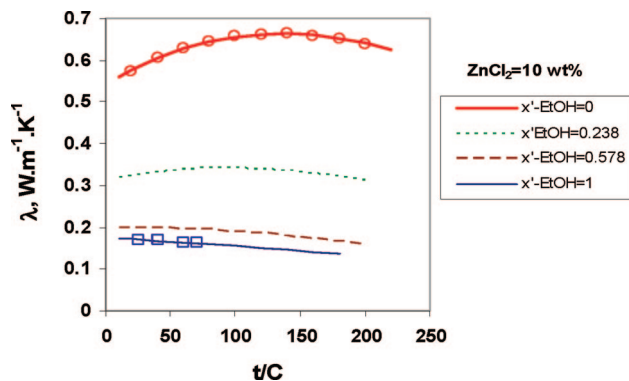
Figure 13. Predicted thermal conductivities of the $ZnCl_2$ + ethanol + water system as a function of temperature at various mole fractions of ethanol (on a salt-free basis). All solutions contain 10% $ZnCl_2$ (weight). The experimental data (symbols) are from Abdulagatov and Magomedov (at $x_{EtOH}' = 0$)[64] and El'darov (at $x_{EtOH}' = 1$).[63]

and f_i and f_k are the solute-only mole fractions of the ith and kth species, respectively, adjusted for the charges of species, i.e.

$$f_i = \frac{x_i/\max(1, |z_i|)}{\sum_m x_m/\max(1, |z_m|)} \qquad (15)$$

and $\beta_{ik,jl}$ is a binary parameter between the species i and k in a solvent mixture $j-l$. It should be noted that, when $j = l$, $\beta_{ik,ll}$ becomes the $i-k$ interaction in pure solvent l. The definition of the charge-adjusted fraction f_i has been introduced following a previous study of mixing rules in a viscosity model.[30] The sum in eq 15 is over the solute species and the factor $\max(1, |z_i|)$ ensures that f_i reduces to the mole fraction for neutral species. In cases when there is only one solvent, such as in aqueous electrolyte solutions, eq 14 reduces to

$$\Delta\lambda^{s-s} = \sum_i \sum_k f_i f_k \beta_{ik} \qquad (14a)$$

Parameter Evaluation

Interaction Parameter, k_{ji}, in the Mixed Solvent λ_m Model. The model for the thermal conductivity of mixed solvents (eqs 2, 8, 10) includes only a single adjustable parameter, k_{ji}, which can be determined using experimental data for binary mixtures. While the temperature dependence of the thermal conductivity of the solvent mixture, λ_m, is primarily determined by the variations with temperature of the thermal conductivities of the pure components, λ_i^0, it has been found that the accuracy of the calculated thermal conductivity can be improved if an additional temperature dependence is introduced into the binary parameter k_{ji}:

$$k_{ji} = k_{ji}^{(0)} + k_{ji}^{(1)} T \qquad (16)$$

The α Coefficients. The α coefficients as defined by Riedel[5] for aqueous ions have been traditionally based on molar concentrations. These coefficients must be rescaled to work with the model proposed in this study, in which mole fractions are used as composition variables. The α coefficients are also solvent-dependent. To determine the α coefficients in eq 13, experimental thermal conductivity data of aqueous and non-aqueous electrolyte solutions at low or moderate electrolyte concentrations have been analyzed. For aqueous solutions, data for binary systems from primary literature sources and from the compilation of Aseyev[32] were used to obtain the α
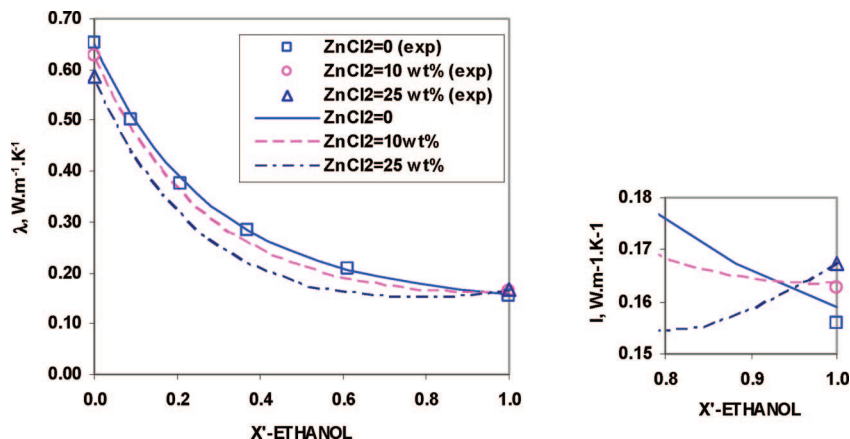
Figure 14. Predicted thermal conductivities of the $ZnCl_2$ + ethanol + water system as a function of the mole fraction of ethanol (on a salt-free basis) at 60 °C. The experimental data (symbols) are from Rastorgu and Ganiev (at $ZnCl_2 = 0\%$),[43] Abdulagatov and Magomedov (at $x_{EtOH}' = 0$),[64] and El'darov (at $x_{EtOH}' = 1$).[63]
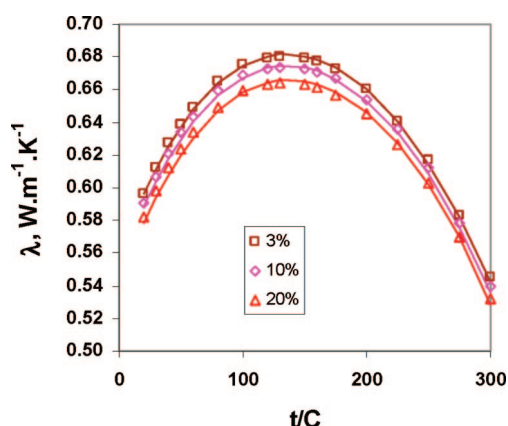
Figure 15. Thermal conductivities of the NaCl + $CaCl_2$ + water system as a function of temperature at various total weight percents of the salts. The mass ratio of NaCl:$CaCl_2$ is 3:1 in all solutions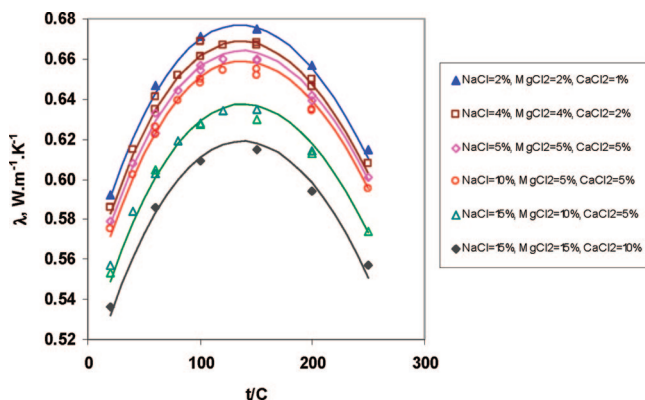. The experimental data are from Abdullaev et al.,[65] and the lines are calculated using the model. The average percentage deviation of the fit is 0.31.

Figure 16. Thermal conductivities of the NaCl + $CaCl_2$ + $MgCl_2$ + water system as a function of temperature at various compositions (in weight percent) of the salts. The experimental data are from Magomedov,[66,67] and the lines are calculated using the model. The average percentage deviation of the fit is 0.74.

coefficients according to the formula $\lambda - \lambda_{H_2O} = x_c\alpha_c + x_a\alpha_a$. As in Riedel's original work,[5] the α coefficient for the Na$^+$ ion has been assigned a value of 0; i.e., $\alpha_{Na^+} = 0$. With this assumption, coefficients for all other ions can be determined. In cases where there is an insufficient amount of experimental thermal conductivity data at relatively low concentrations, or in systems where speciation effects are significant, the α

coefficients have been treated as adjustable parameters, together with the interaction parameters $\beta_{ik,jl}$, and have been determined using thermal conductivity data for binary electrolyte + solvent system.

In Riedel's original work, the thermal conductivity of electrolyte solutions was assumed to have the same temperature dependence as that of pure water.[5,33] At a given temperature, λ was calculated using the α coefficients obtained at 20 °C, together with the ratio of thermal conductivities of pure water at 20 °C and at the temperature of interest, i.e.

$$\lambda^t = (\lambda^t_{H_2O}/\lambda^{20}_{H_2O})(\lambda^{20}_{H_2O} + \sum_i \alpha^{20}_i c_i) \quad (17)$$

A similar approximation was also used by others[10] to estimate thermal conductivities of aqueous solutions at elevated temperatures by using λ data at 20 °C. Although the temperature dependence expressed by eq 17 can give quite reliable predictions at temperatures up to 100 °C,[1] an explicit expression for the α coefficients is expected to be more accurate over a wider temperature range. A temperature-dependent function similar to the one used for the viscosity B coefficients[34] has been determined to be quite effective for this purpose and has been used in this work to calculate the α coefficients as a function of temperature:

$$\alpha = \alpha_1 + \alpha_2 \exp(-K(T - T_0)) \quad (18)$$

where T is the temperature in K, $T_0 = 273.15$ K, and K has been set equal to 0.023. It is of interest to note that the value of the K coefficient is the same for the viscosity B coefficients and for the thermal conductivity α coefficients. This indicates a certain similarity in the shape of the temperature dependence for both properties in electrolyte solutions. The values of the α coefficients are listed in Table 1 for selected ions. Similarly, the α coefficients for ions in solvents other than water can also be determined. However, due to the fact that experimental data are only available for a limited number of nonaqueous electrolyte systems, such parameters are much more difficult to obtain than those for aqueous ions.

The $\beta_{ik,jl}$ Parameters. For concentrated solutions, it has been found that the parameter $\beta_{ik,jl}$ in eq 14 depends on the ionic strength. A function of the form

$$\beta_{ik,jl} = \beta^{(1)}_{ik,jl} + \beta^{(2)}_{ik,jl}I_x^2 + \beta^{(3)}_{ik,jl} \exp(\beta^0_{ik,jl}I_x) \quad (19)$$

has been selected because it gives the best fit when thermal conductivity data extend to higher concentrations and when the

thermal conductivity shows a complex behavior. The quantity I_x in eq 19 is the extended, mole fraction based ionic strength defined by eq 20 to include the concentrations of neutral ion pairs (as opposed to solvent molecules), which typically become predominant at high concentrations because of speciation equilibria.

$$I_x = \frac{1}{2} \sum_{\text{ions}} z_i^2 x_i + \sum_{\text{ion pair}} x_n \qquad (20)$$

The temperature dependence of each of the $\beta_{ik,jl}^{(m)}$ ($m = 1, 2, 3$) parameters is given by

$$\beta_{ik,jl}^{(m)} = \beta_{ik,jl}^{(m0)} \exp(\beta_{ik,jl}^{(m1)}(T - T_0)) \qquad (21)$$

Results and Discussion

Thermal Conductivities of Solvent Mixtures. Experimental data for a number of binary and ternary solvent mixtures have been used for validating the correlation described in the preceding section. Table 2 lists the parameters k_{ji} for selected systems, together with the average percentage error, which is defined by

$$\text{AAD} = \left[\sum_{k}^{m} 100 |\lambda_{\text{exp}} - \lambda_{\text{cal}}| / \lambda_{\text{exp}} \right] / m \qquad (22)$$

where m is the number of experimental data points. Results for selected binary systems are shown in Figures 2 and 3. To validate the model against ternary or higher order systems, the parameters k_{ji} obtained from binary data were used to predict the thermal conductivity of ternary systems. The results are illustrated in Figure 4 in the form of relative deviations of the calculated thermal conductivities from experimental data for four ternary mixtures containing cyclohexane. The results shown in these figures and in Table 2 indicate that the model (eqs 2, 8, and 10) can accurately reproduce experimental data for solvent mixtures of any composition.

Thermal Conductivities of Electrolyte Solutions. Validation of the new thermal conductivity model for the effect of electrolyte concentration has been focused on two classes of systems: (1) aqueous electrolyte solutions (salts, acids, and bases) ranging from the dilute region to fused salts or pure acids or bases; (2) electrolytes in pure organic and mixed solvents. Experimental thermal conductivity data for aqueous electrolyte systems are available from extensive compilations[32,35] and from other literature sources. Compared to aqueous solutions, there is much less thermal conductivity data available for nonaqueous electrolyte systems and the experimental coverage is even sparser for mixed-solvent electrolyte solutions. Nonetheless, the available literature data provide a sound basis on which the new model can be tested. For all of the systems for which the thermal conductivity model has been tested, thermodynamic model parameters[36] were first developed to provide accurate speciation input for thermal conductivity modeling.

Table 3 lists the adjustable parameters in eqs 12–14 and, in some cases, those in eqs 2 and 10 for selected aqueous and nonaqueous electrolyte systems. The performance of the model for binary aqueous systems is illustrated in Figures 5–10. In these figures, literature thermal conductivity data for the systems LiCl + water, NaF + water, KNO_3 + water, KOH + water, H_3PO_4 + water, and H_2SO_4 + water are compared with calculated results at various temperatures and electrolyte concentrations. The average percentage deviations, AAD, as defined by eq 22, are given in the captions to the figures.

The thermal conductivities of most electrolyte solutions decrease as the concentration increases, as shown in Figure 5 for aqueous LiCl solutions. In contrast, the thermal conductivities of some other systems may exhibit a more complex behavior. For example, in aqueous solutions of LiOH, NaF, NaOH, Na_3PO_4, and Na_2CO_3, the thermal conductivity increases with rising concentration and may then decrease after a maximum is reached, as shown in Figure 6 for the NaF solution. Such complex behavior of thermal conductivity in various binary aqueous electrolyte solutions can be accurately reproduced by the model.

Metal nitrates in water can be continuously miscible from infinite dilution to the fused salt limit. Experimental thermal conductivity data are available for such systems over a moderate concentration range, i.e. $x_{\text{nitrate}} = 0.01-0.12$ ($0.5-8$ mol·kg^{-1})[37] and in the limit of molten salts.[38,39] These data provide a good test case for evaluating the performance of the model over the full concentration range of electrolyte components. Figure 7 shows the results for the system KNO_3 + water at temperatures ranging from 20 to 338 °C and concentrations ranging from $x_w = 0$ to $x_w = 1.0$. Within the concentration and temperature range where experimental data are available, the agreement between the calculated and experimental values is excellent. The model results between the upper end of the concentration range in aqueous solutions (i.e., 8 mol·kg^{-1}) and the molten salt limit can be validated when new experimental data become available. However, the predicted trend appears to be reasonable.

Fully miscible aqueous acids and bases are another important class of mixtures. Because of their usually strong association effects, such systems provide not only good test cases, but also offer an excellent opportunity to examine the effect of speciation on thermal conductivity. When modeling fully miscible acids, both water and the undissociated acid molecules (e.g., $H_2SO_4^0$, $H_3PO_4^0$, HNO_3^0) have been treated as solvent components. In these systems, speciation can change dramatically as acid concentration increases. In particular, a significant amount of neutral acid molecules may exist as the acid concentration approaches a mole fraction of unity and the association is nearly complete in a pure acid.[40] The interaction parameters that are used in the model for this type of systems include the β parameters in eq 14 between ionic species and the k_{ji} parameters in eq 10 between the solvent components (e.g., H_2O and HNO_3^0). For example, the best fit was obtained for the HNO_3 + H_2O system when the parameters $\beta_{H_3O^+,NO_3^-/H_2O,H_2O}$ and k_{H_2O,HNO_3} were introduced. In the H_3PO_4 + P_2O_5 + H_2O system, only the k_{H_2O,H_3PO_4} and $k_{P_2O_3,H_3PO_4}$ parameters are used to reproduce the data from dilute to extremely concentrated solutions that go beyond pure H_3PO_4 (i.e., in the system H_3PO_4 + P_2O_5). Speciation results for this system indicated that ionic species are only important at infinitely dilute solutions where thermal conductivity of the solution approaches that of pure water, while undissociated acid molecules are the predominant species elsewhere. These undissociated molecules have been treated as solvents; therefore treatment of this system is similar to those of the solvent mixtures, and its thermal conductivity can be solely represented by the solvent interaction parameters, $k_{j,i}$. Figures 9 and 10 show the results for the H_3PO_4 + P_2O_5 + H_2O and H_2SO_4 + SO_3 + H_2O systems, respectively, at various temperatures and concentrations. For both systems, data are available beyond the pure acid composition. In the moderately concentrated phosphoric acid solutions (i.e., $x_{P_2O_5} \geq 0.05$), data from Aseyev[32] are inconsistent with those of Luff and Wakefield.[41] Aseyev's data are smoothed values while the data of

Luff and Wakefield are consistent with the pure liquid H_3PO_4 data of Daubert and Danner,[28] which were critically evaluated. Therefore, Aseyev's data at these concentrations were excluded from the determination of model parameters, but were plotted in Figure 9 for comparison. Results for the KOH + water system are shown in Figure 8. Excellent agreement between experimental data and calculated results has been obtained for all of the investigated acids and bases over wide ranges of temperature and concentration.

Results for modeling nonaqueous electrolyte solutions can be demonstrated using the $SbCl_3$ + acetone and $ZnCl_2$ + ethanol systems as examples. The effect of speciation on the model predictions can also be analyzed in these cases. The prevailing complex, $SbCl_3^0$, in acetone solutions necessitated the introduction of the β parameters for the $\{Cl^-, SbCl_3^0\}$ and $\{Sb^{3+}, SbCl_3^0\}$ interactions, i.e., $\beta_{Sb^{3+},SbCl_3/acetone,acetone}$ and $\beta_{Cl^-,SbCl_3/acetone,acetone}$, to reproduce the experimental results within experimental uncertainty. The results for this system are shown in Figure 11. Similarly, thermal conductivities for the system $ZnCl_2$ + ethanol can be accurately reproduced when the interaction parameters $\beta_{Zn^{2+},ZnCl_4^{2-}/EtOH,EtOH}$ and $\beta_{Zn^{2+},Cl^-/EtOH,EtOH}$ are used, as shown in Figure 12.

Due to the lack of experimental data for electrolytes in mixed organic + water systems, only predictions can be made using the parameters obtained from the constituent binary solutions. The predicted thermal conductivities for the $ZnCl_2$ + ethanol + water system are shown in Figures 13 and 14, where the results for $ZnCl_2$ in pure water and in pure ethanol are also plotted to illustrate the predicted trends with changing solvent composition. The model predicts that the solvent composition has the most significant effect on thermal conductivity compared to the effects of electrolyte concentration and temperature. It also predicts a crossover in the λ vs x_{EtOH}' plot (Figure 14) due to the opposite trends of λ with respect to $ZnCl_2$ concentration in water and in ethanol. When experimental data become available for the mixed system, the model results may be improved, if necessary, by introducing additional interaction parameters that are pertinent to the mixed solvent, such as $\beta_{Zn^{2+},Cl^-/EtOH,H_2O}$.

The capability of the model for predicting thermal conductivities in multicomponent electrolyte solutions has also been tested and is demonstrated in Figures 15 and 16 for the ternary system $NaCl + CaCl_2$ + water and the quaternary system $NaCl + CaCl_2 + MgCl_2$ + water. In each case, λ shows a temperature dependence that is similar to that observed for pure water; i.e., a maximum value is reached at approximately 140 °C[29] at various fixed electrolyte concentrations. Also, λ decreases as the total electrolyte concentration increases in these systems. This behavior has been accurately reproduced. It should be noted that, for the multicomponent electrolyte solutions tested in this work, thermal conductivities can be generally predicted within 2.0% using only parameters from binary fits, with most points being within 1%. A further improvement can be obtained when like-ion interactions are introduced.

Conclusion

A general model has been developed for calculating the thermal conductivity of aqueous, nonaqueous, and mixed-solvent electrolyte solutions. The model consists of two main parts, i.e., a correlation for computing the thermal conductivity of solvent mixtures as a function of temperature and solvent composition, and an expression for the effect of electrolyte concentration. The correlation for the solvent mixtures has been derived from

the local composition concept. It has been subsequently simplified to use only the surface area parameters and thermal conductivities for pure components as well as a single adjustable parameter for each binary pair. It has been shown to be very effective for representing experimental data for a variety of solvent mixtures. In particular, the thermal conductivity of ternary solvent mixtures can be accurately predicted using parameters determined from only binary data. To represent the dependence of thermal conductivity on electrolyte concentration, the model includes a contribution of individual ions ($\Delta\lambda^s$), as quantified by a Riedel-type coefficient, and a contribution of specific interactions between ions or neutral species ($\Delta\lambda^{s-s}$). Formulations have been developed for both the $\Delta\lambda^s$ and $\Delta\lambda^{s-s}$ terms to account for the effects of multiple solvents. The thermal conductivity of multicomponent electrolyte solutions can be predicted within 2% by using parameters derived from only binary data. The predictions can be further improved by introducing like-ion interactions. The thermal conductivity model has been coupled with a thermodynamic equilibrium model[36] to provide speciation, which is necessary for thermal conductivity calculations for a large class of electrolyte systems. 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 new model has been shown to be accurate for reproducing thermal conductivities over wide ranges of temperature and concentration.

It should be noted that although the thermal conductivity model described in this paper does not explicitly give the pressure dependence, it should be applicable to higher pressures with good accuracy, as long as the pressure effect in the solvent thermal conductivities are correctly accounted for. This can be demonstrated by comparisons made in this study for pure water and for aqueous LiCl solutions where experimental data are available up to 100 MPa.[59] At 200 °C, thermal conductivity of pure water increases from 0.663 $W \cdot m^{-1} \cdot K^{-1}$ at saturated vapor pressure (1.56 MPa) to 0.733 $W \cdot m^{-1} \cdot K^{-1}$ at 100 MPa; while the increase in the thermal conductivity of the 0.1 mass fraction LiCl solution under the same conditions is from 0.637 to 0.700 $W \cdot m^{-1} \cdot K^{-1}$.[59] The calculated λ in this solution is 0.638 $W \cdot m^{-1} \cdot K^{-1}$ at saturated vapor pressure and 0.710 $W \cdot m^{-1} \cdot K^{-1}$ at 200 MPa using the new model, without explicitly including a pressure-dependent term. This indicates that the pressure effect on thermal conductivity of electrolyte solutions can be adequately represented by that of the solvent. An improved accuracy in calculating the pressure effect on the thermal conductivity can be obtained by introducing a pressure dependence in interaction parameters.

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