

Andrzej Anderko
Malgorzata M. Lencka

Modeling Transport Properties of Electrolyte Solutions in Wide Concentration and Temperature Ranges

INTRODUCTION

Transport properties of electrolyte solutions are needed for the design and optimization of various industrial processes and, at the same time, provide insights into solution structure and interactions. In particular, they are required for modeling the transport processes that are inherent in corrosion phenomena and various electrochemical manufacturing processes. The development of theories of transport properties of dilute electrolyte solutions has been a classical subject of statistical mechanics since the pioneering works of Onsager and Fuoss [1]. However, engineering-oriented models that cover wide ranges of concentration and temperature have a much shorter history and have not been available until recently. In this paper, we summarize the features of recently developed engineering models for self-diffusivity, electrical conductivity and viscosity.

PROPERTIES OF INDIVIDUAL IONS AT INFINITE DILUTION

Limiting conductivities and diffusion coefficients at infinite dilution provide a starting point for the computation of transport properties at finite concentrations. Unlike the finite-concentration properties, the limiting properties are additive with respect to individual ions. For a practical model, a procedure is necessary to compute the limiting properties as functions of temperature.

In the dense liquid phase region at temperatures up to ca. 550 K, the temperature dependence of limiting conductivity λ^0 can be accurately represented as

$$\ln \lambda^0(T)\eta(T) = A + \frac{B}{T} \quad (1)$$

where η is the viscosity of pure water and A and B are adjustable constants. The limiting diffusivity is directly related to the limiting conductivity by the Nernst-Einstein equation.

Anderko and Lencka [2] developed a correlation between the parameter B (eq. 1) and the structural entropy of ions [3], which makes it possible to predict the temperature dependence of λ^0 with good accuracy when experimental data are available only at a single temperature. This correlation is shown in Figure 1. A common curve is obtained for the structure-breaking ions (i.e., for $\Delta S_{str}^0 > 0$) and weak structure-making ones (i.e., for $-100 < \Delta S_{str}^0 < 0$ J/mol K). This line splits in two for ΔS_{str}^0 values below -100 J/mol K. For strongly electrostrictive structure-makers, a horizontal line at $B/|z|=0$ is obtained. Figure 2 shows the calculated temperature dependence of limiting conductivities for selected ions. The dashed lines show the conductivities predicted by calculating the parameter B from the generalized correlation (Figure 1) and the parameter A from a single experimental point at 25 °C. In this way, limiting conductivities and diffusivities can be predicted over wide temperature ranges even when only one experimental point is available.

In the case of viscosity, individual ions are characterized by the Jones-Dole B_{vis} coefficients. The temperature dependence of the B_{vis} parameters can be expressed using the equation developed by Out and Los [4]:

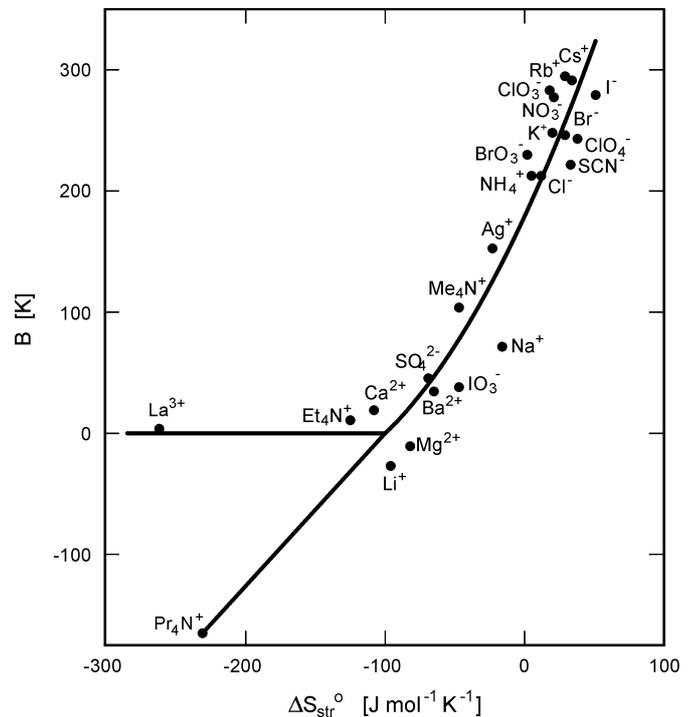


Figure 1: Relationship between the Parameter B /Eq. (1)/, and the Structural Entropy ΔS_{str}^0 for Ions. The circles represent the values of B , divided by ionic charge, that have been obtained by fitting limiting conductivity data for individual ions.

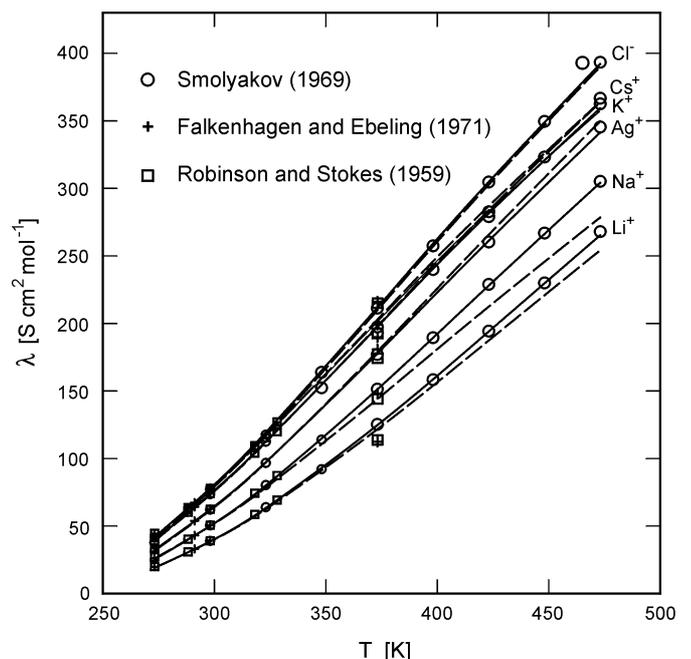


Figure 2: Limiting Ionic Conductivities of Li^+ , Na^+ , K^+ , Cs^+ , Ag^+ and Cl^- . The solid lines have been calculated by fitting the parameters A and B /Eq. (1)/ to individual

data. The dashed lines have been obtained by computing the parameter B from the generalized correlation (Figure 1) and utilizing a single experimental point at 298.15 K to calculate A .

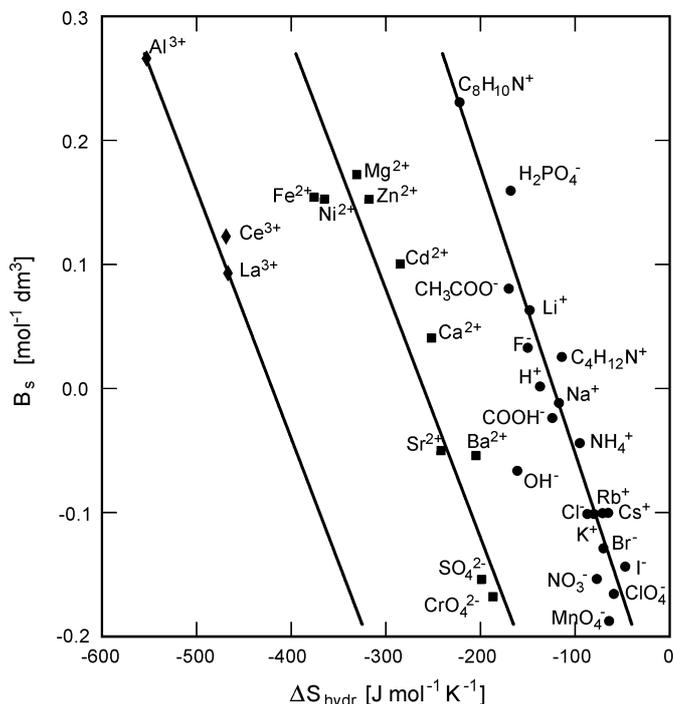


Figure 3: Relationship between the Parameter B_s /Eq. (2) and the Entropy of Hydration of Ions.

The symbols represent the values obtained by fitting Eq. (2) to experimental values of viscosity B_{vis} coefficients and the lines represent model values for mono-, di- and trivalent ions.

$$B_{vis} = B_E + B_s \exp[-0.023(T - 273.15)] \quad (2)$$

As with limiting conductivity, the temperature dependence of B_{vis} is determined by the structural effects caused by the interactions of ions with the H_2O hydrogen-bonded network. Lencka et al. [5] found that the parameter B_s can be correlated with the entropy of hydration. This correlation is shown in Figure 3 for mono-, di- and trivalent ions. With this correlation, the B_{vis} coefficient can be predicted over a wide range of temperatures using only one experimental point at ambient temperatures. Figure 4 illustrates such predictions for selected ions.

CONCENTRATION DEPENDENCE

In relatively dilute electrolyte solutions, the main effects that determine the deviations of transport properties from ideal behavior are the relaxation and electrophoretic effects [6]. However, the concentrations that are of interest for industrial applications range from 0 to ca. 30 M. In systems with a substantial ionic concentration, the long-range interionic forces are effectively screened to short-range by patterns of alternating charges. Then, interionic forces can be combined with all other interparticle forces on the same basis. Thus, all interparticle forces in concentrated solutions can be effectively treated as short-range forces and the solution properties can be calculated by methods similar to those for nonelectrolytes. At the same time, the alternating charge pattern and its accompanying screening effect are lost in the

dilute solution range and, therefore, the effects of long-range electrostatic interactions are significant at low concentrations. This rationale has been used to develop thermodynamic models by combining a long-range electrostatic interaction term with terms developed for nonelectrolyte solutions [7-8]. This approach is also applicable to transport properties.

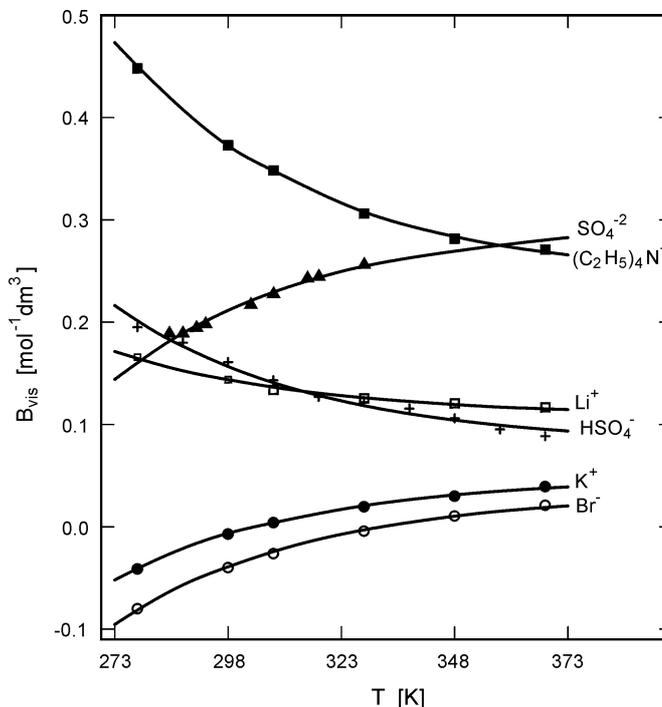


Figure 4: Viscosity B_{vis} Parameters for Selected Ions. The symbols denote experimental data and the lines have been obtained by computing the parameter B_s from the generalized correlation (Figure 3) and utilizing a single experimental point at 298.15 K to calculate B_E in Eq. (2).

Diffusivity

In the case of self-diffusion, long-range electrostatic interactions manifest themselves in the relaxation effect. The concentration dependence of self-diffusion in concentrated solutions can be, at the same time, represented by the hard-sphere theory, which is adequate for nonelectrolyte solutions. As described in a previous paper [9], the electrostatic and hard-sphere contributions can be combined as:

$$D_i = D_i^0 \left(\frac{D_i^{HS}}{D_i^0} \right) \left(1 + \frac{\delta k_i}{k_i} \right) \quad (3)$$

where D_i^0 is the limiting diffusivity and the two terms in parentheses denote the hard sphere and relaxation contributions. For binary systems, expressions for the hard-sphere and relaxation terms were developed by Tham and Gubbins [10] and Bernard et al. [11], respectively. Both terms can be computed if the radii of all ions and neutral species are known. As a first approximation, crystallographic radii can be used. In fact, this approximation works for relatively dilute solutions (up to ca. 1 M). For more concentrated solutions, it is necessary to use effective species radii defined as:

$$\sigma_i = 2 \frac{\sum_j c_j \sigma_{i(j)}}{\sum_j c_j} \quad (4)$$

where $\sigma_{i(j)}$ accounts for the effect of species j on the effective diameter of species i . The $\sigma_{i(j)}$ parameter has the meaning of a molecular or ionic radius (i.e., a half of the diameter). For consistency, $\sigma_{i(i)}$ is equal to the crystallographic radius of the species i . Since closed-form expressions for the electrostatic and hard-sphere terms are available only for binary systems, Anderko and Lencka developed a mixing rule based on the Stefan-Maxwell formalism of multicomponent diffusion [9].

Electrical Conductivity

The conductivity of an ion in a finite-concentration solution (λ_i) is related to the limiting conductivity of this ion (λ_{i0}) by

$$\lambda_i = \lambda_{i0} \left(I + \frac{\delta v_i^{el}}{v_i^0} \right) \left(I + \frac{\delta X}{X} \right) \quad (5)$$

where $\delta X/X$ is the relaxation effect and $\delta v_i^{el}/v_i^0$ is the electrophoretic correction. As with diffusivity, the expressions for the relaxation and electrophoretic terms depend on the ionic radii [11]. To make calculations for concentrated solutions, Anderko and Lencka [2] introduced effective ionic radii. Also, a mixing rule was introduced to extend Eq. (5) to multicomponent systems.

Viscosity

The concentration dependence of the viscosity of electrolyte solutions is calculated as a sum of a long-range electrostatic term, contributions of individual ions (as quantified by the B_{vis} coefficients) and contributions of interactions between ions or neutral species. A general expression for the relative viscosity η_r is written as:

$$\eta_r = 1 + \eta_r^{LR} + \eta_r^s + \eta_r^{s-s} \quad (6)$$

where the terms η_r^{LR} , η_r^s and η_r^{s-s} are the contributions of long-range electrostatic effects, individual species and species-species interactions, respectively [5]. The η_r^{LR} term is calculated from a model that recognizes electrostatic interactions between point charges in a dielectric continuum [1]. The η_r^s contribution is calculated from the B_{vis} coefficients for all species. The η_r^{s-s} term is expressed using a function developed in [5] and contains binary parameters that are regressed from experimental data at finite concentration.

Results and Discussion

The performance of the transport property models has been tested for a large number of single-solute and multicomponent systems. Figures 5-8 show the results for self-diffusivity. In Figure 5, self-diffusivities are shown for all three species that exist in the $\text{CaCl}_2 + \text{H}_2\text{O}$ system. The dotted lines in Figure 5 show the results obtained using only crystallographic diameters. As expected, a reasonable agreement with experimental data has been obtained only for relatively dilute solutions, i.e., for concentrations below 1 m. At higher concentrations, the model with crystallographic parameters fails to reproduce the experimentally observed rapid decrease of diffusivities with concentration. On the other hand, the model with effective ionic diameters (eq. 4) reproduces the data with very good accuracy. This is shown by the solid lines in Figure 5. After verifying the performance of the model for single-solute systems, calculations were performed for mixed systems. Figure 6 shows the results for

the self-diffusion coefficients of H_2O and Na^+ in the $\text{NaCl} + \text{MgCl}_2 + \text{H}_2\text{O}$ system. For this system, the effective ion diameters were regressed from experimental data for the constituent binary systems. The dashed lines in Figure 6 show the diffusivities in the single-solute solutions containing NaCl and MgCl_2 . The solid lines show the predicted diffusivities in a mixed solution with a 1:1 ratio of NaCl to MgCl_2 . As shown in Figure 6, the diffusivities in the mixed solution are represented with the same accuracy as those in the single-solute solutions.

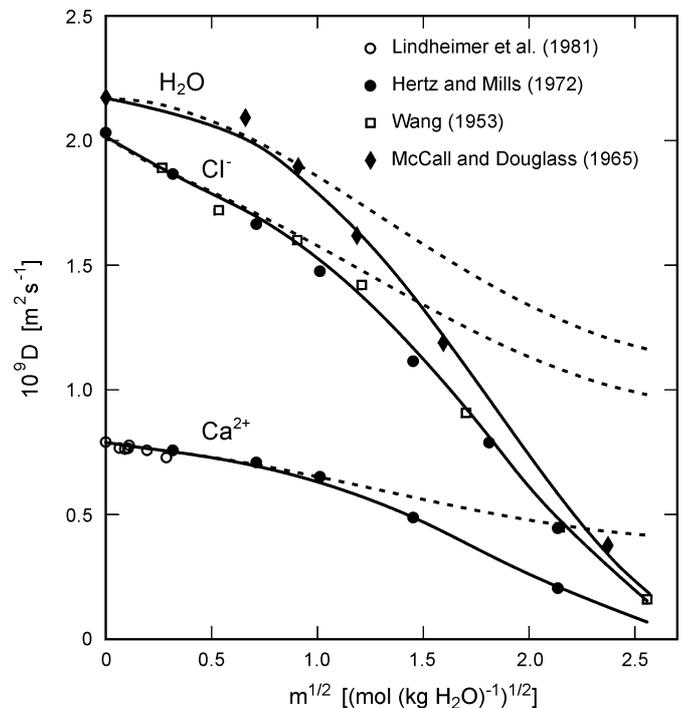


Figure 5: Self-Diffusion Coefficients of Ca^{2+} and Cl^- at 298.15 K and H_2O at 296.15 K in the $\text{CaCl}_2 + \text{H}_2\text{O}$ System.

The lines have been obtained from the model using crystallographic ion radii (dotted lines) and effective radii (solid lines). The symbols denote experimental data from various authors cited in [14], pp. 49-51.

For practical applications, it is particularly important to calculate the diffusivities of species in systems containing transition metals, which show appreciable complexation. For systems with aqueous complexes, the measured diffusion coefficients should usually be regarded as weighted averages of diffusion coefficients for individual (simple and complexed) species. As derived in a previous paper [9], the aggregate diffusivity of a species that undergoes complexation (denoted by X) is related to the diffusivities of individual complexes $Q_i X_i$ by

$$D_{X_T} = \sum_i i D_{Q_i X_i} \frac{\partial c_{Q_i X_i}}{\partial c_X} \quad (7)$$

The derivative in eq. (7) can be computed using a thermodynamic speciation model. In this study, we use the model developed by OLI Systems [12-13]. Figure 7 shows the effects of both weak and strong complexation on the aggregate diffusivity of iodide ions in several aqueous solutions. In the case of the HI and NaCl solutions, the self-diffusivity of

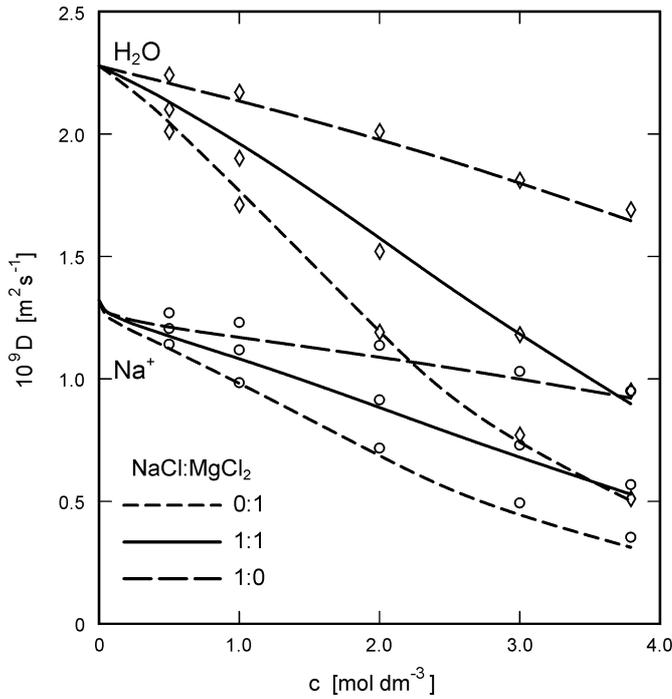


Figure 6: Self-Diffusion Coefficients of Na^+ and H_2O at 298.15 K in the $\text{NaCl} + \text{MgCl}_2 + \text{H}_2\text{O}$ System. The lines have been obtained for various $\text{NaCl}/\text{MgCl}_2$ ratios. The data were taken from the compilation [14], pp. 266-267.

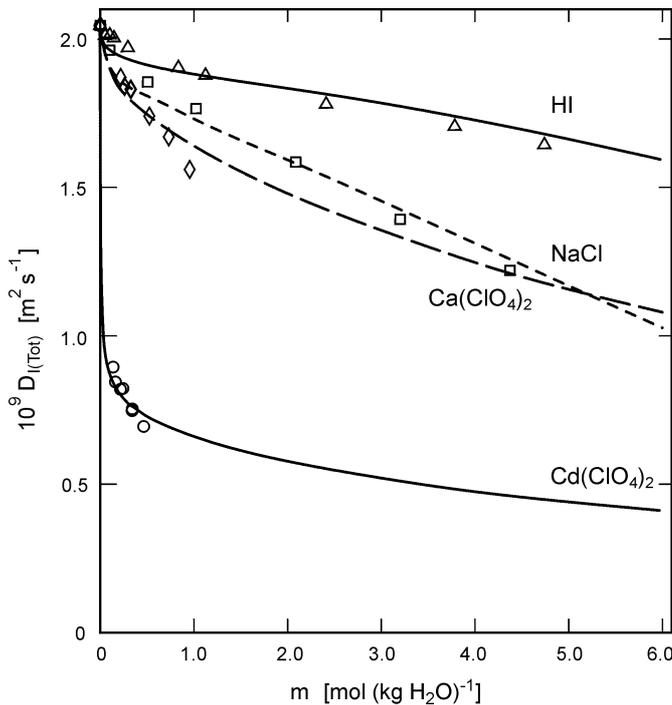


Figure 7: Aggregate Self-Diffusion Coefficients for Iodide-Containing Species in Aqueous Solutions of HI , NaCl , $\text{Ca}(\text{ClO}_4)_2$ and $\text{Cd}(\text{ClO}_4)_2$. The lines have been obtained from the model. Experimental data were taken from various authors cited in [14].

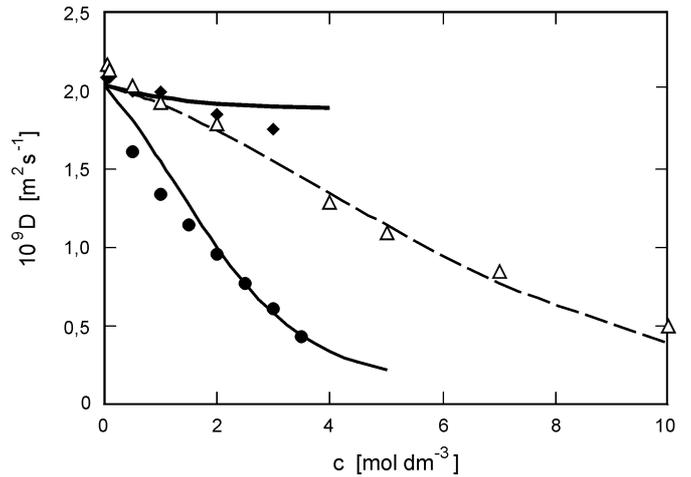


Figure 8: Diffusion Coefficients of Oxygen in KCl (upper line), LiCl (center line) and MgCl_2 (lower line) Solutions. The lines have been obtained from the model and the symbols represent experimental data of Ikeuchi et al. [15].

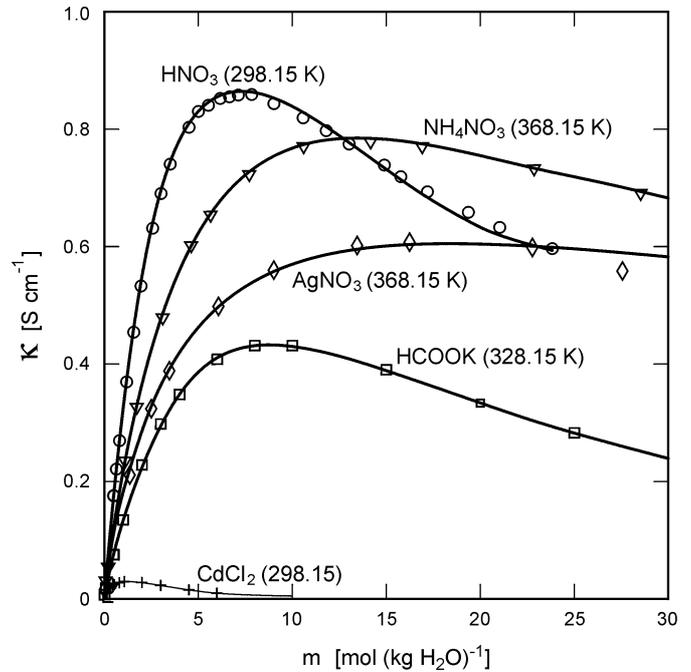


Figure 9: Specific Conductivity for Concentrated Electrolytes. The data for NH_4NO_3 and AgNO_3 are from Campbell and Kartzmark (1952) and the data for HNO_3 , HCOOK and CdCl_2 are from Haase et al. (1965), Isono (1985) and McQuillan (1974), respectively (all cited by Lobo and Quaresma in [16]).

iodide ions in several aqueous solutions moderately decreases with concentration. For the $\text{Ca}(\text{ClO}_4)_2$ solution, the initial decrease of D_T with concentration is stronger than in the case of NaCl because the relaxation effect in 2:1 electrolytes is stronger than in 1:1 electrolytes. Finally, D_T in the $\text{Cd}(\text{ClO}_4)_2$ solution decreases very rapidly at low concentrations because of strong complexation between Cd and I .

The diffusivity model is also applicable to the diffusion of neutral molecules (e.g., gases) in electrolyte solutions. For example, Figure 8 shows the diffusivity of oxygen in three chloride solutions with different cations.

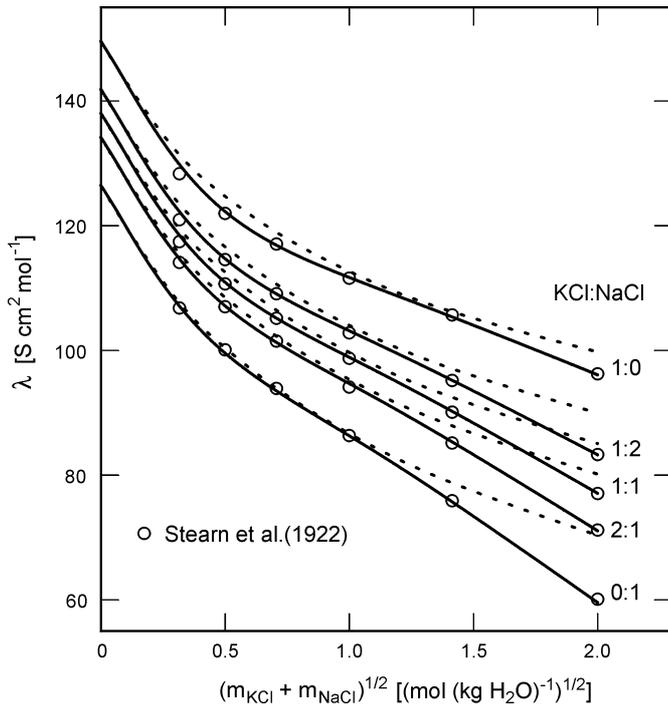


Figure 10: Equivalent Conductivity of the Ternary System KCl + NaCl + H₂O at 298.15 K for Various Molar Ratios of KCl to NaCl. The solid lines have been calculated using the effective ion radii. The dotted lines have been obtained using crystallographic radii.

The results obtained from the electrical conductivity model are compared with experimental data in Figures 9 and 10. Figure 9 shows specific conductivities as functions of concentration for systems for which experimental data extend over wide concentration ranges (up to 30 mol/kg H₂O). The specific conductivities exhibit maxima followed by a slow, nonasymptotic decrease of κ versus m . The location of the maximum and the shape of the κ versus m curve is characteristic for each solution. The parameters regressed from binary data have then been used to predict the conductivity for ternary or quaternary systems. In general, the quality of predicting the conductivity for multicomponent systems is similar to the quality of reproducing the data for the binary subsystems. This is shown in Figure 10 for the system KCl + NaCl + H₂O. Figure 10 also shows the prediction of conductivity without any empirical parameters, i.e., with the ionic radii equal to the crystalline radii (dotted lines). Such a prediction is in reasonable agreement with experiments for 1:1 electrolytes for concentrations up to ca. 1 mol/dm³. Beyond this concentration limit, it is necessary to utilize the effective, ionic strength-dependent radii (solid lines).

Figures 11 and 12 show the results of computations using the viscosity model. Fig. 11 shows the results for both strong and weak 1:1 electrolytes. It is noteworthy that the viscosity of strong electrolytes rapidly increases with concentration whereas that of weak electrolytes slowly increases or decreases. The behavior of weak electrolytes, such as acetic

acid or HCN, is similar to the behavior of nonelectrolyte solutions. Figure 12 shows the results for 2:1 electrolytes. In general, the viscosity of 2:1 electrolytes rises more rapidly with concentration than that of 1:1 electrolytes.

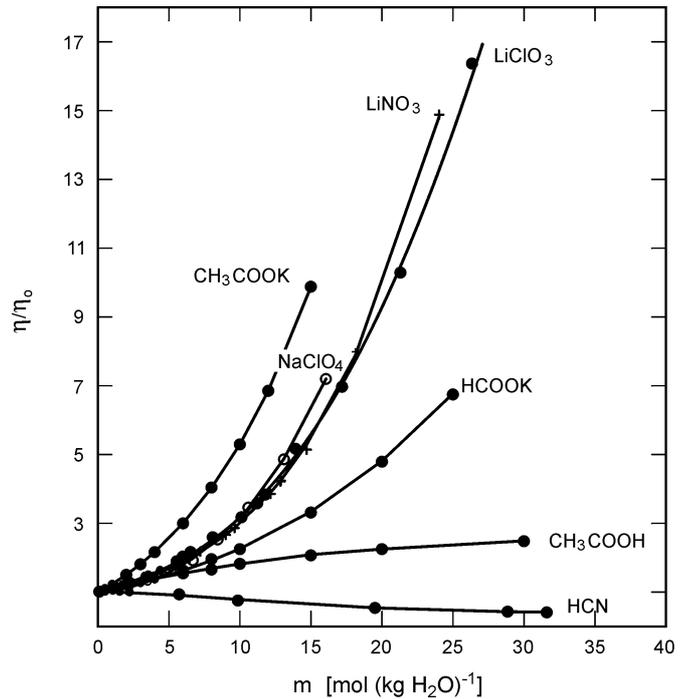


Figure 11: Representation of Viscosity for Strong and Weak 1:1 Electrolytes at 298.15 K. The symbols denote experimental data [16] and the lines have been calculated using the model.

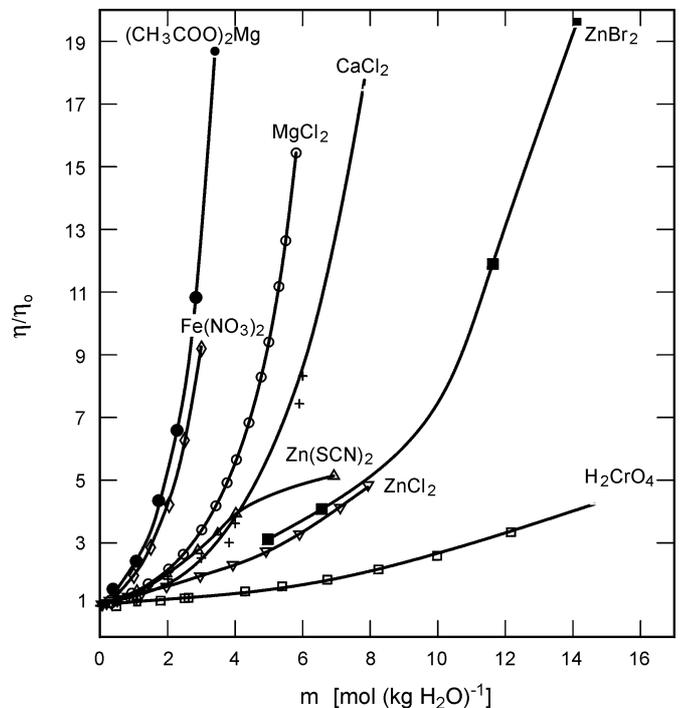


Figure 12: Representation of Viscosity for 2:1 Electrolytes at 298.15 K. The symbols denote experimental data [16] and the lines have been calculated using the model.

CONCLUSIONS

Models have been established for the computation of several transport properties (i.e., self-diffusivity, electrical conductivity and viscosity) of multicomponent aqueous solutions. The models share a number of features that make them applicable over wide ranges of temperatures and concentrations, i.e.,

- At infinite dilution, the models reproduce the temperature dependence of single-ion properties (i.e., the limiting conductivities/diffusivities and viscosity B_{vis} coefficients). This is accomplished by establishing relationships between these properties and thermodynamic functions of hydration.
- For finite concentrations, the models reproduce the contributions of electrostatic and nonelectrostatic interactions to the concentration dependence of transport properties.
- The models contain mixing rules that make it possible to predict the properties of multicomponent systems using parameters developed for simple binary systems.
- The models are combined with a thermodynamic speciation model, which makes it possible to reproduce the effects of complexation or other reactions in solution.

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Introducing the Authors of this Issue

Continued from page #514.

David J. Wesolowski (Ph.D. in Geochemistry and Mineralogy, The Pennsylvania State University) joined Oak Ridge National Laboratory in 1983 as a Eugene P. Wigner Fellow. He is a former group leader of and currently a senior researcher in the Geochemistry Group, Chemical and Analytical Sciences Division. He also serves as the secretary of the Geochemical Society, as an associate editor of *Geochimica et Cosmochimica Acta*, and on the editorial advisory board of *Chemical Geology*. He has authored or co-authored more than 60 publications on aqueous and stable isotope geochemistry and the thermodynamic properties of hydrothermal fluid/solid interactions.

Scott A. Wood (Ph.D. in Geology, Princeton University) has been a professor of Geochemistry at the University of Idaho in Moscow, Idaho since 1992. Prior to that he was employed as an assistant and then associate professor at McGill University in Montreal. He is an associate editor of the journal *Geochimica et Cosmochimica Acta* and editor-in-chief of *Geochemical Transactions*. He has published more than 60 full refereed scientific articles.

Caibin Xiao (Ph. D. in physical chemistry, Memorial University of Newfoundland, Canada) is a senior staff scientist in the Technology Department of the BetzDearborn Division of Hercules Incorporated. His work at BetzDearborn involves the research and development of boiler internal treatment programs. He spent two years as a postdoctoral fellow at Oak Ridge National Laboratory. He has 15 scientific publications in the experimental investigation and modeling of the thermodynamic properties of aqueous solutions.

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