Computation of Electrical Conductivity of Multicomponent Aqueous Systems in Wide Concentration and Temperature Ranges

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A comprehensive model for calculating the electrical conductivity of multicomponent aqueous systems has been developed. In the infinite-dilution limit, the temperature dependence of ionic conductivities is calculated on the basis of the concept of structure-breaking and structure-making ions. At finite concentrations, the concentration dependence of conductivity is calculated from the dielectric continuum-based mean-spherical-approximation (MSA) theory for the unrestricted primitive model. The MSA theory has been extended to concentrated solutions by using effective ionic radii. A mixing rule has been developed to predict the conductivity of multicomponent systems from those of constituent binary cation−anion subsystems. The effects of complexation are taken into account through a comprehensive speciation model coupled with a technique for predicting the limiting conductivities of complex species from those of simple ions. The model reproduces the conductivity of aqueous systems ranging from dilute to concentrated solutions (up to 30 mol/kg) at temperatures up to 573 K with an accuracy that is sufficient for modeling industrially important systems. In particular, the conductivity of multicomponent systems can be accurately predicted using data for single-solute systems.

Introduction

Electrical conductivity is one of the principal transport properties of aqueous electrolyte systems. In engineering applications, the knowledge of electrical conductivity is important for the design and optimization of electrolysis processes and electrochemical power sources. In the area of corrosion protection, electrical conductivity provides useful information for assessing the corrosivity of aqueous media and for the design of cathodic protection systems. Also, conductivity is used to gain insight into the properties of electrolyte solutions and to evaluate characteristic quantities such as dissociation constants.

A comprehensive model for electrical conductivity has to include methods for computing limiting conductivities of ions and the composition dependence of conductivity at finite concentrations. Limiting ionic conductivities characterize the mobility of ions in the infinite-dilution limit. They provide a starting point for the computation of electrical conductivity at finite concentrations and are necessary as input for most theories of the concentration dependence of conductivity. The available theories of limiting conductivity are based on the continuum-mechanics dielectric friction approach (Hubbard, 1978; Hubbard and Kayser, 1982). The dielectric friction theory makes it possible to gain insight into the mobility of charged spheres in a dielectric continuum. However, it is not suitable as an engineering-oriented, predictive model because it does not include structural effects of ion−water interactions (cf. a review by Evans et al., 1979; Ibuki and Nakahara, 1987). Using a more empirical approach, Marshall (1987) has developed a reduced-state relationship that emphasizes density effects at high temperatures. This relationship has been developed for a limited number of ions for which extensive data are available. Several studies have shown that limiting conductivity is primarily determined by structural effects caused by interactions of ions with the hydrogen-bonded network of water molecules (Kay and Evans, 1966; Kay et al., 1968). Accordingly, the temperature dependence of limiting conductivities depends on the structure-breaking and structure-making properties of ions. However, no fully quantitative technique is available that would make it possible to correlate and extrapolate limiting conductivity data with respect to temperature for all ions that are of industrial interest.

The concentration dependence of electrical conductivity has been extensively investigated for dilute aqueous solutions. A limiting law for conductivity was developed by Onsager (1926) by using the Debye−Hückel (1924) equilibrium distribution functions. This law was later extended by several authors as a power series in $c^{1/2}$, with additional nonanalytic terms in $c \ln c$. Various classical theories of electrical conductivity in dilute solutions have been reviewed by Justice (1983). The classical theories, based on combining Onsager's continuity expressions with the Debye−Hückel distribution functions, are generally valid for concentrations up to 10^{-2} mol/dm³. Recently, Bernard et al. (1992) and Turq et al. (1995) combined the Onsager continuity equations with equilibrium distribution functions calculated for the unrestricted primitive model using the mean spherical approximation (MSA). The MSA theory accurately represents the properties of electrolyte solutions in the limit of the primitive model, i.e., up to approximately 1 mol/dm³. Thus, it provides a major improvement over the Debye−Hückel theory. However, the analytical MSA theory has been developed for systems containing only a single cation−anion pair. Therefore, there is a need for a comprehensive model that would be capable of reproducing the conductivity of multicomponent systems in a full concentration range that is of interest for industrial applications.

A comprehensive, engineering-oriented model should satisfy a number of requirements:

(1) The model should predict the limiting conductivities of individual ions in wide temperature ranges even when experimental data are available only at ambient temperatures.

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(2) It should reproduce the conductivity of systems ranging from infinitely dilute to very concentrated.

(3) The conductivity of multicomponent systems should be reasonably predicted on the basis of information obtained from single-solute systems.

(4) The effects of complexation or hydrolysis on conductivity should be taken into account in accordance with reasonable speciation models.

In this work, we develop a model that satisfies these requirements and verify its performance for selected aqueous systems with single and multiple solutes.

Temperature Dependence of Limiting Conductivities

The limiting ionic conductivities are usually known at one temperature (such as 298.15 K) or over narrow temperature ranges. There are only 20 ions (i.e., H^+, Li^+, Na^+, K^+, Rb^+, Cs^+, Ag^+, NH_4^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Cl^-, Br^-, NO_3^-, CNS^-, ClO_4^-, I^-, OH^-, HSO_4^-, and SO_4^{2-}) for which the available experimental data extend at least up to 473 K (Horvath, 1985; Quist and Marshall, 1965; Marshall, 1987). To express the temperature dependence of limiting conductivities, it is convenient to use the equation of Smolyakov (1969), i.e.

$$\ln \lambda^0(T)\,\eta(T) = A + B/T \qquad (1)$$

where λ^0 is the limiting conductivity, η is the viscosity of pure water, and A and B are adjustable constants. Equation 1 does not include any density effects, which have been shown to become important at high pressures and temperatures. Thus, eq 1 is limited to the dense liquid phase region at temperatures extending up to ca. 573 K. In this work, eq 1 is used as a starting point for developing a generalized correlation for predicting limiting conductivities as functions of temperature.

Application of this equation to the correlation of limiting conductivities for the 20 ions for which the data are available up to 473 K gives an average deviation of 0.96%. For some of these ions, the correlation was extended to 573 K if high-temperature data were available (Quist and Marshall, 1965; Marshall, 1987). The coefficients A and B and the relative deviations for these ions are collected in Table 1. The viscosity of water was calculated from the equation of Watson et al. (1980). In all cases, the deviations are very satisfactory and are reasonably close to experimental uncertainty. It is also important that eq 1 provides a reliable extrapolation beyond the temperature range of available experimental data. Therefore, eq 1 can be further used to generalize the temperature dependence of λ^0.

A generalized expression for the temperature dependence of λ^0 has to recognize the structural effects that are caused by interactions of ions with the H_2O hydrogen-bonded network. These effects are the primary factor that determines the temperature dependence of λ^0 (Kay and Evans, 1966; Kay et al., 1968). A convenient quantitative measure of the structural effects has been defined by Marcus (1985). This measure, called the structural entropy ΔS_{str}^0, is defined as the structural component of the entropy of hydration ΔS_{hydr}^0 and is calculated as

$$\Delta S_{str}^0 = \Delta S_{hyd}^0 - \Delta S_{hyd}^0(\text{Born}) -$$
$$\Delta S_{hyd}^0(\text{nonstructural, nonelectrostatic}) \qquad (2)$$

where $\Delta S_{hyd}^0(\text{Born})$ is the electrostatic contribution to

Table 1. Representation of Limiting Ionic Conductivities Using Equation 1 for the Ions for Which Experimental Data Extend from 273 to at Least 473 K[a]

ion	A	B	AAD
H^+	−3.9726	837.79	0.51
Li^+	−3.2762	−26.894	0.53
Na^+	−3.3594	75.492	0.52
K^+	−3.5730	254.36	0.97
Rb^+	−3.6517	294.79	1.22
Cs^+	−3.6512	291.42	1.58
Ag^+	−3.4036	152.70	0.96
NH_4^+	−3.3368	187.06	1.06
Mg^{2+}	−3.0347	−3.505	0.98
Ca^{2+}	−3.0470	33.503	0.30
Ba^{2+}	−3.0994	69.134	0.53
Cl^-	−3.4051	216.03	0.73
Br^-	−3.4910	249.33	0.85
I^-	−3.5660	265.28	0.45
NO_3^-	−3.6743	277.43	1.20
CNS^-	−3.5544	221.74	1.15
ClO_4^-	−3.6181	243.13	0.93
OH^-	−3.3346	468.13	2.64
HSO_4^-	−3.5038	119.58	2.02
SO_4^{2-}	−2.9457	90.983	0.26
average			0.74

[a] The average deviation for each ion is calculated as AAD = $(100/N)\Sigma|\lambda_{cal}^0 - \lambda_{exp}^0|/\lambda_{exp}^0$ where N is the number of experimental data points. The data were taken from Horvath (1985), Quist and Marshall (1965), and Marshall (1987).

the hydration entropy and ΔS_{hyd}^0(nonstructural, nonelectrostatic) is a contribution due to the immobilization of water molecules around the ions and a change of standard state between the ideal gas and aqueous phase. The ΔS_{hyd}^0(Born) contribution is calculated from the Born (1920) equation for the hydration of charged spheres in dielectric continuum and ΔS_{hyd}^0(nonstructural, nonelectrostatic) is assigned an average value of −80 J K^{-1} mol^{-1}. An ion is predominantly structure-breaking if $\Delta S_{str}^0 > 0$. Similarly, an ion is mostly structure-making if $\Delta S_{str}^0 < 0$. The values of ΔS_{str}^0 have been computed by Marcus (1985) for most ions.

In this work, we develop a generalized, predictive formula for the coefficient B of eq 1 by seeking a correlation between B and the structural entropy ΔS_{str}^0. The experimental data base for this correlation consists of ions for which the temperature range of the available limiting conductivity data extends over more than 35 K (Quist and Marshall, 1965; Smolyakov, 1969; Falkenhagen and Ebeling, 1971; Harned and Owen, 1958; Robinson and Stokes, 1959; Kay and Evans, 1966; Pebler, 1981; Marshall, 1987). This minimum range is necessary to obtain a statistically significant value of B. Overall, there are 30 ions for which the limiting conductivity data extend over more than 35 K (i.e., the ions from Table 1 and an additional 10 ions for which the temperature range is between 35 and 100 K). It should be noted that the limiting conductivity of the H^+ and OH^- ions in water is a manifestation of the prototropic mechanism of ionic mobility (Erdey-Gruz, 1974), which is different from the general mechanism of mobility of other ions. Thus, the H^+ and OH^- ions cannot be expected to follow the same relationship between B and ΔS_{str}^0 as other ions. The correlation between B and ΔS_{str}^0 can be established only for the ions that share a common mechanism of ionic mobility based on the interplay between hydrodynamic motion and dielectric relaxation in a molecular solvent.
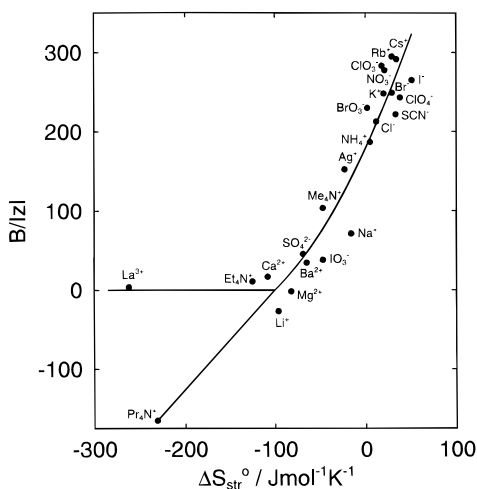
Figure 1. Relationship between the parameter B (eq 1) and the structural entropy ΔS_{str}^0 for ions. The circles represent the values of B, divided by ionic charge, that have been obtained by fitting eq 1 to limiting conductivity data for individual ions. The lines are obtained from eqs 3−5.

We have found that a reasonably significant correlation exists between the $B/|z|$ ratio (where z is the charge of the ion) and ΔS_{str}^0. This correlation is shown in Figure 1. A common curve is obtained for the structure breakers (i.e., for $\Delta S_{str}^0 > 0$) and weak structure makers (i.e., for $-100 < \Delta S_{str}^0 < 0$ J mol^{-1}K^{-1}). This line splits in two for ΔS_{str}^0 values below -100 J mol^{-1} K^{-1}. For strongly electrostrictive structure makers, a horizontal line at $B/|z| = 0$ is obtained. At present, the location of this line is not very precisely known because the temperature dependence of limiting conductivities of many transition-metal cations (which are electrostrictive structure makers) has not been measured. For hydrophobic structure makers, a separate line is established that drops to negative $B/|z|$ values. The algebraic representation of the correlation shown in Figure 1 is

$$B/|z| = 0.006946(\Delta S_{str}^0)^2 + 2.485\Delta S_{str}^0 + 179.1$$
$$\text{for } \Delta S_{str}^0 > -100 \text{ J mol}^{-1} \text{ K}^{-1} \quad (3)$$

$$B/|z| = 0 \quad \text{for } \Delta S_{str}^0 < -100, \text{ electrostrictive}$$
$$\text{structure makers} \quad (4)$$

$$B/|z| = 126.0 + 1.260\Delta S_{str}^0 \quad \text{for } \Delta S_{str}^0 < -100,$$
$$\text{hydrophobic structure makers} \quad (5)$$

The above correlation can be used in conjunction with a single experimental data point to predict the complete temperature dependence of limiting ionic conductivities according to eq 1. Such predictions are illustrated in Figures 2−4 for selected ions. The dashed lines show the conductivities predicted by calculating the parameters of eq 1 as (1) parameter B from eqs 3−5 and (2) parameter A from one experimental λ^0 point at 298.15 K and the value of B.

In Figures 2 and 3, the predictions are shown for selected groups of ions for which experimental data are available in a wide temperature range (up to 473 K). In Figure 4, the results are shown for ions for which experimental data are more limited. As shown in Figures 2−4, the predictions are very satisfactory. This procedure provides an accurate method for calculating the limiting conductivities when experimental data are available only at one temperature or in a narrow range.
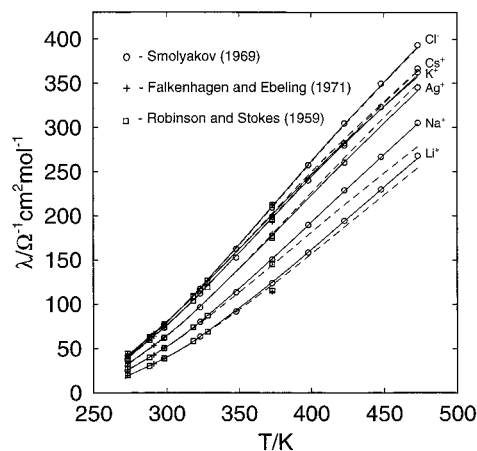
Figure 2. Limiting ionic conductivities of Li$^+$, Na$^+$, K$^+$, Cs$^+$, Ag$^+$, and Cl$^-$. The solid lines have been calculated by fitting the parameters A and B (eq 1) to individual data. The dashed lines have been obtained by computing the parameter B from the generalized correlation (eqs 3−5) and utilizing a single experimental point at 298.15 K to calculate A.
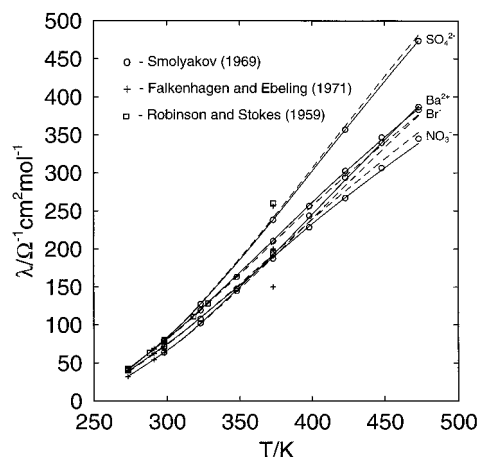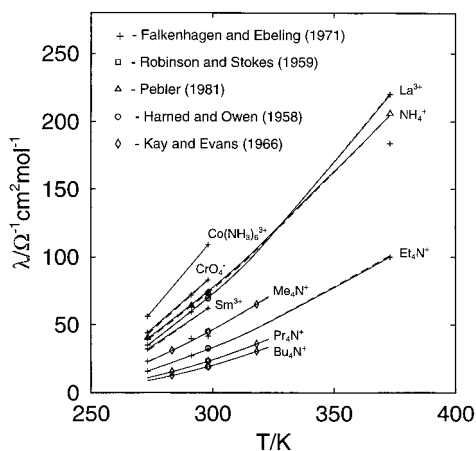

Figure 3. Limiting ionic conductivities of NO$_3^-$, Br$^-$, Ba^{2+}, and SO$_4^{2-}$. The solid lines have been calculated by fitting the parameters A and B (eq 1) to individual data. The dashed lines have been obtained by computing the parameter B from the generalized correlation (eqs 3−5) and utilizing a single experimental point at 298.15 K to calculate A.

This is the case for a large number of ions (cf. Horvath, 1985; Erdey-Gruz, 1974). For comparison, the solid lines in Figures 2−4 show the results of correlating the available λ^0 data in the whole temperature range by fitting individual values of A and B. The deviations between the dashed and solid lines are reasonably small for most of the ions, which indicates that the predicted values can be used with confidence outside of the range of experimental data.

In general, the proposed technique for calculating the limiting conductivities is accurate for temperatures up to 523 K and, in favorable cases, up to 573 K at saturated vapor pressures. Beyond 573 K, the behavior of limiting conductivities becomes dominated by density effects (Marshall, 1987) and cannot be approximated by eq 1.

Limiting Conductivities of Complex Ions

Complex ions of the Me(X^{m-})$_n$ type ($X =$ OH$^-$, Cl$^-$, Br$^-$, CN$^-$, SCN$^-$, etc.) play a very important role in most aqueous systems of industrial interest. At the same time, limiting conductivities for such ions are difficult to measure because the complex ions always occur

Figure 4. Limiting ionic conductivities of Bu_4N^+, Pr_4N^+, Et_4N^+, Me_4N^+, NH_4^+, Sm^{3+}, La^{3+}, CrO_4^{2-}, and $Co(NH_3)_6^{3+}$. 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 (eqs 3–5) and utilizing a single experimental point at 298.15 K to calculate A.

together with simple ions (i.e., Me^{z+} and X^{m-}). Therefore, it is difficult to separate the contributions of simple and complex ions to the electrical conductivity of dilute solutions. The dearth of experimental limiting conductivity data for complex ions makes it necessary to develop a procedure for estimating them from the limiting conductivities of simple ions. For this purpose, we utilize the relationship between the limiting conductivity of an ion λ_i^0 and the Stokes radius $r_{i,S}$ (Marcus, 1985), i.e.

$$r_{i,S} = \frac{F^2}{6\pi N_A \eta} \frac{|z_i|}{\lambda_i^0} \tag{6}$$

where F, N_A, and η are the Faraday constant, Avogadro's number, and the viscosity of the solvent, respectively. The Stokes radius is a measure of the size of a hydrated ion and is greater than the crystallographic radius. In fact, the Stokes radii are used to estimate the hydration numbers of ions (Marcus, 1985).

In this work, we postulate that the volume of a hydrated complex ion is, to a first approximation, equal to the sum of the hydrated volumes of the constituent simple ions. If a complex is made up of n simple ions, the Stokes radius of the complex ($r_{complex,S}$) is then related to the Stokes radii of the constituent simple ions ($r_{i,S}$) by

$$r_{complex,S}^3 = \sum_{i=1}^{n} r_{i,S}^3 \tag{7}$$

According to the definition of the Stokes radius, eq 7 gives us a link between the limiting conductivity of the complex and those of the constituent simple ions. After algebraic rearrangement, a simple formula for the limiting conductivity of the complex is obtained:

$$\lambda_{complex}^0 = \frac{|z_{complex}|}{\left[\sum_{i=1}^{n} \left(\frac{z_i}{\lambda_i^0} \right)^3 \right]^{1/3}} \tag{8}$$

This relationship has been applied to predict the limiting conductivities of the few complexes for which experimental data are available. The results are shown in Table 2. In contrast to simple ions, the experimental values for complexes are subject to considerable uncertainty and depend on the source of data (e.g., conductivity and transference number measurements). The predicted values are well within the range of experimental values that are reported for each complex. Thus, eq 8 is adequate, despite its simplicity, for the prediction of limiting conductivities of complexes.

Concentration Dependence for Binary Cation–Anion Pairs

To calculate the concentration dependence of conductivity, we utilize the MSA theory of Bernard et al. (1992) and develop its semiempirical extension to higher concentrations. According to Bernard et al. (1992), the conductivity of an ion in a finite-concentration solution (λ_i) is related to the limiting conductivity of this ion (λ_i^0) by

$$\lambda_i = \lambda_i^0 \left(1 + \frac{\delta v_i^{el}}{v_i^0} \right) \left(1 + \frac{\delta X}{X} \right) \tag{9}$$

where $\delta X/X$ is the relaxation effect and $\delta v_i^{el}/v_i^0$ is the electrophoretic correction. Detailed expressions for the relaxation and electrophoretic terms are given in the appendix. It should be noted that closed-form expressions for $\delta X/X$ and $\delta v_i^{el}/v_i^0$ have been obtained only for systems containing a single cation and a single anion.

In the unrestricted primitive model, an electrolyte solution is approximated by a system containing charged spheres with different sizes in a dielectric continuum. Therefore, eq 9 can be applied to calculate the concentration dependence of λ_i if the following parameters are known: (1) limiting conductivities λ_i^0 and λ_j^0, (2) ionic diameters σ_i and σ_j, (3) ionic charges z_i and z_j and (4) dielectric constant and viscosity of the solvent as functions of temperature and, to a lesser extent, pressure. These properties can be accurately computed from the equations of Uematsu and Franck (1980) and Watson et al. (1980), respectively.

Although the ionic diameters are difficult to measure in solution, they can be reasonably approximated by crystallographic radii (Marcus, 1985). As shown by Bernard et al. (1992), the predictions for several simple salts are in good agreement with experimental data for concentrations up to ca. 1 mol/dm³ when crystallographic radii are used. In this concentration range, the solvation properties and solvent structure do not change appreciably and the primitive model with ion diameters fixed at their crystallographic values is adequate. Thus, the MSA solution can be then used without any parameters derived from conductivity data (other than the limiting ionic conductivities).

In this work, we extend the applicability of the MSA conductivity model to higher concentrations, i.e., well beyond 1 mol/dm³. For this purpose, we note that a change in viscosity at higher concentrations entails a changing ionic mobility, which is a manifestation of altered solvation structure around ions and short-range interactions between ions. These effects can be taken into account by assuming an effective ion size, which is a function of a changed ionic environment in a concentrated solution. Therefore, we introduce a semiempirical modification of the MSA conductivity model, in which the effective ion radius is a function of the ionic strength in a concentrated solution. The algebraic form

Table 2. Comparison of Predicted Limiting Conductivities of Complex Ions (MeCl⁺) with Experimental Data (All Values Are in Ω^{-1} cm² mol⁻¹)

			$\lambda^0_{MeCl^+}$		
complex	$\lambda^0_{Me^{2+}}$	$\lambda^0_{Cl^-}$	predicted	exptl	ref
BaCl⁺	63.8	76.35	31.2	30	Bianchi et al. (1987), recommended value
				22−38	Bianchi et al. (1987), range of values
MgCl⁺	53.3	76.35	26.3	30	Bianchi et al. (1988)
CdCl⁺	53.95	76.35	26.6	25.5	Indaratna et al. (1986a), from transport numbers
				26.0	
				28.2	
				33	Indaratna et al. (1986b), from conductivity

of the ionic-strength dependence of the effective radius has been found by analyzing a large number of conductivity data sets and is given by

$$\bar{\sigma}_{eff} = \frac{I^{1/2}}{(c_1 + c_2 I^{1/2})^{10}} + c_3 \tag{10}$$

In eq 10, the parameters c_i ($i = 1, 2, 3$) are determined by regressing experimental conductivity data for binary cation−anion pairs in concentrated solutions.

The effective radius of a given ion depends, in contrast to the crystallographic radius, on the chemical identity of the counterion. At the same time, effective radii of a cation and an anion cannot be separately evaluated when only overall conductivity data are used. This is due to the fact that the contributions of individual ions to the overall conductance of a solution can be ascertained only when transference data are available in the same concentration and temperature range as the conductivity data. This is usually not the case. Therefore, it is reasonable to utilize an average effective ionic radius, which is a characteristic quantity for any cation−anion pair. In this study, we regress average effective radii for cation−anion pairs using data for single-solute systems. This makes it possible to cover a full range of concentrations that are important for practical applications.

The parameters c_1, c_2, and c_3 are weakly temperature-dependent. For the representation of conductivity data over wide temperature ranges, a linear temperature dependence is used, i.e.

$$c_i = c_{i,0} + c_{i,1}(T - 298.15) \qquad i = 1, 2, 3 \tag{11}$$

The temperature dependence of the average effective ion radii is relatively weak because the effect of temperature on conductivity is primarily accounted for by the limiting conductivities (eq 1) and, to a lesser extent, by the temperature dependence of the relaxation and electrophoretic terms (cf. Appendix). Therefore, the conductivities can be reasonably predicted in substantial temperature ranges even when the parameters c_i ($i = 1, 2, 3$) are determined only from ambient-temperature data.

Concentration Dependence for Multicomponent Systems

The analytical MSA theory of the concentration dependence of conductivity has been developed for systems containing only a single cation and a single anion. Therefore, it is not directly applicable to systems containing two or more solutes (e.g., NaCl + KCl + H_2O) or even systems with a single solute that dissociates into more than two ions (e.g., $ZnCl_2$ + H_2O, which forms the Zn^{2+}, $ZnCl^+$, $ZnCl_3^-$, $ZnCl_4^{2-}$, and Cl^- ions). An analytical theory for multicomponent systems can be ob-

tained only for very dilute solutions (Onsager and Kim, 1957; Justice, 1983). Therefore, it is necessary to develop a technique for predicting the conductivity of multicomponent solutions in the full concentration range.

Urban et al. (1983) and Miller (1996) studied the prediction of electrical conductivity in two-solute systems on the basis of experimental data for single-solute systems. In particular, Miller (1996) reviewed several linear approximations to the specific conductance, which can be written in terms of various solute fractions (molar, equivalent, or ionic strength) and the specific conductance of constituent binary subsystems, i.e.,

$$\kappa(K) = a_1 \kappa_1(K) + a_2 \kappa_2(K) \tag{12}$$

where a_1 and a_2 are the fractions of binary subsystems 1 and 2, respectively. The specific conductances of the binary subsystems (i.e., κ_1 and κ_2) are evaluated at some type of constant concentration (K) which characterizes the mixture (constant total molarity, constant equivalent concentration, or constant ionic strength). Although the use of constant ionic strength is supported by the theories of dilute solutions, the selection of the type of constant concentration is essentially guided only by its empirical effectiveness (Miller, 1996).

No theoretical methods are available for the prediction of conductivity of concentrated solutions that contain any number of ions. Therefore, it is necessary to develop a method that utilizes the available information for binary cation−anion pairs. In the case of complex multicomponent mixtures, it would be ambiguous to determine a priori the binary subsystems that make up the multicomponent mixture. Instead, it is more convenient to express the specific conductivity of the mixture in terms of the composition-dependent conductivities of the constituent ions. In this work, we derive a mixing rule for the conductivity of multicomponent systems by starting from the definition of the specific conductivity, i.e.

$$\kappa = \sum_k^{N_T} c_k |z_k| \lambda_k \tag{13}$$

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, we can calculate the conductivity of individual ions that belong to binary cation−ion pairs. In other words, we can obtain 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. These quantities will be denoted by $\lambda_{i(j)}$ and $\lambda_{j(i)}$, respectively. It can be postulated that λ_k in eq 13 can be approximated by an average value $\bar{\lambda}_k$, i.e.

$$\lambda_k \cong \bar{\lambda}_k \tag{14}$$

Table 3. Representation of Electrical Conductivity in Binary, Ternary, and Quaternary Systems[a]

system	temp range	AAD	ref
		Binary Systems	
$NaCl + H_2O$	298−573	0.71	Chambers (1956), Stearn (1922), Isono (1980), Noyes and Coolidge (1904), Quist and Marshall (1968a)
$KCl + H_2O$	298−523	0.83	Stearn (1922), Campbell and Ross (1956), Miller (1966), Isono (1980), Noyes and Coolidge (1904), Gorbachev and Kondratev (1961)
$NaBr + H_2O$	298−573	0.94	Stearn (1922), Isono (1985), Quist and Marshall (1968b)
$KBr + H_2O$	298−523	0.81	Stearn (1922), Jones and Bickford (1934), Isono (1985), Kondratev and Gorbachov (1965)
$NaI + H_2O$	298−573	1.50	Stearn (1922), Molenat (1969), Dunn and Marshall (1969)
$KI + H_2O$	298−523	0.92	Stearn (1922), Chambers (1958), Kondratev and Gorbachov (1965)
$MgCl_2 + H_2O$	298−523	1.99	Miller et al. (1984), Isono (1985), Kondratev and Nikich (1963)
$HCl + H_2O$	273−338	1.30	Owen and Sweeton (1941), Haase et al. (1965)
$HNO_3 + H_2O$	273−323	1.05	Haase et al. (1965)
$NH_4NO_3 + H_2O$	298−453	1.33	Sharma and Gaur (1977), Campbell and Kartzmark (1952), Campbell et al. (1954)
$AgNO_3 + H_2O$	298−495	1.24	Campbell and Kartzmark (1952), Campbell et al. (1954), Campbell and Singh (1959)
$HCOOK + H_2O$	288−328	1.47	Isono (1985)
$CdCl_2 + H_2O$	298	0.33	McQuillan (1974), Indaratna et al. (1986b)
		Ternary Systems	
$KCl + NaCl + H_2O$	298	0.24	Stearn (1922)
$KBr + NaBr + H_2O$	298	0.72	Stearn (1922)
$KI + NaI + H_2O$	298	0.59	Stearn (1922)
$NaCl + MgCl_2 + H_2O$	298	0.73	Bianchi et al. (1989)
$MgCl_2 + HCl + H_2O$	298	2.88	Berecz and Báder (1973)
$CdCl_2 + HCl + H_2O$	298	0.92	Török and Berecz (1989)
		Quaternary System	
$NaCl + KCl + HCl + H_2O$	298	1.29	Ruby and Kawai (1926)

[a] The deviations from experimental data are defined as

$$AAD = \frac{100}{N}\sum|(\kappa_{calc} - \kappa_{exp})/\kappa_{exp}|$$

where $\bar{\lambda}_k$ is obtained by a suitable combination of $\lambda_{i(j)}$ and $\lambda_{j(i)}$. The average conductivity of the ith cation ($\bar{\lambda}_i$) is obtained by averaging over all anions that exist in the mixture, i.e.

$$\bar{\lambda}_i = \sum_j^{N_A} f_j \lambda_{i(j)}(I) \tag{15}$$

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.

$$\bar{\lambda}_j = \sum_i^{N_C} f_i \lambda_{j(i)}(I) \tag{16}$$

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 9 is applied at the following concentrations of the ions in a binary pair $i-j$:

$$c_i = \frac{2I}{|z_i|(|z_i| + |z_j|)}; \quad c_j = \frac{2I}{|z_j|(|z_i| + |z_j|)} \tag{17}$$

Equations 17 have been derived to satisfy the condition of a constant ionic strength.

The definition of the fraction of the ith ion (f_i) in eqs 15 and 16 is guided by the empirical effectiveness of the final mixing rule. Tests made using all the ternary and quaternary systems listed in Table 3 revealed that the best agreement is obtained when f_i is the equivalent fraction given by

$$f_i = \frac{|z_i|c_i}{c_{eq}} \tag{18}$$

where the equivalent concentration c_{eq} is defined as

$$c_{eq} = \sum_i^{N_C} c_i|z_i| = \sum_j^{N_A} c_j|z_j| \tag{19}$$

Equations 14−19 make it possible to predict the conductivity of a multicomponent mixture from conductivities of ions computed for binary subsystems containing a single cation and a single anion. It is noteworthy that eqs 14−19 reduce, for a two-solute system, to eq 12 with $K = I$ and a_i defined as equivalent fractions of solutes.

Results and Discussion

The performance of the proposed model has been tested for a large number of binary and ternary aqueous systems. In particular, we focused on the prediction of electrical conductivity for model multicomponent solutions because aqueous systems of industrial importance usually contain more than one solute. First, the available data for the constituent binary subsystems were correlated by regressing the parameters that determine the dependence of the effective average diameter on ionic strength and temperature (eqs 10 and 11). Then, these parameters were used to predict the conductivity of ternary and quaternary systems.

First, calculations have been performed for systems with simple speciation, i.e., electrolytes that show

Table 4. Coefficients That Determine the Ionic Strength Dependence of the Average Effective Radius (Eqs 10 and 11)[a]

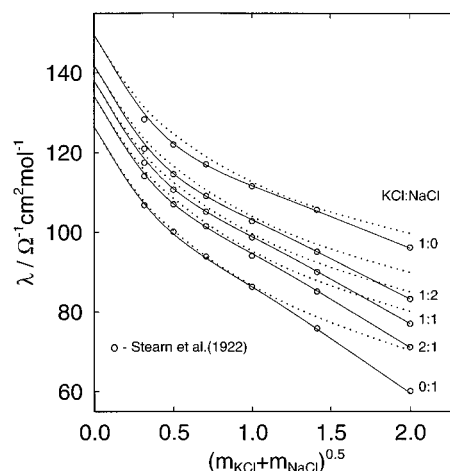| cation–anion pair	$c_{1,0}$	$c_{2,0}$	$c_{3,0}$	$c_{1,1}$	$c_{2,1}$	$c_{3,1}$
Na^+–Cl^-	0.892 69	0.146 90	0.605 11	$0.457\ 16 \times 10^{-3}$	$-0.394\ 0 \times 10^{-3}$	$0.662\ 56 \times 10^{-3}$
K^+–Cl^-	0.937 16	$0.898\ 54 \times 10^{-1}$	0.681 78	$-0.395\ 5 \times 10^{-3}$	$0.331\ 80 \times 10^{-3}$	$-0.188\ 7 \times 10^{-2}$
Na^+–Br^-	0.851 07	0.123 04	0.250 09	$0.596\ 03 \times 10^{-3}$	$-0.114\ 9 \times 10^{-3}$	$0.414\ 67 \times 10^{-2}$
K^+–Br^-	0.921 44	$0.899\ 18 \times 10^{-1}$	0.739 09	$0.761\ 18 \times 10{-3}$	$0.602\ 29 \times 10^{-3}$	$0.202\ 20 \times 10^{-2}$
Na^+–I^-	0.803 78	0.127 23	-0.126 30	$0.858\ 87 \times 10^{-4}$	$-0.618\ 6 \times 10^{-4}$	$0.432\ 52 \times 10^{-2}$
K^+–I^-	0.941 55	$0.829\ 06 \times 10^{-1}$	1.165 3	$0.150\ 73 \times 10^{-1}$	$-0.137\ 2 \times 10^{-1}$	$0.401\ 36 \times 10^{-2}$
Mg^{2+}–Cl^-	0.946 96	0.119 38	0.991 48	$0.125\ 62 \times 10^{-2}$	$-0.813\ 2 \times 10^{-3}$	$0.611\ 66 \times 10^{-3}$
H^+–Cl^-	0.995 67	$0.830\ 35 \times 10^{-2}$	0.382 99	$0.164\ 03 \times 10^{-5}$	$-0.101\ 4 \times 10^{-4}$	$0.896\ 58 \times 10^{-3}$
Cd^{2+}–Cl^-	0.779 22	0.572 47	0.216 37			
$CdCl^+$–$CdCl_4^-$	0.980 53	0.010 64	-0.198 69			
H^+–$CdCl_4^-$	0.914 65	0.0407 16	-1.641 8			
NH_4^+–NO_3^-	0.930 81	0.102 38	0.430 47	$0.648\ 64 \times 10^{-3}$	$0.796\ 89 \times 10^{-5}$	$0.239\ 13 \times 10^{-2}$
Ag^+–NO_3^-	0.996 27	$0.313\ 06 \times 10^{-1}$	0.825 99	$-0.106\ 6 \times 10^{-2}$	$0.217\ 71 \times 10^{-3}$	$-0.607\ 3 \times 10^{-2}$
K^+–$HCOO^-$	0.667 80	0.151 98	2.559 20	$-0.149\ 1 \times 10^{-3}$	$0.374\ 05 \times 10^{-3}$	$0.148\ 13 \times 10^{-1}$

[a] The coefficients $c_{1,1}$, $c_{2,1}$, and $c_{3,1}$ are omitted when they are not necessary for reproducing the experimental data (as listed in Table 3).
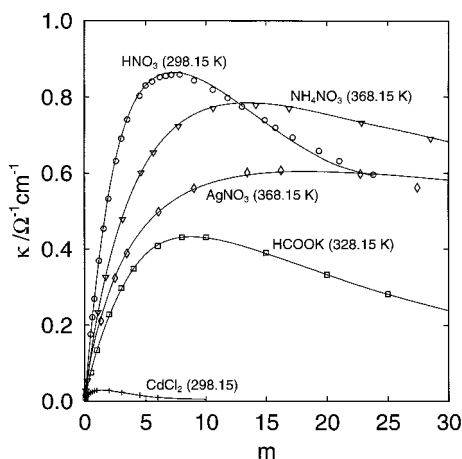
Figure 5. Specific conductivity for electrolytes for which experimental data extend to very high concentrations (up to 30 mol/kg of H_2O). The lines have been calculated using the parameters from Table 4, and the symbols represent experimental data. The data for NH_4NO_3 and $AgNO_3$ are from Campbell 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.

Figure 6. Equivalent conductivity of the ternary system KCl + NaCl + H_2O at 298.15 K for various molar ratios of KCl to NaCl. The solid lines have been calculated using the parameters from Table 4. The dotted lines have been obtained using crystallographic ion radii.

complete dissociation and do not form complexes (e.g., alkali-metal halides). For such systems, a solution with a single solute contains only one cation and one anion. Thus, the selection of the cation–anion pair for regressing the effective diameter is straightforward. For example, the conductivity of the NaCl + H_2O system can be exactly reproduced once the average effective radius for the Na^+–Cl^- pair is determined. Calculations have been performed for binary systems containing H_2O and NaCl, KCl, NaBr, KBr, NaI, KI, $MgCl_2$, HCOOK, $AgNO_3$, NH_4NO_3, HNO_3, or HCl as solutes. The obtained deviations from experimental data are given in Table 3, and the regressed parameters are collected in Table 4. The binary systems shown in Table 3 have been selected in order to include data at high concentrations and/or temperature. Usually, experimental conductivity data are available at either high temperatures or high concentrations. However, data for two of the systems listed in Table 3 (i.e., $AgNO_3$ + H_2O and NH_4NO_3 + H_2O) extend to both high molalities (ca. 29 mol/kg) and high temperatures. For all systems, the representation of experimental data is very satisfactory.

Figure 5 shows specific conductivities as functions of concentration for the systems for which experimental data extend over very wide concentration ranges (up to 30 mol/kg of H_2O). The specific conductivities exhibit maxima followed by a slow, nonasymptotic decrease of κ versus m. The location of the maximum and the shape
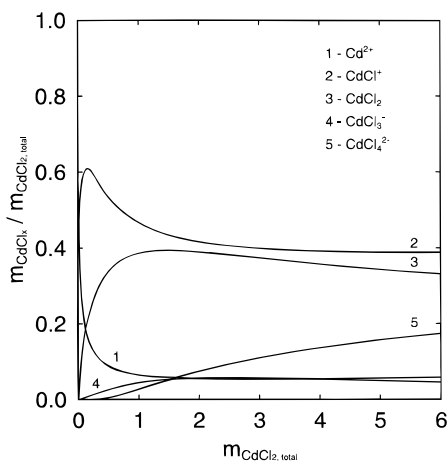
of the κ versus m curve is characteristic for each solution and cannot be easily generalized. It is noteworthy that specific conductivity decreases to very small values at high concentrations for some electrolytes (such as $CdCl_2$), whereas it remains quite high for other electrolytes even at $m = 30$ mol/kg of H_2O. Thus, the high-concentration data provide a stringent test for the concentration dependence of the effective ionic radii (eq 10). As shown in Figure 5, eq 10 makes it possible to reproduce the various shapes of the κ versus m curves with very good accuracy.

The parameters regressed from binary data have then been used to predict the conductivity for the ternary systems KCl + NaCl + H_2O, KBr + NaBr + H_2O, KI + NaI + H_2O, NaCl + $MgCl_2$ + H_2O, and $MgCl_2$ + HCl + H_2O as well as for the quaternary system NaCl + KCl + HCl + H_2O. As shown in Table 3, the quality of predicting the conductivity for multicomponent systems is similar to the quality of reproducing the data for the binary subsystems. This indicates that the mixing rule for multicomponent systems (eqs 14–19) does not introduce any significant error into the calculation of conductivities and yields consistent results for a variety of systems. Additionally, the quality of reproducing experimental data is shown in Figures 6 and 7 for the systems KCl + NaCl + H_2O and NaCl + $MgCl_2$ + H_2O, respectively. As illustrated in Figures 6 and 7, the accuracy of representing the experimental data is close to the experimental uncertainty. Figures 6 and 7 also
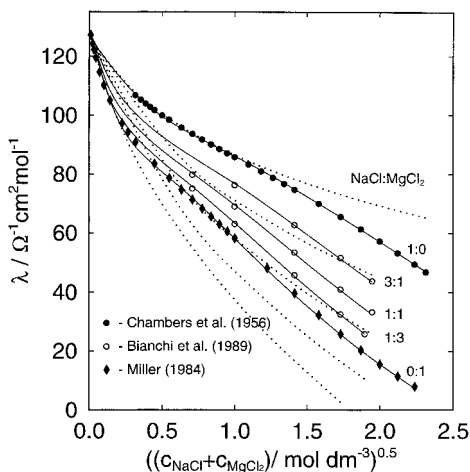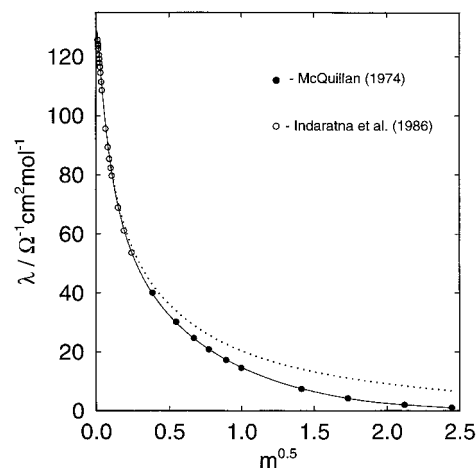
Figure 7. Equivalent conductivity of the ternary system NaCl + MgCl$_2$ + H$_2$O at 298.15 K for various molar ratios of NaCl to MgCl$_2$. The solid lines have been calculated using the parameters from Table 4. The dotted lines have been obtained using crystallographic ion radii.

Figure 9. Equivalent conductivity of the CdCl$_2$ + H$_2$O system. The solid line has been calculated using the parameters from Table 4. The dotted line has been obtained using crystallographic ion radii.
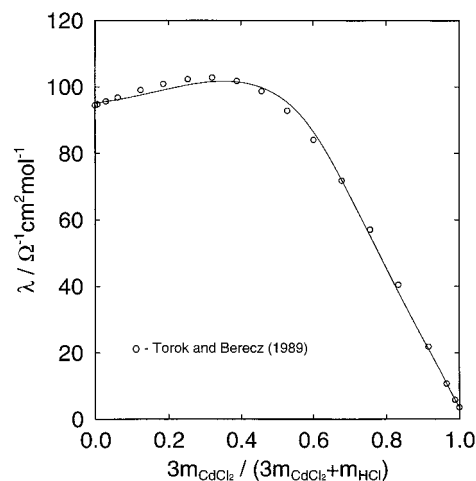

Figure 8. Equilibrium speciation in the CdCl$_2$ + H$_2$O system as a function of the total molality of CdCl$_2$.

Figure 10. Equivalent conductivity of the CdCl$_2$ + HCl + H$_2$O system for the total ionic strength equal to 10 (i.e., $3m_{CdCl_2}$ + m_{HCl} = 10 mol/kg). The solid line has been obtained using the parameters from Table 4.

show 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 experiment for 1:1 electrolytes for concentrations up to ca. 1 mol/dm^3. For electrolytes with higher charges (e.g., 2:1), the predictions from crystalline radii are reliable only up to ca. 0.1–0.2 mol/dm^3. Beyond these concentration limits, it is necessary to rely on the effective, ionic-strength-dependent radii (solid lines).

For practical applications, it is particularly important to calculate the conductivity of systems containing transition metals, which show appreciable complexation. For example, the binary system CdCl$_2$ + H$_2$O contains as many as six distinct species, i.e., Cd^{2+}, CdCl$^+$, CdCl$_{2(aq)}$, CdCl$_3^-$, CdCl$_4^{2-}$, and Cl$^-$. The amounts of various species in an aqueous system are computed in this work by using a thermodynamic model developed by OLI Systems (Zemaitis et al., 1986; Rafal et al., 1995). Figure 8 shows the distribution of various species in the CdCl$_2$ + H$_2$O system obtained from the OLI thermodynamic model. It is evident that this system should be treated as a multicomponent system with two cations (Cd^{2+} and CdCl$^+$), three anions (CdCl$_3^-$, CdCl$_4^{2-}$, and Cl$^-$) and one neutral complex which does not contribute to electrical conductivity (CdCl$_{2(aq)}$). In such systems, it is necessary to select the most impor-

tant cation–anion pairs for which the average effective ion radii have to be adjusted. In the case of the CdCl$_2$ + H$_2$O system, the most important pairs are Cd^{2+}–Cl$^-$ in relatively dilute solutions and CdCl$^+$–CdCl$_4^{2-}$ in more concentrated solutions. The parameters for these pairs are given in Table 4. For the remaining cation–anion pairs, the ion radii were estimated by assuming the additivity of crystalline ion volumes. Figure 9 shows the reproduction of the data for the CdCl$_2$ + H$_2$O system. It can be noted that complexation leads to a more rapid decline of the equivalent conductivity with concentration than that observed for noncomplexing systems (cf. Figures 6 and 7). As shown in Figure 9, the model represents the data within experimental uncertainty (solid lines). Additionally, Figure 10 shows the conductivity in the ternary system CdCl$_2$ + HCl + H$_2$O when the total formal ionic strength (i.e., the ionic strength calculated without regard to complexation) is equal to 10 mol/kg. The maximum of conductivity in Figure 10 is related to the combined effects of complexation and the addition of H$^+$ ions, which are much more mobile. The conductivity in this system is also accurately represented by the model.

As shown in Table 4, temperature-dependent parameters c_i (i = 1, 2, 3) are regressed when experimental data are available in wide temperature ranges. How-

ever, it is worthwhile to note that satisfactory results are also obtained when no temperature dependence of the effective diameter is introduced (i.e., when the coefficients $c_{i,1}$ in eq 11 are set equal to zero). For example, average deviations from experimental data obtained for KCl, KBr, and KI with temperature-dependent parameters c_i are 0.83%, 0.81%, and 0.92%, respectively (cf. Table 3). For all three salts, the experimental data are available in the range from 298.15 to 523.15 K. If a temperature-independent effective diameter was assumed (i.e., $c_{i,1} = 0$, $i = 1, 2, 3$) and established based on the data at the lowest temperature (298.15 K), the average deviations would increase only to 1.98%, 2.71%, and 2.49% for these three salts. This indicates that the model developed in this work can be used to predict electrical conductivities in wide temperature ranges when limited experimental data are available at only one temperature (typically, 298.15 K).

Conclusions

The proposed model for electrical conductivity incorporates four important features, i.e., (1) a technique for predicting the temperature dependence of limiting conductivities on the basis of the concept of structure-breaking and structure-making ions; (2) a method for estimating unknown limiting conductivities of complex species from those of simple ions; (3) an extension of the MSA theory of the concentration dependence of conductivity to high concentrations through the introduction of effective radii; (4) a mixing rule for calculating the conductivity of multicomponent systems. Because of these features, the model is capable of accurately reproducing the conductivity of complex aqueous systems that are encountered in industrial practice. For practical applications, it is particularly important that the conductivity of multicomponent systems can be accurately predicted using parameters obtained from data for single-solute systems. The model is applicable for molalities up to 30 mol/kg of H_2O and temperatures up to 573 K. The predictions are expected to be somewhat less accurate in the 473−573 K temperature range than at temperatures below 473 K because the model parameters were obtained using mostly data for low- and moderate-temperature systems. However, extrapolations with respect to both temperature and concentration are made possible by the use of parameters with a straightforward physical meaning.

Although the model has been applied only to aqueous solutions, it is also applicable to nonaqueous and mixed-solvent systems. However, new parametrization procedures would be necessary for each solvent.

Appendix

According to Bernard et al. (1992), the relaxation term in eq 9 is given by

$$\frac{\delta X}{X} = \frac{\delta X_1^{rel}}{X} + \frac{\delta X_2^{rel}}{X} + \frac{\delta X_1^{hyd}}{X} \quad \text{(A-1)}$$

where $\delta X_1^{rel}/X$, $\delta X_2^{rel}/X$, and $\delta X_1^{hyd}/X$ are the first-order, second-order, and hydrodynamic relaxation terms. The first-order term is

$$\frac{\delta X_1^{rel}}{X} = -\frac{\kappa_q^2}{3}\left[i_0(\kappa_q\sigma_{ij}) - \frac{\epsilon k_B T}{e_i e_j}\kappa_q\sigma_{ij}^2 i_1(\kappa_q\sigma_{ij})\right]I_1 \quad \text{(A-2)}$$

where

$$\kappa_q^2 = \frac{4\pi}{\epsilon k_B T}\frac{\rho_i e_i^2 D_i^0 + \rho_j e_j^2 D_j^0}{D_i^0 + D_j^0} \quad \text{(A-3)}$$

$$i_0(\kappa_q\sigma_{ij}) = \frac{\sinh(\kappa_q\sigma_{ij})}{\kappa_q\sigma_{ij}} \quad \text{(A-4)}$$

$$i_1(\kappa_q\sigma_{ij}) = \frac{\cosh(\kappa_q\sigma_{ij})}{\kappa_q\sigma_{ij}} - \frac{\sinh(\kappa_q\sigma_{ij})}{(\kappa_q\sigma_{ij})^2} \quad \text{(A-5)}$$

In these expressions, ρ_i is the number density of the ith ion, σ_{ij} is given by eq 11, ϵ is defined as

$$\epsilon = 4\pi\epsilon_0\epsilon_s \quad \text{(A-6)}$$

and D_i is the infinite-dilution diffusion coefficient of the ith ion, which is related to the limiting conductivity by

$$\frac{D_i^0}{\lambda_i^0} = \frac{RT}{z_i F^2} \quad \text{(A-7)}$$

where F is the Faraday constant. The integral I_1 in eq A-2 is given by

$$I_1 = \frac{-\kappa_q A_{ij}\exp(-\kappa_q\sigma_{ij})}{\kappa_q^2 + 2\Gamma\kappa_q + 2\Gamma^2 - (2\Gamma^2/\alpha^2)\sum_k \rho_k a_k^2 \exp(-\kappa_q\sigma_{ij})} \quad \text{(A-8)}$$

with

$$A_{ij} = \frac{e_{ij}}{\epsilon k_B T(1 + \Gamma\sigma_i)(1 + \Gamma\sigma_j)} \quad \text{(A-9)}$$

$$a_k = \frac{4\pi e^2}{\epsilon k_B T}\frac{1}{2\Gamma}\frac{z_k}{1 + \Gamma\sigma_k} \quad \text{(A-10)}$$

Γ is the screening parameter from the MSA theory:

$$4\Gamma^2 = \frac{4\pi}{\epsilon k_B T}\sum_i \rho_i\left(\frac{z_i - (\pi/2\Delta)P_n\sigma_i^2}{1 + \Gamma\sigma_i}\right)^2 \quad \text{(A-11)}$$

where

$$P_n = \frac{1}{\Omega}\sum_k \frac{\rho_k\sigma_k z_k}{1 + \Gamma\sigma_k} \quad \text{(A-12)}$$

$$\Omega = 1 + \frac{\pi}{2\Delta}\sum_k \frac{\rho_k\sigma_k^3}{1 + \Gamma\sigma_k} \quad \text{(A-13)}$$

$$\Delta = 1 - \frac{\pi}{6}\sum_k \rho_k\sigma_k^3 \quad \text{(A-14)}$$

The second-order relaxation term is

$$\frac{\delta X_2^{\text{rel}}}{X} =$$

$$-\frac{\kappa_q^2}{3}\left[i_0(\kappa_q\sigma_{ij}) - \frac{\epsilon k_B T}{e_i e_j}\kappa_q\sigma_{ij}^2 i_1(\kappa_q\sigma_{ij})\right]A_{ij}^2\left\{\left(\frac{x^2 + \kappa_q^2}{x^2 - \kappa_q^2}\right)\times\right.$$

$$\left[\frac{\kappa_q^2}{4x^2}\exp(2x\sigma_{ij})E_1[(2x + \kappa_q)\sigma_{ij}] +\right.$$

$$\left.\frac{\exp(-\kappa_q\sigma_{iij})}{4x^2\sigma_{ij}^2}[1 + (2x - \kappa_q)\sigma_{ij}]\right] +$$

$$\frac{\kappa_q C_{ij}}{x - \kappa_q}\left[\frac{x^2 - 2\kappa_q^2}{2\kappa_q(x + \kappa_q)}\exp(x\sigma_{ij})E_1[(x + 2\kappa_q)\sigma_{ij}] -\right.$$

$$\left.\frac{\exp(-2\kappa_q\sigma_{ij})}{2\kappa_q(x + \kappa_q)\sigma_{ij}^2}[1 + x\sigma_{ij}]\right] +$$

$$(1 + x\sigma_{ij})\left[\frac{(x^2 - \kappa_q^2)^2}{4x^2\kappa_q^2}\exp(x\sigma_{ij})E_1[(x + \kappa_q)\sigma_{ij}] -\right.$$

$$\frac{x^2}{4\kappa_q^2}\exp((x - \kappa_q)\sigma_{ij})E_1(x\sigma_{ij})(1 + \kappa_q\sigma_{ij}) +$$

$$\left.\left.\frac{\exp(-2\kappa_q\sigma_{ij})}{4x^2\sigma_{ij}^2}\left(1 + (x - \kappa_q)\sigma_{ij} + \frac{x^3\sigma_{ij}^2}{\kappa_q}\right)\right]\right\} \quad \text{(A-15)}$$

where

$$C_{ij} = \cosh(\kappa_q\sigma_{ij}) + \frac{x}{\kappa_q}\sinh(\kappa_q\sigma_{ij}) \quad \text{(A-16)}$$

$$x = 2\Gamma(1 + \Gamma\bar{\sigma}) \quad \text{(A-17)}$$

$$\bar{\sigma}^n = \frac{\epsilon k_B T}{4\pi e^2}\sum_k \rho_k a_k^2 \sigma_k^n \quad \text{(A-18)}$$

$$E_1(\kappa_q r) = \int_r^\infty \frac{\exp(-\kappa_q r)}{r}\,dr \quad \text{(A-19)}$$

The integral E_1 is evaluated numerically. The hydrodynamic relaxation term is given by

$$\frac{\delta X_1^{\text{hyd}}}{X} =$$

$$\frac{-4\Gamma^2 A_{ij}k_B T}{48\pi\eta(D_i^0 + D_j^0)}\left[i_0(\kappa_q\sigma_{ij}) - \frac{\epsilon k_B T}{e_i e_j}\kappa_q\sigma_{ij}^2 i_1(\kappa_q\sigma_{ij})\right]\times$$

$$\left\{\left(1 + x\sigma_{ij} + \frac{x^2\sigma_{ij}^2}{3}\right)\left[\frac{x^2}{\kappa_q^2}(\exp((x - \kappa_q)\sigma_{ij}))E_1(x\sigma_{ij})(1 +\right.\right.$$

$$\left.\kappa_q\sigma_{ij}) - \frac{x^2\exp(-\kappa_q\sigma_{ij})}{\kappa_q(x + \kappa_q)} - \frac{x^2}{\kappa_q^2}E_1[(x + \kappa_q)\sigma_{ij}] +\right.$$

$$\left(\frac{2x^2 - \kappa_q^2}{x^2}\right)\exp(x\sigma_{ij})E_1[(x + \kappa_q)\sigma_{ij}] -$$

$$\frac{\exp(-\kappa_q\sigma_{ij})}{x^2\sigma_{ij}^2}(1 + (x - \kappa_q)\sigma_{ij}) - \frac{x\exp(-\kappa_q\sigma_{ij})}{x + \kappa_q}\right] +$$

$$\frac{\exp(-\kappa_q\sigma_{ij})}{x^2\sigma_{ij}^2}(1 + (2x - \kappa_q)\sigma_{ij}) -$$

$$\left.\left(\frac{4x^2 - \kappa_q^2}{x^2}\right)\exp(2x\sigma_{ij})E_1[(2x + \kappa_q)\sigma_{ij}]\right\} \quad \text{(A-20)}$$

where η is the viscosity of the solvent.

The electrophoretic term is the sum of a first-order and a second-order term:

$$\frac{\delta\nu_i^{\text{el}}}{\nu_i^0} = \frac{\delta\nu_{i1}^{\text{el}}}{\nu_i^0} + \frac{\delta\nu_{i2}^{\text{el}}}{\nu_i^0} \quad \text{(A-21)}$$

where

$$\nu_i^0 = e_i E \frac{D_i^0}{k_B T} \quad \text{(A-22)}$$

In eq A-22, E is the electric field, which cancels when the terms in eq A-21 are computed. The first-order electrophoretic term is given by

$$\delta\nu_{i1}^{\text{el}} = -\frac{e_i E}{3\pi\eta}\left(\frac{\Gamma}{1 + \Gamma\sigma_i} + \frac{\pi}{2\Delta}\frac{P_n\sigma_i}{z_i(1 + \Gamma\sigma_i)} + \frac{\pi}{z_i}\sum_i \rho_j z_j \sigma_{ij}^2\right) \quad \text{(A-23)}$$

The second-order term consists of two parts, I and J, i.e.

$$\delta\nu_{i2}^{\text{el}} = I + J \quad \text{(A-24)}$$

$$I = \frac{e_i E \kappa_q^2 A_{ij}}{24\pi\eta(x^2 - \kappa_q^2)\sigma_{ij}^2(1 + \Gamma\sigma_i)(1 + \Gamma\sigma_j)}\{(1 + 2x\sigma_{ij}) -$$

$$C_{ij}\exp(-\kappa_q\sigma_{ij})(1 + (x - \kappa_q)\sigma_{ij}) -$$

$$2x^2\sigma_{ij}^2\exp(2x\sigma_{ij})E_1(2x\sigma_{ij}) +$$

$$C_{ij}(x^2 + \kappa_q^2)\sigma_{ij}^2\exp(x\sigma_{ij})E_1[(x + \kappa_q)\sigma_{ij}]\} \quad \text{(A-25)}$$

$$J =$$

$$\frac{\dfrac{e_i E}{12\pi\eta(1 + \Gamma\sigma_i)(1 + \Gamma\sigma_j)}\left(\cosh(\kappa_q\sigma_{ij}) - \dfrac{\sinh(\kappa_q\sigma_{ij})}{\kappa_q\sigma_{ij}}\right)\times \kappa_q^3\exp(-\kappa_q\sigma_{ij})}{\kappa_q^2 + 2\Gamma\kappa_q + 2\Gamma^2 - \dfrac{2\Gamma^2\epsilon k_B T}{4\pi e^2}\displaystyle\sum_k \rho_k a_k^2\exp(-\kappa_q\sigma_k)} \quad \text{(A-26)}$$

Literature Cited

Berecz, E.; Báder, I. Physico-Chemical Study of Ternary Aqueous Electrolyte Solutions. VIII. Electric Conductivity of the System MgCl₂–HCl–H₂O. *Acta Chim. Acad. Sci. Hung.* **1973**, *79*, 81.

Bernard, O.; Kunz, W.; Turq, P.; Blum, L. Conductance in Electrolyte Solutions Using the Mean Spherical Approximation. *J. Phys. Chem.* **1992**, *96*, 3833.

Bianchi, H.; Corti, H. R.; Fernandez-Prini, R. The Conductivity of Dilute Solutions of Mixed Electrolytes. Part 1—The System NaCl–BaCl₂–H₂O at 298.2 K. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 3027.

Bianchi, H.; Corti, H. R.; Fernandez-Prini, R. The Conductivity of Dilute Aqueous Solutions of Magnesium Chloride at 25 °C. *J. Solution Chem.* **1988**, *17*, 1059.

Bianchi, H.; Corti, H. R.; Fernandez-Prini, R. The Conductivity of Concentrated Aqueous Mixtures of NaCl and MgCl₂ at 25 °C. *J. Solution Chem.* **1989**, *18*, 485.

Born, M. Volumes and Heats of Hydration of Ions. *Z. Phys.* **1920**, *1*, 45.

Campbell, A. N.; Ross, L. Application of the Wishaw–Stokes Equation to the Conductances of Potassium Chloride Solutions at 25 °C. *Can. J. Chem.* **1956**, *34*, 566.

Campbell, A. N.; Singh, K. P. Transference Numbers and Conductances in Concentrated Solutions: Silver Nitrate and Silver Perchlorate at 25 °C. *Can. J. Chem.* **1959**, *37*, 1959.

Campbell, A. N.; Kartzmark, E. M. The Conductivity of Strong Solutions of Strong Electrolytes. *Can. J. Chem.* **1952**, *30*, 128.

Campbell, A. N.; Kartzmark, E. M.; Bednas, M. E.; Herron, J. T. The Electrical Conductances of Aqueous Solutions of Silver Nitrate at the Temperatures 221.7 °C and 180.0 °C, Respectively. *Can. J. Chem.* **1954**, *32*, 1051.

Chambers, J. F. The Conductance of Concentrated Aqueous Solutions of Potassium Iodide at 25 °C and of Potassium and Sodium Chlorides at 50 °C. *J. Phys. Chem.* **1958**, *62*, 1136.

Chambers, J. F.; Stokes, J. M.; Stokes, R. H. Conductances of Concentrated Aqueous Sodium and Potassium Chloride Solutions at 25 °C. *J. Phys. Chem.* **1956**, *60*, 985.

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

Dunn, L. A.; Marshall, W. L. Electrical Conductances of Aqueous Sodium Iodide and the Comparative Thermodynamic Behavior of Aqueous Sodium Halide Solutions to 800 °C and 4000 Bars. *J. Phys. Chem.* **1969**, *73*, 723.

Erdey-Gruz, T. *Transport Phenomena in Aqueous Solutions*; Wiley: New York, 1974.

Evans, D. F.; Tominaga, T.; Hubbard, J. B.; Wolynes, P. G. Ionic Mobility. Theory Meets Experiment. *J. Phys. Chem.* **1979**, *83*, 2669.

Falkenhagen, H.; Ebeling, W. *Theorie der Elektrolyte*; S. Hirzel Verlag: Leipzig, Germany, 1971.

Gorbachev, S. V.; Kondratev, V. P. Conductivity of Aqueous Potassium Chloride Solutions at High Temperatures. *Zh. Fiz. Khim.* **1961**, *35*, 1235.

Haase, R.; Sauermann, P.-F.; Dücker, K.-H. Conductivities of Concentrated Electrolyte Solutions. IV. Hydrochloric Acids. *Z. Phys. Chem.* **1965**, *47*, 224.

Harned, H. S.; Owen, B. B. *The Physical Chemistry of Electrolyte Solutions*, 2nd Ed.; Reinhold: New York, 1958.

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

Hubbard, J. B. Dielectric Dispersion and Dielectric Friction in Electrolyte Solutions. II. *J. Chem. Phys.* **1978**, *68*, 1649.

Hubbard, J. B.; Kayser, R. F. Dielectric Saturation and Dielectric Friction on an Ion in a Polar Solvent. *Chem. Phys.* **1982**, *66*, 377.

Ibuki, K.; Nakahara, M. Test of the Hubbard-Onsager Dielectric Friction Theory of Ion Mobility in Nonaqueous Solvents. 2. Temperature Effect. *J. Phys. Chem.* **1987**, *91*, 4411.

Indaratna, K.; McQuillan, A. J.; Matheson, R. A. Transport Numbers of Dilute Aqueous Cadmium Chloride Solutions at 298.15 K. *J. Chem. Soc., Faraday Trans. 1* **1986a**, *82*, 2763.

Indaratna, K.; McQuillan, A. J.; Matheson, R. A. Conductivity of Unsymmetrical and Mixed Electrolytes. Dilute Aqueous Cadmium Chloride and Barium Chloride−Hydrochloric Acid Mixtures at 298.15 K. *J. Chem. Soc., Faraday Trans. 1* **1986b**, *82*, 2755.

Isono, T. Measurements of Density, Viscosity and Electrolytic Conductivity of Concentrated Electrolyte Solutions. I. LiCl, NaCl, KCl, RbCl, CsCl, MgSO₄, ZnSO₄ and NiSO₄. *Rikagaku Kenkyusho Hokoku* **1980**, *56*, 103.

Isono, T. Densities, Viscosities and Electrolytic Conductivities of Concentrated Aqueous Solutions of 31 Solutes in the Temperature Range 15−55 °C and Empirical Equations for the Relative Viscosity. *Rikagaku Kenkysho Hokoku* **1985**, *61*, 53.

Jones, G.; Bickford, C. F. The Conductance of Aqueous Solutions as a Function of the Concentration. I. Potassium Bromide and Lanthanum Chloride. *J. Am. Chem. Soc.* **1934**, *56*, 602.

Justice, J.-C. Conductance of Electrolyte Solutions. In *Comprehensive Treatise of Electrochemistry*; Conway, B. E., Bockris, J. O'M., Yeager, E., Eds.; Plenum Press: New York, 1983; vol. 5, Chapter 3.

Kay, R. L.; Evans, D. F. The Effect of Solvent Structure on the Mobility of Symmetrical Ions in Aqueous Solutions. *J. Phys. Chem.* **1966**, *70*, 2325.

Kay, R. L.; Cunningham, G. P.; Evans, D. F. The Effect of Solvent Structure on Ionic Mobilities in Aqueous Solvent Mixtures. In *Hydrogen-Bonded Solvent Systems*; Covington, A. K., Jones, P., Eds.; Taylor and Francis: London, 1968; p 249.

Kondratev, V. P.; Nikich, V. I. Specific Conductance of Aqueous Solutions of Alkaline Earth Metal Chlorides at High Temperatures. *Z. Phys. Chem.* **1963**, *37*, 100.

Kondratev, V. P.; Gorbachov, S. V. Electrical Conductivity of Aqueous Solutions of Potassium Salts at High Temperatures. *Russ. J. Phys. Chem.* **1965**, *39*, 1599.

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

Marshall, W. L. Reduced State Relationship for Limiting Electrical Conductances of Aqueous Ions over Wide Ranges of Temperature and Pressure. *J. Chem. Phys.* **1987**, *87*, 3639.

McQuillan, A. J. Irreversible Thermodynamics and the Transference Numbers of Aqueous Cadmium Chloride Solutions. *J. Chem. Soc., Faraday Trans. 1* **1974**, *70*, 1558.

Miller, D. G. Application of Irreversible Thermodynamics to Electrolyte Solutions. Determination of Ionic Transport Coefficients l_{ij} for Isothermal Vector Transport Processes in Binary Electrolyte Systems. *J. Phys. Chem.* **1966**, *70*, 2639.

Miller, D. G. Binary Mixing Approximations and Relations Between Specific Conductance, Molar Conductance, Equivalent Conductance and Ionar Conductance for Mixtures. *J. Phys. Chem.* **1996**, *100*, 1220.

Miller, D. G.; Rard, J. A.; Eppstein, L. B.; Albright, J. G. Mutual Diffusion Coefficients and Ionic Coefficients l_{ij} of MgCl₂−H₂O at 25 °C. *J. Phys. Chem.* **1984**, *88*, 5739.

Molenat, J. Systematic Study of Conductivity at 25 °C in Concentrated Alkali Halide Solutions. *J. Chim. Phys.* **1969**, *66*, 825.

Noyes, A. A.; Coolidge, W. D. The Electrical Conductivity of Aqueous Solutions at High Temperatures. *J. Am. Chem. Soc.* **1904**, *26*, 134.

Onsager, L. The Theory of Electrolytes. *Phys. Z.* **1926**, *27*, 388.

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

Owen, B. B.; Sweeton, F. H. The Conductance of Hydrochloric Acid in Aqueous Solutions from 5 to 65 °C. *J. Am. Chem. Soc.* **1941**, *63*, 2811.

Pebler, A. Temperature Correction for the Specific Conductivity of Dilute Aqueous Ammonia Solutions. *Anal. Chem.* **1981**, *53*, 1134.

Quist, A. S.; Marshall, W. L. Assignment of Limiting Equivalent Conductances for Single Ions to 400°. *J. Phys. Chem.* **1965**, *69*, 2984.

Quist, A. S.; Marshall, W. L. Electrical Conductances of Aqueous Sodium Chloride Solutions from 0 to 800 °C and at Pressures to 4000 Bars. *J. Phys. Chem.* **1968a**, *72*, 684.

Quist, A. S.; Marshall, W. L. Electrical Conductances of Aqueous Sodium Bromide Solutions from 0 to 800 °C and at Pressures to 4000 Bars. *J. Phys. Chem.* **1968b**, *72*, 2100.

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

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

Ruby, C. E.; Kawai, J. The Densities, Equivalent Conductances and Relative Viscosities at 25 °C, of Solutions of Hydrochloric Acid, Potassium Chloride and Sodium Chloride and of Their Binary and Ternary Mixtures of Constant Chloride-Ion-Constituent Content. *J. Am. Chem. Soc.* **1926**, *48*, 1119.

Sharma, R. C.; Gaur, H. C. Conductivity of Highly Concentrated Aqueous Electrolyte Solutions: Ammonium Nitrate−Water System. *Indian J. Chem.* **1977**, *15A*, 84.

Smedley, S. I. *The Interpretation of Ionic Conductivity in Liquids*; Plenum Press: New York, 1980.

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

Stearn, A. Ionic Equilibria of Strong Electrolytes. *J. Am. Chem. Soc.* **1922**, *44*, 670.

Török, T. I.; Berecz, E. Volumetric Properties and Electrolytic Conductances of Aqueous Ternary Mixtures of Hydrogen Chloride and Some Transition Metal Chlorides at 25 °C. *J. Solution Chem.* **1989**, *18*, 1117.

Turq, P.; Blum, L.; Bernard, O.; Kunz, W. Conductance in Associated Electrolytes Using the Mean Spherical Approximation. *J. Phys. Chem.* **1995**, *99*, 822.

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

Urban, D.; Gerets, A.; Kiggen, H.-J.; Schönert, H. Ionic Mobilities in the Ternary Solution H_2O + KCl + NaCl at 25 °C. *Z. Phys. Chem. (Neue Folge)* **1983**, *137*, 69.

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

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