Predicting the Diffusion Coefficients of Concentrated Mixed Electrolyte Solutions from Binary Solution Data. $NaCl + MgCl_2 + H_2O$ and $NaCl + SrCl_2 + H_2O$ at 25 °C

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The model used by Stokes to interpret binary mutual diffusion in concentrated electrolyte solutions can be generalized to estimate mixed electrolyte diffusion coefficients (including cross-coefficients for coupled diffusion) from binary solution activities, viscosities, and diffusion coefficients which are available for many aqueous electrolytes. To test the accuracy of this estimation procedure, ternary D_{ik} coefficients are predicted for NaCl (1) + $MgCl_2$ (2) + H_2O solutions and compared with accurate measured values over a wide composition range. At high NaCl concentrations the cross-coefficient D_{12} is larger than the main coefficients D_{11} and D_{22}. This behavior is correctly predicted together with the crossover of D_{11} and D_{22} observed at low NaCl concentrations. The strong composition dependence of the D_{ik} coefficients is caused by changes in the viscosity and the thermodynamic driving forces for diffusion. For NaCl + $MgCl_2$ + H_2O solutions the average value of $|D_{\mathrm{ik}}(\text{measured}) - D_{ik}(\text{predicted})|$ is (0.04×10^{-5}) $cm^2\ s^{-1}$ at ionic strengths from 0.015 to 9 mol dm^{-3}. Similar agreement is obtained for the extensive ternary diffusion data available for NaCl + $SrCl_2$ + H_2O solutions.

Introduction

Diffusion in solutions of mixed electrolytes plays a key role in processes such as desalination, ion exchange, crystallization, dissolution, corrosion, electroplating, and battery chemistry (Cussler, 1976; Pletcher, 1982; Tuwiner, 1962). In view of the considerable effort devoted to understanding these important processes, mixed-electrolyte diffusion data are scarce (Rard and Miller, 1987). Much more is known about binary diffusion in solutions containing a single electrolyte (Tyrrell and Harris, 1984), such as NaCl + H_2O. In practice, however, binary diffusion coefficients are unreliable indicators of mixed-electrolyte diffusion because of the strong interactions between dissolved electrolytes. For example, adding $MgCl_2$ to a binary aqueous solution of NaCl can reduce the diffusion coefficient of NaCl by >70% (Paduano et al., 1989). There is the additional complication that fluxes of electrolytes tend to be strongly coupled. It is not uncommon for a mole of a diffusing electrolyte to cotransport or countertransport several moles of another electrolyte (Leaist and Curtis, 1999), even in very dilute solutions. Coupled electrolyte diffusion is not observed in binary electrolyte solutions.

Nernst−Planck and related equations can be used to estimate the diffusion properties of mixed-electrolyte solutions, but these predictions are reliable only for dilute solutions (Newman, 1973). Significant progress was made when Stokes and Agar showed that the Hartley−Crank equations for diffusion in nonelectrolyte mixtures (Hartley and Crank, 1949) can be extended to concentrated electrolyte solutions by including terms for ionic hydration (Robinson and Stokes, 1959). Treating the hydration number as an adjustable parameter, the concentration dependence of the binary diffusion coefficient of strong univalent electrolytes is accurately represented at concentrations up to several moles per liter (Wishaw and Stokes, 1954).

In a recent study the model developed by Stokes and Agar was generalized to help interpret the diffusion properties of mixed electrolyte solutions (Leaist and Curtis, 1999). The generalized model can also be used to estimate mixed electrolyte diffusion coefficients (including cross-coefficients for coupled diffusion) from binary solution diffusion coefficients, viscosities, and activities which are available for many aqueous electrolytes. In this paper the accuracy of the estimation procedure is tested by comparing predicted ternary diffusion coefficients with accurate measured values for NaCl + $MgCl_2$ + H_2O solutions (Albright et al., 1989; Leaist, 1988; Mathew et al., 1989; Mathew et al., 1990; Miller et al., 1993; Paduano et al., 1989). The exceptional amount of data reported for this system allows a meaningful comparison of the trends in the measured and predicted diffusion properties over a wide composition range.

At high NaCl concentrations, a gradient in the concentration of $MgCl_2$ produces a coupled flow of NaCl which is larger than the main flow of $MgCl_2$ (Albright et al., 1989). One of the goals of the present study is to provide an explanation for this behavior. In addition, predicted ternary diffusion coefficients are compared with the extensive measurements reported for NaCl + $SrCl_2$ + H_2O solutions (Rard and Miller, 1987, 1988).

The concentration dependence of mutual diffusion coefficients is dominated by changes in the viscosity and thermodynamic driving forces (Robinson and Stokes, 1959; Wishaw and Stokes, 1954). In this paper Pitzer's equations (Pitzer and Kim, 1974) are used to evaluate the thermodynamic contributions to the predicted diffusion coefficients. Accurate viscosity data have been reported for aqueous solutions of NaCl (Gonçalves and Kesting, 1977), $MgCl_2$ (Phang and Stokes, 1980), $SrCl_2$ (Zaytsev and Aseyev, 1992), and NaCl + $MgCl_2$ (Mills et al., 1987). We report here viscosities for aqueous NaCl + $SrCl_2$ solutions.

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Experimental Section

An Ubbelohde viscometer was used to measure relative viscosities with an estimated accuracy of ±1%. Distilled, deionized water and reagent-grade (BDH AnalaR) NaCl and $SrCl_2{\cdot}6H_2O$ were used. A concentrated stock solution of $SrCl_2$ was prepared and analyzed by mass titration against silver nitrate. Solutions for the viscosity measurements were prepared by mixing weighed amounts of water, NaCl, and the $SrCl_2$ stock solution.

Results and Discussion

Binary Diffusion of Aqueous NaCl, $MgCl_2$, and $SrCl_2$. In this section data for binary aqueous solutions of NaCl, $MgCl_2$, and $SrCl_2$ are used to evaluate hydration numbers for the diffusion of the electrolytes. This information is required to predict the diffusion coefficients of the mixed electrolytes.

Mutual diffusion (chemical interdiffusion) in a binary solution of water (0) + electrolyte (1) is described by Fick's equation

$$J_1 = -D\nabla c_1 \tag{1}$$

J_1 is the molar flux of electrolyte in the volume-fixed frame of reference, D is the binary diffusion coefficient, and c_1 is the electrolyte concentration in moles per unit volume.

To develop a model for the concentration dependence of D, the following assumptions are made (Robinson and Stokes, 1959): (1) each mole of electrolyte diffuses with a fixed number (h_1) of moles of bound water; (2) the diffusion mobilities are inversely proportional to the solution viscosity; (3) the pure-diffusion fluxes of free water and hydrated electrolyte are driven by the negative gradient in the chemical potential of each component. These assumptions lead to the expression (Leaist and Curtis, 1999)

$$D = (1 - c_1V_1')D_1' + c_1V_1'D_0' \tag{2}$$

for the binary diffusion coefficient. D_0' and D_1' are the pure diffusion coefficients of free water and hydrated electrolyte defined by

$$D_0' = \frac{D_0^*}{\eta_r}\frac{\mathrm{d}\ln a_0}{\mathrm{d}\ln c_0'} \tag{3}$$

$$D_1' = \frac{D_1^*}{\eta_r}\left[\frac{1}{\nu}\frac{\mathrm{d}\ln a_1}{\mathrm{d}\ln c_1} + h_1\frac{\mathrm{d}\ln a_0}{\mathrm{d}\ln c_1}\right] \tag{4}$$

and V_1' is the partial molar volume of the hydrated electrolyte. In the notation used here D_0^* is the self-diffusion coefficient of pure water (2.29×10^{-5} cm^2 s^{-1} at 25 °C (Easteal, 1991)), D_1^* is the limiting electrolyte diffusion coefficient at infinite dilution, η_r is the relative viscosity, a_1 and a_0 are the stoichiometric activities of water and the electrolyte (treated as an anhydrous component), and ν is the number of moles of ions per mole of electrolyte (e.g., 3 for $MgCl_2$). The concentration of free water, $c_0' = c_0 - h_1c_1$, is obtained by subtracting the concentration of bound water from the stoichiometric (total) water concentration.

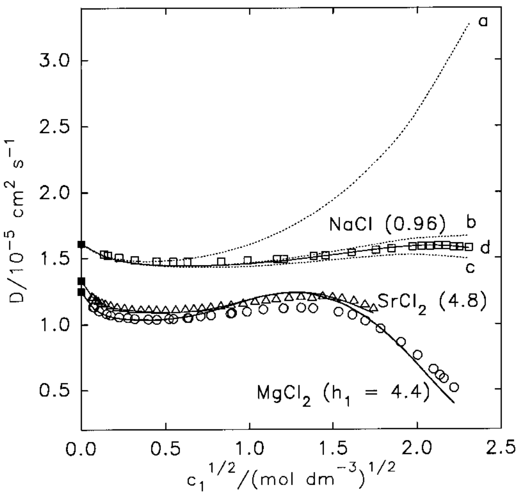

Figure 1. Binary mutual diffusion coefficients at 25 °C plotted against the square root of the electrolyte concentration. Measured D values: □, NaCl (Rard and Miller, 1979); ○, $MgCl_2$ (Miller et al., 1984); △, $SrCl_2$ (Rard and Miller, 1982). Nernst limiting D^* values: ■. Solid curves: fitted D values (eq 2) with hydration numbers 0.96 for NaCl, 4.4 for $MgCl_2$, and 4.8 for $SrCl_2$. Dotted curves: predicted D values for NaCl with terms included for (a) nonideal solution thermodynamics, (b) viscosity changes, (c) ionic hydration, and (d) zero-volume flow.

The hydration numbers indicated in Figure 1 were evaluated by fitting eq 2 to accurate D values measured for aqueous NaCl (Rard and Miller, 1979), $MgCl_2$ (Miller et al., 1984), and $SrCl_2$ (Rard and Miller, 1982) at 25 °C and concentrations up to 5.3, 4.9, and 3.0 mol dm^{-3}, respectively. Despite the high ionic strengths, the agreement between the measured and fitted D values is nearly quantitative for NaCl and $SrCl_2$, though poorer for $MgCl_2$. The average values of $|D(\text{measured}) - D(\text{predicted})|$ for aqueous NaCl, $MgCl_2$, and $SrCl_2$ are 0.02×10^{-5}, 0.05×10^{-5}, and 0.02×10^{-5} cm^2 s^{-1}, respectively.

The relative importance of the factors influencing the concentration dependence of the binary diffusion coefficient is illustrated in Figure 1 for aqueous NaCl by plotting the predicted D values with successive corrections applied for (a) nonideal solution thermodynamics, (b) viscosity changes, (c) hydration, and (d) zero-volume flow (Leaist and Curtis, 1999). In this case thermodynamic and viscosity factors make the largest contribution to changes in D with concentration.

The electrolyte activities used to calculate the binary diffusion coefficients were evaluated from Pitzer's equations and the $\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ} parameters listed in Table 1 (Pitzer and Mayorga, 1973). These equations give the stoichiometric electrolyte activity a_1 as a function of the electrolyte molality m_1 and the mean ionic activity coefficient γ_1 ($a_1 = \gamma_1^2m_1^2$ for NaCl and $a_1 = 4\gamma_1^3m_1^3$ for $MgCl_2$ and $SrCl_2$). The density equation

$$\rho(c_1) = \rho_0^* + \sum_{q=2}^{7}A_{1q}(c_1/\mathrm{mol\ dm^{-3}})^{q/2} \tag{5}$$

and the A_{1q} parameters listed in Table 1 (Miller et al., 1984; Rard and Miller, 1979, 1982) were used to convert electrolyte molalities to molarities. ρ is the density of pure water (0.997 045 g cm^{-3} at 25 °C). The Gibbs−Duhem relation $\mathrm{d}\ln a_0 = -55.51m_1\,\mathrm{d}\ln a_1$ was used in eqs 3 and 4 to calculate the changes in the water activity.

The relation $V_1 = (M_1 - \mathrm{d}\rho/\mathrm{d}c_1)/(\rho - c_1\,\mathrm{d}\rho/\mathrm{d}c_1)$ was used to evaluate the partial molar volume of each electrolyte (Dunlop and Gosting, 1959), where M_1 is the molar mass of the anhydrous electrolyte. The partial molar volume of the stoichiometric water component, V_0, was evaluated from the identity 1000 cm^3 dm^{-3} = $c_0V_0 + c_1V_1$. Provided there is sufficient water to hydrate the ions ($c_0 > h_1c_1$), added water increases the number of moles of free water, leaving the amount of water of hydration unchanged. The

Table 1. Thermodynamic, Density, Viscosity, Conductivity, and Hydration Parameters for Binary Aqueous Solutions of NaCl, $MgCl_2$, and $SrCl_2$ at 25 °C

parameter	NaCl	$MgCl_2$	$SrCl_2$
Thermodynamic Parameters (Pitzer and Mayorga, 1973)			
$\beta^{(0)}$/kg mol^{-1}	0.0765	0.3524	0.2858
$\beta^{(1)}$/kg mol^{-1}	0.2664	1.682	1.667
C^{ϕ}/kg^2 mol^{-2}	0.001 27	0.005 19	−0.001 30
max. molality/ mol kg^{-1}	6	4.5	4
Density Parameters (Albright et al., 1982; Rard and Miller, 1979, 1982)			
A_{i2}/g cm^{-3}	0.041 540	0.082 947 10	0.139 262 4
A_{i3}/g cm^{-3}	−0.000 829 7	−0.018 765 29	−0.003 276 04
A_{i4}/g cm^{-3}	−0.000 910 5	0.026 802 78	−0.003 004 48
A_{i5}/g cm^{-3}	0.000 192 1	−0.024 313 55	0.000 733 619 3
A_{i6}/g cm^{-3}	0.0	0.009 888 612	0.0
A_{i7}/g cm^{-3}	0.0	−0.001 481 259	0.0
max. molarity/ mol dm^{-3}	5.4	5.0	3.1
Viscosity Parameters			
B_{i1}	0.006 436	−0.073 79	−0.116 074
B_{i2}	0.078 185	0.635 04	0.530 185
B_{i3}	0.008 629	−0.294 91	−0.222 251
B_{i4}	0.002 759	0.281 15	0.150 074
B_{i5}	−0.000 404	−0.081 82	−0.026 855
B_{i6}	0.000 046	0.010 62	0.001 198
max. molarity/ mol dm^{-3}	5.2	5.0	3.5
Limiting Diffusion Coefficients and Molar Ionic Conductivities (Robinson and Stokes, 1959)			
Λ_{cation}*/S cm^2 mol^{-1}	50.10	106.10	118.90
Λ_{anion}*/S cm^2 mol^{-1}	76.35	76.35	76.35
D_{cation}*/10^{-5} cm^2 s^{-1}	1.334	0.7063	0.7915
D_{anion}*/10^{-5} cm^2 s^{-1}	2.033	2.033	2.033
Hydration Numbers			
h_1	0.96	4.4	4.8

partial molar volumes of stoichiometric water and free water are therefore identical: $V_0 = V_0'$. The partial molar volume of the hydrated electrolyte is $V_1' = V_1 + h_1V_0$.

Relative viscosities were calculated from the equation (Phang and Stokes, 1980)

$$\eta_r(c_1) = 1 + \sum_{q=1}^{6} B_{1q}(c_1/\text{mol dm}^{-3})^{q/2} \tag{6}$$

which was fitted to accurate viscosity data reported for binary aqueous solutions of NaCl (Gonçalves and Kestin, 1977), $MgCl_2$ (Phang and Stokes, 1980), and $SrCl_2$ (Zaytsev and Aseyev, 1992). The B_{1q} parameters for each electrolyte are listed in Table 1.

The intercepts plotted in Figure 1 are the limiting binary electrolyte diffusion coefficients calculated from the Nernst relations $D_1^* = 2D_{Na}^*D_{Cl}^*/(D_{Na}^* + D_{Cl}^*)$ for NaCl and $D_1^* = 3D_M^*D_{Cl}^*/(2D_M^* + D_{Cl}^*)$ for $MgCl_2$ and $SrCl_2$. The subscript M denotes Mg or Sr. Accurate limiting ionic diffusion coefficients D_Q^* were evaluated from limiting molar ionic conductivities Λ_Q^* (Robinson and Stokes, 1959) by using the identity $D_Q^* = RT\Lambda_Q^*/z_Q^2F^2$, where z_Q is the charge number for ion Q and F is the Faraday constant.

Ternary Diffusion in Aqueous NaCl (1) + $MgCl_2$ (2) Solutions. Mutual diffusion in ternary NaCl (1) + $MgCl_2$ (2) + H_2O solutions is described by the coupled Fick equations (Tyrrell and Harris, 1984)

$$J_1 = -D_{11}\nabla c_1 - D_{12}\nabla c_2 \tag{7}$$

$$J_2 = -D_{21}\nabla c_1 - D_{22}\nabla c_2 \tag{8}$$

The ternary diffusion coefficient D_{ik} gives the molar flux of electrolyte i produced by the gradient in the concentration of electrolyte k in the volume-fixed frame of reference.

Electrolyte fluxes can be strongly coupled by electrostatic forces, even in very dilute solutions (Leaist and Curtis, 1999). A $MgCl_2$ concentration gradient, for example, generates an electric field which slows down the diffusing Cl^- ions and speeds up the less-mobile Mg^{2+}, thereby preventing charge separation. If the solution also contains NaCl, the electric field produced by the $MgCl_2$ gradient will drive a coupled flux of Na^+ ions cocurrent to the diffusing Mg^{2+} ions. This electrostatic mechanism makes a positive contribution to the cross-coefficient D_{12} for NaCl (1) + $MgCl_2$ (2) + H_2O solutions.

The treatment of diffusion in concentrated binary electrolyte solutions is extended to mixed electrolytes by including cross-mobility terms L_{ik}' ($i \neq k$) for the electrostatic coupling of the diffusing electrolyte components (Leaist and Curtis, 1999). For a ternary mixed electrolyte solution, the expressions for the pure diffusion coefficients are

$$D_{ik}' = RT\sum_{q=1}^{2} L_{iq}'\left[\left(\frac{\partial \ln a_q}{\partial c_k}\right)_{c_{p\neq k}} + h_q\left(\frac{\partial \ln a_0}{\partial c_k}\right)_{c_{p\neq k}}\right] \tag{9}$$

The mobility coefficients for the aqueous NaCl (c_1) + MCl_2 (c_2) solutions (M = Mg or Sr) considered in this paper are (Leaist, 1982)

$$L_{11}' = c_1D_{Na}^*[4c_2D_M^* + (c_1 + 2c_2)D_{Cl}^*]/B \tag{10}$$

$$L_{12}' = L_{21}' = -2c_1c_2D_{Na}^*D_M^*/B \tag{11}$$

$$L_{22}' = c_2D_M^*[c_1D_{Na}^* + (c_1 + 2c_2)D_{Cl}^*]/B \tag{12}$$

where B is an abbreviation for

$$B = RT\eta_r[c_1D_{Na}^* + 4c_2D_M^* + (c_1 + 2c_2)D_{Cl}^*] \tag{13}$$

The predicted ternary diffusion coefficients are (Leaist and Curtis, 1999)

$$D_{ik} = D_{ik}' - c_i\left[\sum_{q=1}^{2} V_q'D_{qk}' + c_0'V_0D_0'\left(\frac{\partial \ln a_0}{\partial c_k}\right)_{c_{p\neq k}}\right] \tag{14}$$

The ternary diffusion coefficients predicted by eq 14 for aqueous NaCl (1) + $MgCl_2$ (2) solutions are plotted in Figures 2−6 together with the measured coefficients for this extensively studied system. In Figures 2−4 the D_{ik} coefficients are plotted against the total electrolyte concentration for solutions containing NaCl and $MgCl_2$ at molar ratios of 1:1, 1:3, and 3:1 (Albright et al., 1989; Mathew et al., 1990; Leaist, 1988; Miller et al., 1993). Figure 5 gives the results for solutions containing a fixed concentration of $MgCl_2$ and a large excess of NaCl (Mathew et al., 1989). The results for a fixed concentration of NaCl and a large excess of $MgCl_2$ (Paduano et al., 1989) are plotted in Figure 6.

The binary solution parameters $\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ} (Pitzer and Mayorga, 1973) listed in Table 1 and Pitzer's mixed-electrolyte equations (Pitzer and Kim, 1974) were used to calculate the stoichiometric electrolyte activities, a_1 and a_2. Solution densities were used to convert the molalities of

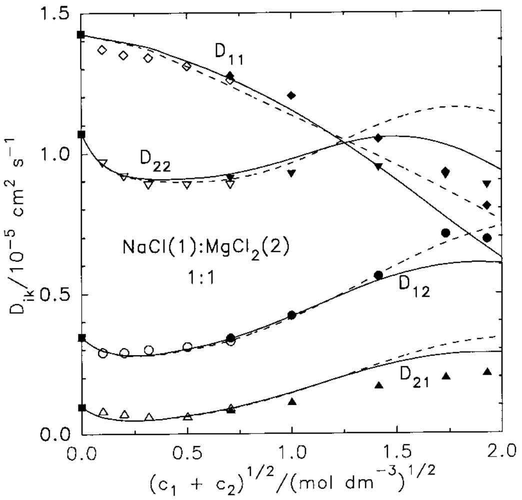

Figure 2. Ternary mutual diffusion coefficients of aqueous NaCl (c_1) + MgCl$_2$ (c_2) solutions at 25 °C plotted against the square root of the total electrolyte concentration. 1:1 molar ratio of NaCl/MgCl$_2$. Measured D_{ik} values: ◆, D_{11}; ●, D_{12}; ▲, D_{21}; ▼, D_{22} (Miller et al., 1993); ◇, D_{11}; ○, D_{12}; △, D_{21}; ▽, D_{22} (Leaist, 1988). Limiting Nernst values: ■. Predicted D_{ik} values: —, using ternary solution densities and viscosities; – – –, using binary solution data.

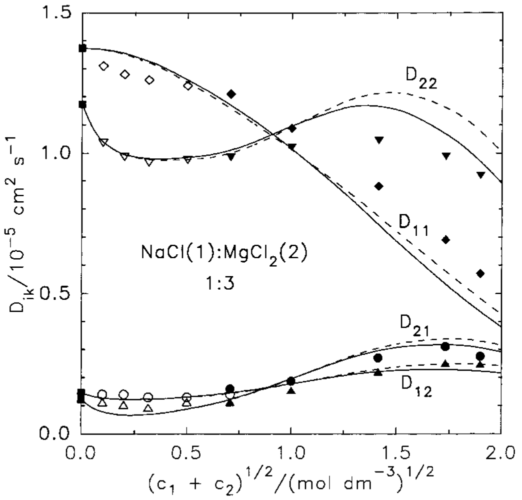

Figure 3. Ternary mutual diffusion coefficients of aqueous NaCl (c_1) + MgCl$_2$ (c_2) solutions. 1:3 molar ratio of NaCl/MgCl$_2$. Measured D_{ik} values: ●, ◆, ▼, ▲ (Mathew et al., 1990); ○, ◇, ▽, △ (Leaist, 1988). See caption of Figure 2.

NaCl and MgCl$_2$ to molarities (Dunlop and Gosting, 1959)

$$c_i = \frac{(1000\ \text{cm}^3\ \text{dm}^{-3})\rho m_i}{(1000\ \text{g kg}^{-1}) + m_1M_1 + m_2M_2} \qquad (15)$$

and to calculate the stoichiometric electrolyte partial molar volumes.

$$V_i = \frac{M_i - (\partial\rho/\partial c_i)_{c_{k\neq i}}}{\rho - c_1(\partial\rho/\partial c_1)_{c_2} - c_2(\partial\rho/\partial c_2)_{c_1}} \qquad (16)$$

The partial molar volume of water was evaluated from the identity 1000 cm^3 dm^{-3} = $c_0V_0 + c_1V_1 + c_2V_2$.

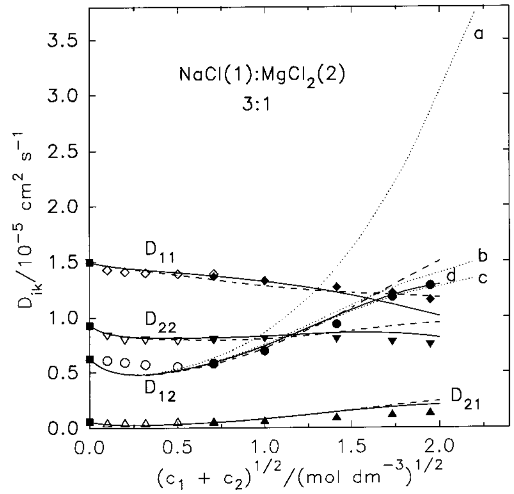

Figure 4. Ternary mutual diffusion coefficients of aqueous NaCl (c_1) + MgCl$_2$ (c_2) solutions. 3:1 molar ratio of NaCl/MgCl$_2$. Measured D_{ik} values: ●, ◆, ▼, ▲ (Albright et al., 1989); ○, ◇, ▽, △ (Leaist, 1988). The dotted curves give predicted D_{12} values with terms included for (a) nonideal solution thermodynamics, (b) viscosity changes, (c) ionic hydration, and (d) zero-volume flow. See caption of Figure 2.

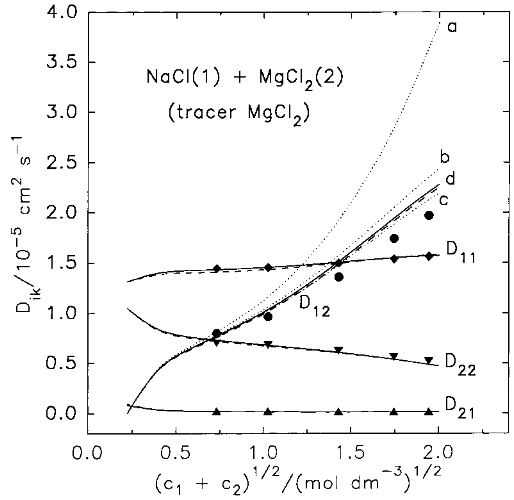

Figure 5. Ternary mutual diffusion coefficients of aqueous NaCl (c_1) + MgCl$_2$ (c_2 = 0.050 mol dm^{-3}) solutions. Large excess of NaCl relative to MgCl$_2$. Measured D_{ik} values: ●, ◆, ▼, ▲ (Mathew et al., 1989). The dotted curves give predicted D_{12} values with corrections applied in succession for (a) nonideal solution thermodynamics, (b) viscosity changes, (c) ionic hydration, and (d) zero-volume flow. See caption of Figure 2.

The dashed curves in Figures 2–6 give the ternary diffusion coefficients of aqueous NaCl (1) + MgCl$_2$ (2) solutions predicted entirely from the properties of binary solutions of NaCl and MgCl$_2$ using the parameters listed in Table 1. In these calculations the increments in the density and relative viscosity caused by each dissolved electrolyte were assumed to be additive and identical to those for the binary solution of each electrolyte at the same concentration.

$$\rho_{\text{bin}}(c_1,c_2) = \rho_0{}^* + \sum_{q=2}^{7}[A_{1q}(c_1/\text{mol dm}^{-3})^{q/2} + A_{2q}(c_2/\text{mol dm}^{-3})^{q/2}] \qquad (17)$$

$$\eta_{\text{rbin}}(c_1,c_2) = 1 + \sum_{q=1}^{6}[B_{1q}(c_1/\text{mol dm}^{-3})^{q/2} + B_{2q}(c_2/\text{mol dm}^{-3})^{q/2}] \qquad (18)$$

The solid curves shown in Figures 2–6 give a second set of predicted D_{ik} coefficients. These calculations employed

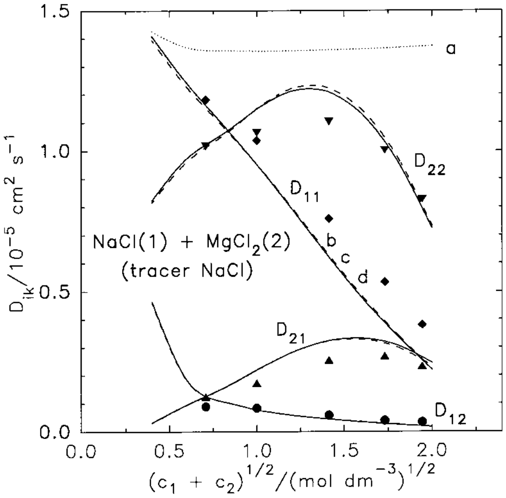

Figure 6. Ternary mutual diffusion coefficients of aqueous NaCl (c_1 = 0.115 mol dm^{-3}) + MgCl$_2$ (c_2) solutions plotted against the square root of the total electrolyte concentration. Large excess of MgCl$_2$ relative to NaCl. Measured D_{ik} values: ●, ◆, ▼, ▲ (Paduano et al., 1989). The dotted curves give predicted D_{11} values with corrections included for (a) nonideal solution thermodynamics, (b) viscosity changes, (c) ionic hydration, and (d) zero-volume flow. See caption of Figure 2.

accurate densities and viscosities for the ternary solutions evaluated from the equations

$$\rho(c_1,c_2) = \rho_{\text{bin}}(c_1,c_2) + E_{\rho1}y_1y_2I + E_{\rho2}y_1y_2I^2 + E_{\rho3}y_1y_2^{\,2}I \tag{19}$$

$$\eta_{\text{r}}(c_1,c_2) = \eta_{\text{rbin}}(c_1,c_2) + E_{\eta1}y_1y_2I + E_{\eta2}y_1y_2I^2 + E_{\eta3}y_1y_2^{\,2}I \tag{20}$$

where $I = c_1 + 3c_2$ is the ionic strength, $y_1 = c_1/I$ is the ionic strength fraction of NaCl, and $y_2 = 3c_2/I$ is the MgCl$_2$ ionic strength fraction. The excess density parameters $E_{\rho i}$ listed in Table 2 were evaluated by fitting eq 19 to accurate densities reported for ternary NaCl (1) + MgCl$_2$ (2) solutions (Albright et al., 1989; Mathew et al., 1990; Miller et al., 1993). The ternary viscosity data reported by Mills et al. (1987) were used to evaluate the $E_{\eta i}$ parameters. The rms deviations between the measured and fitted densities and relative viscosities are 0.0001 g cm^{-3} and 0.01, respectively.

The intercepts plotted in Figures 2–4 are the accurate limiting ternary diffusion coefficients evaluated from the Nernst relations (Leaist and Lyons, 1982)

$$D_{11}{}^* = D_{\text{Na}}{}^* + t_{\text{Na}}(D_{\text{Cl}}{}^* - D_{\text{Na}}{}^*) \tag{21}$$

$$D_{12}{}^* = 2t_{\text{Na}}(D_{\text{Cl}}{}^* - D_{\text{Mg}}{}^*) \tag{22}$$

$$D_{21}{}^* = t_{\text{Mg}}(D_{\text{Cl}}{}^* - D_{\text{Na}}{}^*)/2 \tag{23}$$

$$D_{22}{}^* = D_{\text{Mg}}{}^* + t_{\text{Mg}}(D_{\text{Cl}}{}^* - D_{\text{Mg}}{}^*) \tag{24}$$

where t_{Q} is the limiting transference number of ion Q.

$$t_{\text{Q}} = \frac{c_{\text{Q}}z_{\text{Q}}{}^2D_{\text{Q}}{}^*}{\sum_{K=1}^{3} c_Kz_K{}^2D_K{}^*} \tag{25}$$

The D_{ik} values are predicted by applying thermodynamic, viscosity, hydration, and zero-volume flow corrections to accurate limiting D_{ik}* values. For this reason the predictions are generally more reliable at low ionic strengths. If ternary solution densities and viscosities are employed in the predictions (solid curves), the average values of $|D_{ik}(\text{measured}) - D_{ik}(\text{predicted})|$ for D_{11}, D_{12}, D_{21}, and D_{22} are 0.06 × 10^{-5}, 0.04 × 10^{-5}, 0.03 × 10^{-5}, and 0.04 × 10^{-5} cm^2 s^{-1}, respectively. If the predictions are based entirely on binary solution data (dashed curves), the respective deviations are 0.05 × 10^{-5}, 0.04 × 10^{-5}, 0.04 × 10^{-5}, and 0.06 × 10^{-5} cm^2 s^{-1}. It is noteworthy that the differences between the measured and predicted D_{ik} values are not significantly larger if pseudobinary densities and viscosities are used instead of the more accurate ternary data. This result suggests that relatively plentiful data for binary electrolyte solutions can be used to estimate ternary diffusion coefficients without impairing the accuracy of the predictions.

Table 2. Ternary Density and Viscosity Parameters for NaCl + MgCl$_2$ + H$_2$O and NaCl + SrCl$_2$ + H$_2$O Solutions at 25 °C

parameter	NaCl + MgCl$_2$ + H$_2$O	NaCl + SrCl$_2$ + H$_2$O
$E_{1\rho}$/g cm^{-3} (mol dm^{-3})$^{-1}$	−0.001 48	−0.001 32
$E_{2\rho}$/g cm^{-3} (mol dm^{-3})$^{-2}$	−0.000 45	−0.000 55
$E_{3\rho}$/g cm^{-3} (mol dm^{-3})$^{-1}$	−0.000 72	−0.000 74
$E_{1\eta}$/(mol dm^{-3})$^{-1}$	−0.146 697	−0.129 861
$E_{2\eta}$/(mol dm^{-3})$^{-2}$	0.058 694	0.049 877
$E_{3\eta}$/(mol dm^{-3})$^{-1}$	0.011 090	0.036 843

The diffusion measurements reported by Albright et al. (1989) show that the cross-coefficient D_{12} becomes larger than the main coefficients D_{11} and D_{22} at high NaCl concentrations (see Figure 4). In this composition region the coupled flux $-D_{12}\nabla c_2$ of NaCl driven by the MgCl$_2$ gradient is larger than the main flux $-D_{22}\nabla c_2$ of MgCl$_2$ driven by its own gradient. Moreover, the coupled flux of NaCl is larger than the main flux $-D_{11}\nabla c_1$ of NaCl driven by an equivalent gradient in NaCl. So far no explanation has been offered for the sharp increase in D_{12} at high NaCl concentrations. To help interpret this behavior, predicted D_{12} values are plotted in Figure 4 with terms included for (a) nonideal solution thermodynamics, (b) viscosity changes, (c) hydration, and (d) zero-volume flow. Although these predictions are not quantitatively accurate, the sharp increase in D_{12} is evidently a thermodynamic effect resulting from nonideal solution behavior. Specifically, added MgCl$_2$ increases the activity coefficient of NaCl, causing "salted-out" NaCl to diffuse down the MgCl$_2$ gradient to regions of lower NaCl activity. For a solution containing 2.845 mol dm^{-3} NaCl (1) + 0.948 mol dm^{-3} MgCl$_2$ (2), the most concentrated solution of NaCl used by Albright et al. (1989), we calculate $(\partial \ln a_1/\partial c_2)_{c_1} = 1.44$ dm^3 mol^{-1} and $(\partial \ln a_1/\partial c_1)_{c_2} = 0.92$ dm^3 mol^{-1}. At this composition a gradient in the concentration of MgCl$_2$ produces a larger thermodynamic driving force for the diffusion of NaCl than an equivalent concentration gradient in NaCl, and hence $D_{12} > D_{11}$. Another interesting result is the crossover of D_{11} and D_{22} observed for solutions containing a large excess of MgCl$_2$ relative to NaCl (Paduano et al., 1989). At these compositions the activity coefficient of NaCl is effectively constant along the diffusion path. The thermodynamic contribution, which tends to increase diffusion coefficients for concentration solutions, is therefore negligible for D_{11} (see Figure 6). As the concentration of MgCl$_2$ is raised, the solution becomes significantly more viscous, causing D_{11} to drop well below D_{22}. In this case D_{22} is nearly identical to the binary diffusion coefficient of aqueous MgCl$_2$.

Ternary Diffusion in Aqueous NaCl + SrCl$_2$ Solutions. Rard and Miller (1987, 1988) have measured ac-

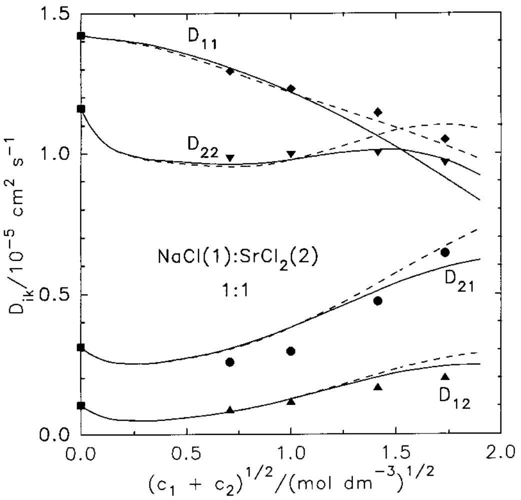

Figure 7. Ternary mutual diffusion coefficients of aqueous NaCl (c_1) + $SrCl_2$ (c_2) solutions at 25 °C plotted against the square root of the total electrolyte concentration. 1:1 molar ratio of NaCl/$SrCl_2$. Measured D_{ik} values: ●, ◆, ▼, ▲ (Rard and Miller, 1987, 1988). Limiting Nernst values: ■. Predicted D_{ik} values: —, using ternary solution densities and viscosities; — — —, using binary solution data.

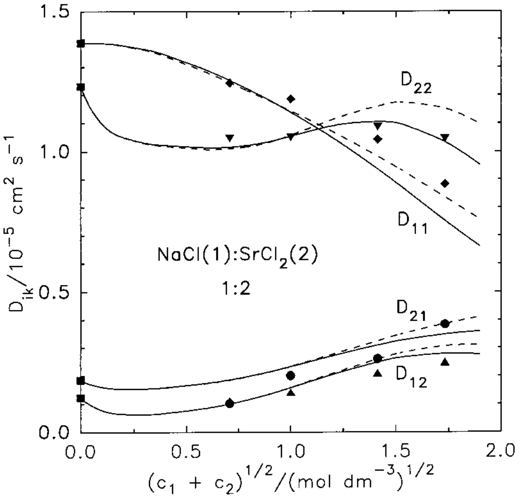

Figure 8. Ternary mutual diffusion coefficients of aqueous NaCl (c_1) + $SrCl_2$ (c_2) solutions at 25 °C plotted against the square root of the total electrolyte concentration. 1:2 molar ratio of NaCl/$SrCl_2$. See caption of Figure 7.

curate ternary diffusion coefficients for aqueous NaCl + $SrCl_2$ solutions at 25 °C and ionic strengths from 0.8 to 7.0 mol dm^{-3}. These results are plotted in Figures 7−9 for NaCl/$SrCl_2$ ratios of 1:1, 1:2, and 2:1. The dashed curves give the ternary D_{ik} coefficients predicted from the properties of the binary NaCl + H_2O and $SrCl_2$ + H_2O solutions represented by the parameters listed in Table 1. For this system the average values of $|D_{ik}(\text{measured}) - D_{ik}(\text{predicted})|$ for D_{11}, D_{12}, D_{21}, and D_{22} are 0.02×10^{-5}, 0.06×10^{-5}, 0.03×10^{-5}, and 0.05×10^{-5} cm^2 s^{-1}, respectively.

Rard and Miller (1987, 1988) also reported accurate densities for ternary NaCl + $SrCl_2$ solutions. Fitting eq 19 to their data gave the excess density parameters listed in Table 2. Table 3 gives the relative viscosities measured in the present study for NaCl + $SrCl_2$ solutions. Fitting eq 20 to these data gave the excess viscosity parameters listed in Table 3.

Ternary densities and viscosities were used to predict the D_{ik} values given by the solid curves in Figures 7−9. In this case the average values of $|D_{ik}(\text{measured}) - D_{ik}(\text{predicted})|$ are 0.06×10^{-5}, 0.06×10^{-5}, 0.02×10^{-5}, and 0.02×10^{-5} cm^2 s^{-1} for D_{11}, D_{12}, D_{21}, and D_{22}. Once again the overall agreement between the measured and predicted coefficients is not significantly improved by using the ternary densities and viscosities instead of the pseudobinary values.

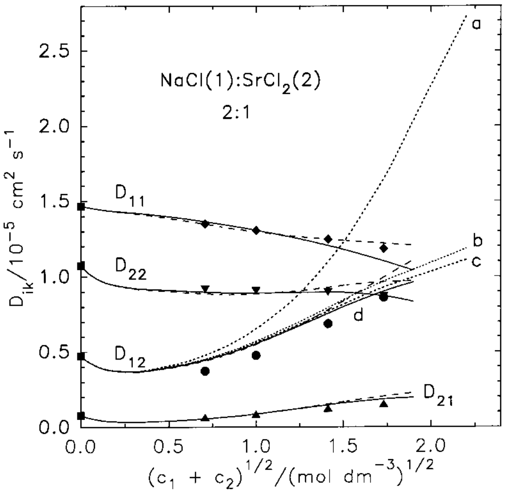

Figure 9. Ternary mutual diffusion coefficients of aqueous NaCl (c_1) + $SrCl_2$ (c_2) solutions at 25 °C plotted against the square root of the total electrolyte concentration. 2:1 molar ratio of NaCl/$SrCl_2$. See caption of Figure 7.

Table 3. Densities and Viscosities of Ternary NaCl (c_1) + $SrCl_2$ (c_2) + H_2O Solutions at 25 °C

c_1/mol dm^{-3}	c_2/mol dm^{-3}	ρ/g cm^{-3} (eq 19)	η_r (measured)	η_r (eq 20)
0.7518	0.7527	1.12924	1.328	1.325
1.5017	0.7518	1.15669	1.450	1.452
0.7505	1.5040	1.22260	1.708	1.710
2.2473	0.7496	1.18061	1.607	1.606
1.5061	1.5063	1.24963	1.914	1.913

Conclusions

The model of mutual diffusion in mixed electrolyte predicts with useful accuracy ternary diffusion coefficients for concentrated NaCl + $MgCl_2$ + H_2O and NaCl + $SrCl_2$ + H_2O solutions. The model also helps to explain interesting properties of these systems, such as the large values of the cross-coefficient D_{12} and the crossover of the main coefficients D_{11} and D_{22}. Although the measured and predicted diffusion coefficients are generally in close agreement, the D_{ik} predictions cannot match the accuracy of ternary diffusion measurements, especially at the highest electrolyte concentrations.

Mutual diffusion measurements become enormously difficult as the number of solution components increases beyond three or four. The present results suggest that reasonably accurate mixed-electrolyte diffusion coefficients can be predicted from activity, viscosity, and diffusion data which are available for many binary aqueous electrolyte solutions. These predictions might be the only practical way to obtain mutual diffusion coefficients for concentrated solutions containing a number of different electrolytes.

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