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Mutual Diffusion Coefficients and Densities at 298.15 K of Aqueous Mixtures of NaCl and Na_2SO_4 at High Concentrations with NaCl Solute Fractions of 0.9000

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Isothermal mutual diffusion coefficients (interdiffusion coefficients) were measured for ternary aqueous mixtures of NaCl and Na_2SO_4 at a constant NaCl molarity fraction $z_1 = 0.9000$ at 298.15 K, using high precision Rayleigh interferometry with computerized data acquisition. The experiments were performed at total molarities of (2.0000, 3.0003, 4.0010, and 5.0071) mol·dm^{-3}. Diffusion coefficients of NaCl(aq) were also measured at essentially these same four concentrations, those of Na_2SO_4(aq) at (1.3500 and 1.6998) mol·dm^{-3}, as were the densities of all solutions. These measurements supplement our earlier ones at total molarities of (0.5000, 1.0002_5, and 1.4990) mol·dm^{-3} with various ratios of NaCl to Na_2SO_4, which also included compositions with $z_1 = 0.9000$. At nearly all of the ternary solution compositions, the Na_2SO_4 cross-term diffusion coefficient is small and negative whereas the NaCl cross-term diffusion coefficient is larger and positive. However, at the fixed NaCl molarity fraction $z_1 = 0.9000$, the Na_2SO_4 cross-term diffusion coefficient changes from negative to positive values as the total concentration exceeds about 4.0 mol·dm^{-3}, and above 3.0 mol·dm^{-3} the size of the NaCl cross-term diffusion coefficient exceeds that of the corresponding Na_2SO_4 main-term diffusion coefficient. This indicates that, at high concentrations, a concentration gradient of Na_2SO_4 causes the transport of more NaCl than of itself. In contrast, cotransport of Na_2SO_4 by a concentration gradient of NaCl is quite small.

Introduction

The salt NaCl is the major electrolyte constituent of seawater and most natural waters. Another constituent of many natural waters is Na_2SO_4, which can be present at high concentrations in calcium-deficient brines. Because of their importance, extensive thermodynamic measurements have been made for NaCl(aq) and Na_2SO_4(aq).[1−3] A preliminary literature search for thermodynamic data for the NaCl + Na_2SO_4 + H_2O system by one of the present authors indicates that its thermodynamic characterization is relatively complete only at 298.15 K.

Diffusion coefficients are needed for modeling the transport of aqueous electrolytes in many chemical, geochemical, and industrial processes,[4−6] as well as for calculation of various types of generalized transport coefficients.[7−11] Diffusion data for aqueous NaCl, Na_2SO_4, and their mixtures complement ongoing work at Texas Christian University to provide fundamental data for modeling liquid-phase transport during protein crystal growth,[12] and supplement our earlier studies of aqueous solutions of the various soluble salts present in seawater and natural brines.[13−25]

Felmy and Weare[5] examined available diffusion data for various subsystems derived from the six-ion Na−K−Ca−Mg−Cl−SO_4−H_2O seawater model. Diffusion data were lacking for the majority of its ternary solution subsystems, with most of the available data being for common-ion chloride salt mixtures. Relatively fewer diffusion studies have been reported for common-cation aqueous mixtures.[23−27]

Binary and ternary solution diffusion coefficients D and D_{ij} cannot be predicted quantitatively by the Nernst−Hartley equations,[7,8,20,23,28,29] which are based on an infinite dilution model, except at fairly low concentrations, even when activity coefficient derivative corrections and other factors are included.[29] Consequently, we are determining accurate D_{ij} values for some representative ternary and quaternary aqueous salt systems to characterize experimentally the dependences of these diffusion coefficients on total concentration and on the solute mole ratio, so that they may be used for testing methods to estimate multicomponent solution D_{ij}.

Leaist and co-workers[30,31] generalized the binary electrolyte solution diffusion model of Stokes and Agar[32] to common-ion ternary solution diffusion. Miller[8] earlier investigated several mixing rules based on the Onsager transport coefficients of irreversible thermodynamics. Both approaches were able to represent the D_{ij} values of several such ternary systems with reasonable accuracy to ionic strengths as high as $I = 3.0$ mol·dm^{-3}, but so far none of these models have been applied to solutions containing both chloride and sulfate ions.

In 1995 we began a systematic investigation of the D_{ij} for NaCl + Na_2SO_4 + H_2O at 298.15 K, and have reported our results at total concentrations of (0.500, 1.000, and 1.499) mol·dm^{-3} over the composition fraction range z_1 = 0.25 to 0.90.[23−25] Because of solubility limitations resulting from the precipitation of $Na_2SO_4\cdot10H_2O$(cr), 1.500 mol·dm^{-3} is very close to the maximum concentration for which

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diffusion coefficient measurements can be made over the full range of z_1 values. Inspection of the solubility diagram[33] for the $NaCl + Na_2SO_4 + H_2O$ system at 298.15 K indicates that it should still be possible to prepare and study thermodynamically stable $NaCl + Na_2SO_4 + H_2O$ solutions with concentrations up to and slightly above 5.0 $mol{\cdot}dm^{-3}$ for NaCl composition fractions $z_1 \geq 0.85$. In the present report we extend our earlier measurements at $z_1 = 0.9000$ to include these higher concentrations.

Experimental Section

All experiments were performed at Texas Christian University. Most details of the experimental measurements and data processing are identical to those reported in the earlier studies, so we refer the readers to a previous paper.[23]

Diffusion Coefficient Measurements. Diffusion experiments were performed by Rayleigh interferometry[20,34] at $(298.15 \pm 0.00_5)$ K with free-diffusion boundary conditions, using the high-quality Gosting diffusiometer[35] with automated data recording.

At each overall ternary solution composition, four diffusion experiments were performed at essentially the same average concentrations of each solute, $\bar{C}_1$ and $\bar{C}_2$, but with different values of ΔC_1 and ΔC_2, where the ΔC_i are the differences between the concentrations of electrolyte i at the bottom and top sides of the initial diffusion boundary. Subscript 1 denotes NaCl, and subscript 2 denotes Na_2SO_4. These ratios were selected to correspond to the refractive index fractions of $\alpha_i \approx 0$, 0.2, 0.8, and 1 as recommended by Dunlop[36] and O'Donnell and Gosting.[37] The α_i are defined by

$$\alpha_i = R_i\Delta C_i/(R_1\Delta C_1 + R_2\Delta C_2) = R_i\Delta C_i/J \qquad (1)$$

where J is the total number of Rayleigh interference fringes and R_i is the refractive index increment of J with respect to the concentration increment of solute i. The α_i and R_i are obtained by the method of least squares from each set of four experimental J and eight ΔC_i values measured for the same overall composition in the same diffusion cell.

A more fundamental refractive index increment R_i^* describes the difference in refractive index Δn between the top and bottom solutions forming the diffusion boundary, as given by the equation $\Delta n = \lambda J/a = R_1^*\Delta C_1 + R_2^*\Delta C_2$, where $\lambda = 543.366$ nm is the wavelength in air of the helium−neon laser green line used by our interferometer and a is the path length of the light inside the diffusion cell. We report the R_i because J is the directly observed experimental quantity. Several different cells were used in this and our previous investigations of this system,[23−25] and because each cell has a slightly different value of a, the R_i^* should be used when comparing refractive indices or refractive index increments.

A scanning, computer-controlled photodiode array was used for the "real time" recording of positions of the Rayleigh fringe patterns during the diffusion experiments.[23] The 66 MHz 486 DX and 166 MHz Pentium computers used in our earlier studies[23−25] were replaced with a 550 MHz Pentium 3 Dell Computer to increase the speed of acquiring and processing the experimental information. The extraction of diffusion coefficients and their standard errors was done exactly as described previously.[20,23,38]

Solution Preparations and Density Measurements. Solutions were prepared by mass from samples of Mallinckrodt Analytical reagent NaCl(cr) that had previously been dried in air at 723 K,[39] from samples of stock solutions of Na_2SO_4(aq), and from purified water. The water purification was described previously.[23] Assumed molar masses are 58.443 $g{\cdot}mol^{-1}$ for NaCl, 142.037 $g{\cdot}mol^{-1}$ for Na_2SO_4, and 18.0153 $g{\cdot}mol^{-1}$ for H_2O. All apparent masses were converted to true masses by using buoyancy corrections.

Three stock solutions of Na_2SO_4(aq) were used, and all were prepared from recrystallized Baker "Analyzed" Na_2SO_4(s) and purified water. All three Na_2SO_4(aq) stock solutions were filtered through a prewashed 0.2 μm Corning Low Extractable Membrane Filtering Unit before use. The molalities of these stock solutions were calculated from their measured densities using eq 6 of Rard et al., as described previously.[23]

At each investigated ternary solution composition at constant total molarity, the eight densities from the four solution pairs were represented by the linear Taylor series expansion[36,40]

$$\rho = \bar{\rho} + H_1(C_1 - \langle\bar{C}_1\rangle) + H_2(C_2 - \langle\bar{C}_2\rangle) \qquad (2)$$

using the method of least squares. The C_1 and C_2 are the concentrations of NaCl and Na_2SO_4, respectively, for each individual solution, $\langle\bar{C}_1\rangle$ and $\langle\bar{C}_2\rangle$ are the corresponding overall concentration averages of the $\bar{C}_1$ and $\bar{C}_2$ for all four solution pairs at the same overall composition, the H_i are least squares parameters, and $\bar{\rho}$ is a least squares parameter representing the density of a ternary solution with molar concentrations corresponding to $\langle\bar{C}_1\rangle$ and $\langle\bar{C}_2\rangle$. These H_1 and H_2 parameters are needed for calculating the partial molar volumes $\bar{V}_i$ of the two solutes and water,[23,40] which in turn are needed to convert the experimentally based volume-fixed diffusion coefficients $(D_{ij})_V$ to solvent-fixed ones $(D_{ij})_0$. The appropriate equation for calculation of the $\bar{V}_i$ from these parameters is

$$\bar{V}_i = (M_i - H_i)/(\bar{\rho} - H_1\langle\bar{C}_1\rangle - H_2\langle\bar{C}_2\rangle) \qquad (3)$$

where M_i is the molar mass of component i and $H_0 = 0$ for the solvent.

Calculations for Ternary Solutions

The complete description of diffusion of solutes in a ternary solution under isothermal and isobaric conditions requires four diffusion coefficients D_{ij}, where i and $j = 1$ or 2.[8,41] The main-term diffusion coefficients D_{ii} describe the flow of each solute i due to its own concentration gradient, and the cross-term diffusion coefficients D_{ij} $(i \neq j)$ describe the coupled flow of solute i due to a gradient of solute j. Under our experimental conditions of relatively small ΔC_i, the derived values of D_{ij} are in the *volume-fixed reference frame*[42] and are denoted as $(D_{ij})_V$.

All of the diffusion boundaries were found to be statically and dynamically stable. [43−45]

Table 1 contains all concentration information for solutions used in our binary solution diffusion experiments, along with the densities and other experimental and derived information, and Table 2 contains similar information for the ternary solution experiments. Quantities reported for each individual mixture experiment are the $\bar{C}_i$ and ΔC_i for both solutes; J; α_1; Δt, the starting time correction which is added to the recorded "clock" times to correct them to the times corresponding to diffusion from an infinitely sharp boundary; and the reduced height−area ratio D_A.[20,23,46]

Both experimental and calculated J values are reported in Table 2. These J(calcd) were obtained from the ΔC_i and the least squares parameters R_i, using the second equality

Table 1. Results from Binary Solution Mutual Diffusion Coefficient and Density Measurements for NaCl(aq) and Na_2SO_4(aq) Solutions at 298.15 K with Rayleigh Interferometry and Vibrating Tube Densimetry[a]

quantity	NaCl(aq)	NaCl(aq)	NaCl(aq)	NaCl(aq)	Na_2SO_4(aq)[b]	Na_2SO_4(aq)[b]
$\bar{C}$	1.999 94	3.000 19	4.000 17_5	4.999 38	1.349 96	1.699 81
ΔC	0.186 85_5	0.186 91	0.186 76	0.186 74_5	0.087 56_5	0.087 91
ρ(top)	1.071 706	1.108 845	1.144 952	1.180 239_5	1.149 234_5	1.186 759
ρ(bottom)	1.078 686	1.115 660	1.151 592	1.186 760	1.158 921	1.196 444
$m(\bar{C})$	2.0868_8	3.2025	4.3748	5.6094	1.4027_9	1.7887
J	76.606	73.415	70.540	68.216	61.739	58.181
$10^{-2}R_i$	4.0998	3.9278	3.7771	3.6529	7.0506	6.6183
Δt	5.9	16.7_5	7.5	10.5	8.6	13.2
$10^9 D_V$	1.518_2	1.558_6	1.586_8	1.583_4	0.592_2	0.547_8
$10^9 M$	1.371	1.220	1.077	0.942	1.000	0.869

[a] Units of $\bar{C}$ and ΔC are mol·dm^{-3}; those of $m(\bar{C})$ are mol·kg^{-1}; those of $10^{-2}R_i$ are mol^{-1}·dm^3; those of ρ are g·cm^{-3}; those of Δt are s; and those of $10^9 D_V$ and $10^9 M$ are m^2·s^{-1}. The density values were measured with a Mettler-Parr DMA/40 vibrating tube densimeter. Cell C-1335-H-11 was used for the diffusion measurements; for this cell the path length inside the cell is $a = 2.4943$ cm, and the magnification factor is 1.7580. [b] The two stock solutions were prepared using recrystallized Baker “Analyzed” Na_2SO_4 that was separated from the mother liquor by centrifugal draining, and purified water, and they were then filtered through a 0.2 μm Corning ‘Low Extractable’ Membrane Filtering Unit before being used for making solutions for diffusion experiments.

Table 2. Compositions and Results for Ternary Solution Diffusion Experiments for $\{z_1NaCl + (1 - z_1)Na_2SO_4\}$(aq) Solutions at $z_1 = 0.9000$ and 298.15 K Measured with Rayleigh Interferometry[a]

	$\langle \bar{C}_T \rangle = 2.000\ 042$ mol·dm^{-3}				$\langle \bar{C}_T \rangle = 3.000\ 282$ mol·dm^{-3}			
quantity	expt 1	expt 2	expt 3	expt 4	expt 1	expt 2	expt 3	expt 4
$\bar{C}_1$	1.800 102	1.800 074	1.800 054	1.800 034	2.700 203	2.700 400	2.700 076	2.700 306
$\bar{C}_2$	0.200 014	0.199 882	0.200 006	0.200 003	0.300 034	0.300 044	0.300 034	0.300 033
ΔC_1	0.000 167	0.201 904	0.040 389	0.161 445	0.000 758	0.202 273	0.040 818	0.162 083
ΔC_2	0.106 479	0.000 018	0.085 171	0.021 299	0.106 549	0.000 057	0.085 258	0.021 339
J(exptl)	82.154	81.317	81.882	81.327	75.338	77.347	75.824	77.100
J(calcd)	82.131	81.267	81.896	81.386	75.422	77.410	77.732	77.044
α_1	0.000 82	0.999 83	0.198 47	0.798 30	0.003 84	0.999 48	0.206 16	0.804 69
Δt	7.4	5.3	7.5	20.9	12.4	19.6	12.4	15.2
$10^9 D_A$(exptl)	0.8240	1.4236	0.9079	1.2597	0.7958	1.4549	0.8869	1.2740
$10^9 D_A$(calcd)	0.8242	1.4229	0.9080	1.2585	0.7962	1.4537	0.8875	1.2728
ρ(top)	1.084 543	1.086 800	1.084 998	1.086 357	1.128 522	1.130 785	1.128 957	1.130 285
ρ(bottom)	1.096 614	1.094 296	1.096 098	1.094 706	1.140 142	1.138 016	1.139 726	1.138 446

	$\langle \bar{C}_T \rangle = 4.001\ 011$ mol·dm^{-3}				$\langle \bar{C}_T \rangle = 5.007\ 086$ mol·dm^{-3}			
quantity	expt 1	expt 2	expt 3	expt 4	expt 1	expt 2	expt 3	expt 4
$\bar{C}_1$	3.600 824	3.600 956	3.600 874	3.601 008	4.506 294	4.506 431	4.506 506	4.506 296
$\bar{C}_2$	0.400 082	0.400 100	0.400 094	0.400 108	0.500 690	0.500 712	0.500 718	0.500 697
ΔC_1	−0.000 503	0.226 158	0.045 121	0.180 967	−0.000 781	0.223 890	0.044 465	0.178 654
ΔC_2	0.130 268	0.000 041	0.104 259	0.026 105	0.130 320	−0.000 052	0.104 286	0.025 990
J(exptl)	83.748_5	82.543	83.721	83.017	77.634	78.230	77.753	78.210
J(calcd)	83.793	82.625	83.689	82.922	77.577	78.332	77.816_5	78.056
α_1	−0.002 19	0.999 68	0.196 91	0.797 06	−0.003 52	1.000 40	0.199 88	0.801 09
Δt	8.3	5.6	4.9	8.0	10.0_5	6.8	34.6	11.9
$10^9 D_A$(exptl)	0.7795	1.4750	0.8719	1.2763	0.7785	1.4575	0.8694	1.2676
$10^9 D_A$(calcd)	0.7801	1.4753	0.8721	1.2745	0.7782	1.4569	0.8705_5	1.2651
ρ(top)	1.169 913	1.172 839	1.170 452	1.172 258	1.211 662	1.214 529	1.212 245	1.213 968
ρ(bottom)	1.183 561	1.180 702	1.183 059	1.181 321	1.224 908	1.222 124	1.224 446	1.222 613

[a] Units of $\bar{C}_i$ and ΔC_i are mol·dm^{-3}, those of Δt are s, those of $10^9 D_A$ are m^2·s^{-1}, and those of ρ are g·cm^{-3}. Densities were measured using a Mettler-Parr DMA/40 vibrating tube densimeter. Cell C-1297-H-11 was used for experiments with $\langle \bar{C}_T \rangle = (2.000\ 042, 3.000\ 282,$ and $4.001\ 011)$ mol·dm^{-3}; the path length inside this cell is $a = 2.4999$ cm, and the magnification factor is 1.7603. The remaining experiments with $\langle \bar{C}_T \rangle = 5.007\ 086$ mol·dm^{-3} were done in cell C-1335-H-11; the path length inside this cell is $a = 2.4943$ cm, and the magnification factor is 1.7580.

of eq 1. The D_A(exptl) were calculated as described on page 4193 of ref 23.

Values of D_A(calcd) for each experiment were obtained as described elsewhere[20,23] using the α_1 values of that experiment and the four least squares Rayleigh parameters a, b, s_1, and s_2 appropriate to that overall composition, where $s_1 = \sqrt{\sigma_+}$ and $s_2 = \sqrt{\sigma_-}$. The quantities σ_+ and σ_- are defined in terms of the $(D_{ij})_V$ by eqs 12 and 13 of ref 23 and are the reciprocals of the eigenvalues λ_1 and λ_2 of the diffusion coefficient matrix. The a and b parameters are defined in terms of the $(D_{ij})_V$ and R_i by eqs 8 and 9 of ref 20.

Comparing these calculated D_A values with the corresponding experimental ones provides a measure of the internal consistency of the four experiments at each overall composition. Agreement between D_A(exptl) and D_A(calcd) values is generally very good, with $|D_A(\text{exptl}) - D_A(\text{calcd})| \leq 0.0012 \times 10^{-9}$ m^2·s^{-1}, except for the fourth experiments of the two series of experiments with $\langle C_T \rangle = (4.001\ 011$ and $5.007\ 086)$ mol·dm^{-3}, where $\langle C_T \rangle = \langle \bar{C}_1 \rangle + \langle \bar{C}_2 \rangle$. For those two experiments, $|D_A(\text{exptl}) - D_A(\text{calcd})| = 0.0018 \times 10^{-9}$ m^2·s^{-1} and 0.0025×10^{-9} m^2·s^{-1}, respectively. We note that the values of D_A(exptl) obtained with Rayleigh interferometry are determined mainly by the position of the fringes closest to the center of the diffusion boundary, where the effects of measurement errors are largest, and the resulting D_A are not known as precisely as values determined from Gouy interferometry.[20]

Results

Binary Solutions. Isothermal diffusion in a binary solution is characterized by a single, concentration dependent, volume-fixed diffusion coefficient D_V. Table 1 contains our experimental results for the limiting binary solutions NaCl(aq) ($z_1 = 1$) and Na_2SO_4(aq) ($z_1 = 0$) at 298.15 K. Also reported are the thermodynamic diffusion coefficients $M = D_V/\{d(m\phi)/dm\}$, where ϕ is the molality-based or "practical" osmotic coefficient of the solution. These derivatives were evaluated at the molality $m(\bar{C})$ corresponding to $\bar{C}$, using published equations for ϕ of Na_2SO_4(aq) and NaCl(aq).[47,48] Newer and significantly more accurate extended Pitzer models[2] are available for the thermodynamic properties of both NaCl(aq) and Na_2SO_4(aq),[1,3] but the differences are not large for the chemical potential derivatives $\{d(m\phi)/dm\}$ at 298.15 K. However, we used the older empirical isothermal activity equations to maintain consistency with the values of M reported by us previously.[13,23−25,49]

Our experimental values of D_V for NaCl(aq) at 298.15 K are $D_V = 1.518_2 \times 10^{-9}$ m^2·s^{-1} at $\bar{C} = 1.999\ 94$ mol·dm^{-3}, $D_V = 1.558_6 \times 10^{-9}$ m^2·s^{-1} at $\bar{C} = 3.000\ 19$ mol·dm^{-3}, $D_V = 1.586_8 \times 10^{-9}$ m^2·s^{-1} at $\bar{C} = 4.000\ 17_5$ mol·dm^{-3}, and $D_V = 1.583_4 \times 10^{-9}$ m^2·s^{-1} at $\bar{C} = 4.999\ 38$ mol·dm^{-3}. Rard and Miller[13] reported D_V for NaCl(aq) at 298.15 K from dilute solution to near saturation using Rayleigh interferometry, and reviewed other published D_V values. They subsequently reported a few additional values of D_V.[49] The original large-scale plot for their[13] Figure 2 yields $D_V = (1.515_8 \pm 0.002) \times 10^{-9}$ m^2·s^{-1} at $\bar{C} = 2.0000$ mol·dm^{-3}, $D_V = (1.556_8 \pm 0.002) \times 10^{-9}$ m^2·s^{-1} at $\bar{C} = 3.0000$ mol·dm^{-3}, $D_V = (1.587_5 \pm 0.002) \times 10^{-9}$ m^2·s^{-1} at $\bar{C} = 4.0000$ mol·dm^{-3}, and $D_V = (1.585_4 \pm 0.002) \times 10^{-9}$ m^2·s^{-1} at $\bar{C} = 5.0000$ mol·dm^{-3}. The experimental values agree to $\leq$0.16% of the published values, which is well within the experimental uncertainty of the published diffusion coefficients.

Our measured diffusion coefficient for Na_2SO_4(aq) at $\bar{C} = 1.349\ 96$ mol·dm^{-3} is $D_V = 0.592_2 \times 10^{-9}$ m^2·s^{-1}, and at $\bar{C} = 1.699\ 81$ mol·dm^{-3} it is $D_V = 0.547_8 \times 10^{-9}$ m^2·s^{-1}. A value of $D_V \approx (0.589_6 \pm 0.001) \times 10^{-9}$ m^2·s^{-1} at 1.3500 mol·dm^{-3} was estimated by graphical interpolation of a large-scale plot of the Rayleigh interferometric values of Rard and Miller,[14] which were measured at Lawrence Livermore National Laboratory using a less precise Beckman-Spinco Model H diffusiometer. These two values at $\bar{C} = 1.3500$ mol·dm^{-3} disagree by $0.002_6 \times 10^{-9}$ m^2·s^{-1} (0.4%), and this minor difference is consistent with similar differences observed at $\bar{C} = (1.2000$ and $1.5000)$ mol·dm^{-3}.[25] However, no significant differences are observed below 1.0 mol·dm^{-3}.[23−25] Extrapolation of the diffusion coefficients of Rard and Miller,[14] which only extend to $\bar{C} = 1.5282$ mol·dm^{-3}, to higher concentrations gives an estimated value of $D_V \approx 0.544 \times 10^{-9}$ m^2·s^{-1} at $\bar{C} = 1.7000$ mol·dm^{-3}. This value is in reasonable agreement with the experimental value of $D_V = 0.547_8 \times 10^{-9}$ m^2·s^{-1}, given that the extrapolated value is somewhat uncertain, owing to the rapid decrease of D_V with increasing concentration.

A comparison was made of the measured densities of the four Na_2SO_4(aq) solutions used for the diffusion measurements to those predicted from the density equations of Rard and Miller.[14] We expected to observe a high degree of consistency, because the molalities of the stock solutions used to prepare these solutions were determined using their densities, as described in the Experimental Section. This consistency was generally observed, except for the top solution of the pair of solutions used for the diffusion experiment at $\bar{C} = 1.699\ 81$ mol·dm^{-3}, where the experimental and calculated densities differed by about 3×10^{-4} g·cm^{-3}. This discrepancy implies that a minor error was made either while preparing that solution or for the density measurement. If the error was made during the density measurement, it would affect $\bar{C}$ by <0.02%. If, instead, it were made during the solution preparation, it would lower the value of $\bar{C}$ by 0.0014 mol·dm^{-3} (0.08%). The diffusion coefficients of Na_2SO_4(aq) solutions at $\bar{C} = (1.699\ 81$ and $1.6984)$ mol·dm^{-3} would be experimentally indistinguishable, even using our highly precise diffusiometer. However, the refractive index increment of J with respect to the concentration increment, R_i, for this experiment has an uncertainty larger than is typical.

On the basis of previous experience with the Gosting diffusiometer, experimental D_V values are reproducible to about 0.03 to 0.05% for binary solutions, whereas the diffusiometer used by Rard and Miller[14] was capable of a precision of 0.1−0.2%. We noted previously[25] that there is a slight disagreement between our results for Na_2SO_4(aq) and those of Rard and Miller at $\bar{C} > 1.0000$ mol·dm^{-3}, which slightly exceeds the reported errors. In contrast, our values measured with the Gosting diffusiometer[23−25] agree very well with the Rard and Miller[14] results when $\bar{C} \leq 1.0000$ mol·dm^{-3}. Rard and Miller[14] reported difficulties with crystallization of Na_2SO_4 while filling their cell with Na_2SO_4(aq) at their highest concentrations, since their laboratory was several degrees below 298 K when those experiments were performed. Consequently, they warmed their solutions and their cell above room temperature before filling it. If the cell and the "bottom" solution were at somewhat different temperatures when the cell was being filled, as is likely, this could have given rise to a small Soret effect and thus slight systematic distortions in the baseline corrections. In our opinion, the combined measurements from this laboratory, including those reported previously,[23−25] those of Rard and Miller,[14] and those of Wendt[50] are the most accurate D_V values for Na_2SO_4(aq) at 298.15 K for concentrations up to 1.0000 mol·dm^{-3} Na_2SO_4(aq), but at higher concentrations our new measurements reported in Table 1 and those reported by Annunziata et al.[25] are to be preferred. In addition, at low concentrations, the diffusion coefficients of Na_2SO_4(aq) measured with Harned's conductometric method[51] merge smoothly and are thus consistent with the lower concentration Rayleigh interferometric values of Rard and Miller.[14] However, the four highest concentration D_V values of Rard and Miller are apparently slightly low by 0.2−0.5%.

Ternary Solutions. Table 3 contains all the derived quantities for the four ternary solution compositions of the system NaCl + Na_2SO_4 + H_2O at 298.15 K and $z_1 = 0.9000$. We report both the experimental volume-fixed $(D_{ij})_V$ and the derived solvent-fixed $(D_{ij})_0$, which can be interconverted as described elsewhere.[8,40,42] The quantities $m_1(\langle\bar{C}_1\rangle,\langle\bar{C}_2\rangle)$ and $m_2(\langle\bar{C}_1\rangle,\langle\bar{C}_2\rangle)$ are the molalities of NaCl and Na_2SO_4, respectively, corresponding to a solution having the molarities of both salts equal to the averages $\langle\bar{C}_1\rangle$ and $\langle\bar{C}_2\rangle$ of all four experiments at that overall composition.

Another quantity reported in Table 3 is S_A,[52] which is related to the D_{ij}, to the R_i, and to σ_+ and σ_- by

$$S_A = [D_{22} - D_{11} + (R_1/R_2)D_{12} - (R_2/R_1)D_{21}]/[(D_{11}D_{22} - D_{12}D_{21})(\sqrt{\sigma_+} + \sqrt{\sigma_-})] = b(\sqrt{\sigma_+} - \sqrt{\sigma_-}) \quad (4)$$

If the value of $|10^{-2}S_A|$ is less than ~(20 to 25) m^{-1}·s$^{1/2}$, then the calculated standard errors of the D_{ij} may be significantly larger than usual.[20,53] Furthermore, if the σ_+ and σ_- values are nearly equal, the nonlinear least squares

Table 3. Results from Ternary Solution Mutual Diffusion Coefficient and Density Measurements for $\{z_1\mathrm{NaCl} + (1 - z_1)\mathrm{Na_2SO_4}\}$(aq) Solutions at $z_1 = 0.9000$ and 298.15 K Using Rayleigh Interferometry[a]

quantity	$z_1 = 0.900\ 01$	$z_1 = 0.900\ 00$	$z_1 = 0.900\ 00$	$z_1 = 0.900\ 00$
$\langle\bar{C}_T\rangle$	2.000 042	3.000 282	4.001 011	5.007 086
$\langle\bar{C}_1\rangle$	1.800 066	2.700 246	3.600 915	4.506 382
$\langle\bar{C}_2\rangle$	0.199 976	0.300 036	0.400 096	0.500 704
$\langle\bar{C}_0\rangle$	53.1185	51.8411	50.4841	49.0598
$m_1(\langle\bar{C}_1\rangle,\langle\bar{C}_2\rangle)$	1.881 053	2.891 262	3.959 282	5.098 715
$m_2(\langle\bar{C}_1\rangle,\langle\bar{C}_2\rangle)$	0.208 973	0.321 261	0.439 914	0.566 518
$10^{-2}R_1$	4.024 35	3.825 00	3.652 27	3.500 06
$10^{-2}R_2$	7.707 05	7.051 45	6.446 43	5.973 81
$\bar{\rho}$	1.090 551	1.134 360	1.176 763$_5$	1.218 312
H_1	36.981 ± 0.146	35.885 ± 0.149	34.844 ± 0.159	33.812 ± 0.208
H_2	113.065 ± 0.277	108.958 ± 0.283	105.276 ± 0.276	102.093 ± 0.401
$s(\rho$ fit$)$	0.000 029	0.000 035	0.000 036	0.000 042
$s(\bar{\rho})$	0.000 009	0.000 010	0.000 011	0.000 016
$\bar{V}_1$	21.433	22.451	23.384$_5$	24.271
$\bar{V}_2$	28.932	32.922	36.427	39.361
$\bar{V}_0$	17.991	17.930	17.852	17.752
$10^{-9}\sigma_+$	0.673 68	0.671 31	0.677 23	0.697 32
$10^{-9}\sigma_-$	1.427 04	1.667 31	1.959 54	2.354 59
$10^{-2}S_A$	−83.31	−92.52	−97.51	−96.10
$10^9(D_{11})_V$	1.4973 ± 0.0011	1.5005 ± 0.0007	1.4770 ± 0.0012	1.4218 ± 0.0007
$10^9(D_{12})_V$	0.3976 ± 0.0016	0.6089 ± 0.0013	0.7938 ± 0.0017	0.9691 ± 0.0025
$10^9(D_{21})_V$	−0.0259 ± 0.0005	−0.0160 ± 0.0003	−0.0005 ± 0.0005	0.0126 ± 0.0003
$10^9(D_{22})_V$	0.6878 ± 0.0006	0.5889 ± 0.0003	0.5099 ± 0.0005	0.4370 ± 0.0003
$10^9(D_{11})_0$	1.5563	1.5968	1.6149	1.6029$_5$
$10^9(D_{12})_0$	0.4511	0.7049	0.9422	1.1798
$10^9(D_{21})_0$	−0.0193	−0.0053	0.0148	0.0328
$10^9(D_{22})_0$	0.6937$_5$	0.5996	0.5264	0.4603$_5$

[a] Units of $\langle\bar{C}_i\rangle$ are mol·dm^{-3}; those of $m_i(\langle\bar{C}_1\rangle,\langle\bar{C}_2\rangle)$ are mol·kg^{-1}; those of $10^{-2}R_i$ are mol^{-1}·dm^3; those of $\bar{\rho}$, $s(\rho$ fit$)$, and $s(\bar{\rho})$ are g·cm^{-3}; those of H_i are g·mol^{-1}; those of $\bar{V}_i$ are cm^3·mol^{-1}; those of $10^{-9}\sigma_+$ and $10^{-9}\sigma_-$ are m^{-2}·s; those of $10^{-2}S_A$ are m^{-1}·s$^{1/2}$; and those of $10^9(D_{ij})_V$ and $10^9(D_{ij})_0$ are m^2·s^{-1}. Here $s(\rho$ fit$)$ and $s(\bar{\rho})$ are the standard deviations of the density fit and of $\bar{\rho}$, respectively. The quantity z_1 is the solute molarity fraction of NaCl, the total solute molarity is $\langle\bar{C}_T\rangle = \langle\bar{C}_1\rangle + \langle\bar{C}_2\rangle$, and $\langle\bar{C}_0\rangle$ is the molar concentration of water in the solution. To obtain densities from eq 2 in units of g·cm^{-3} when C_i and $\langle\bar{C}_i\rangle$ are in units of mol·dm^{-3}, divide the listed values of H_i by 10^3. Similarly, to obtain molar volumes from eq 3 in units of cm^3·mol^{-1}, divide the listed values of H_i by 10^3 in the denominator only. The "±" value given immediately to the right of each $(D_{ij})_V$ value is its standard error as calculated from the data reduction algorithm using standard propagation of error methods.

analysis of the fringe position data may not converge. Fortunately, σ_+ and σ_- differ by ratios of 2.1 to 3.4 for our experiments, and the $|10^{-2}S_A|$ values range from (83.31 to 97.51) m^{-1}·s$^{1/2}$, and no such computational difficulties were encountered.

Reported uncertainties in the $(D_{ij})_V$ values in Table 3 were estimated from the statistical analysis portion of the diffusion coefficient extraction program TFIT[23] using standard propagation of error methods. However, as noted elsewhere, we believe the actual uncertainties are larger than these calculated statistical uncertainties.[20,21,28,53,54] A more realistic "rule of thumb" estimate is that the actual errors are about four times larger than the statistical errors.[16−20]

More realistic estimates of the errors for the $(D_{ij})_V$ values may also be obtained from various subsets of the diffusion experiments.[54] These calculations use the four possible three-experiment subsets of the α_1 for each overall ternary solution composition. The results are reported in Table 4, where the values of $\delta(D_{ij})_V$ are the "$n - 1$" standard deviations calculated from the four resulting values of each $(D_{ij})_V$ obtained from the four subsets.

The calculated uncertainties of several of the $(D_{ij})_V$ values for the $\langle\bar{C}_T\rangle = (2.000\ 042$ and $4.001\ 011)$ mol·dm^{-3} cases are somewhat larger than those given by the four times the statistical errors "rule of thumb", but for the $\langle\bar{C}_T\rangle = 3.000\ 282$ mol·dm^{-3} case there is an approximate agreement between the two different methods of estimating errors for the $(D_{ij})_V$ values. In contrast, at $\langle\bar{C}_T\rangle = 5.007\ 086$ mol·dm^{-3}, the errors from the subset analysis are smaller and are also generally less than expected from the "rule of thumb" estimates, which indicates a high degree of internal consistency among the four diffusion experiments.

Table 4. Comparison of Calculated Errors of Ternary Solution $(D_{ij})_V$ for $\{z_1\mathrm{NaCl} + (1 - z_1)\mathrm{Na_2SO_4}\}$(aq) Solutions at $z_1 = 0.9000$ and 298.15 K[a]

quantity	$z_1 = 0.900\ 01$	$z_1 = 0.900\ 00$	$z_1 = 0.900\ 00$	$z_1 = 0.900\ 00$
$\langle\bar{C}_T\rangle$	2.000 042	3.000 282	4.001 011	5.007 086
$\langle\bar{C}_1\rangle$	1.800 066	2.700 246	3.600 915	4.506 382
$\langle\bar{C}_2\rangle$	0.199 976	0.300 036	0.400 096	0.500 704
$10^9\delta(D_{11})_V$[b]	0.0011	0.0007	0.0012	0.0007
$10^9\delta(D_{12})_V$[b]	0.0016	0.0013	0.0017	0.0025
$10^9\delta(D_{21})_V$[b]	0.0005	0.0003	0.0005	0.0003
$10^9\delta(D_{22})_V$[b]	0.0006	0.0003	0.0005	0.0003
$10^9\delta(D_{11})_V$[c]	0.0069	0.0045	0.0104	0.0014$_5$
$10^9\delta(D_{12})_V$[c]	0.0103	0.0026	0.0031	0.0061
$10^9\delta(D_{21})_V$[c]	0.0025	0.0014	0.0036	0.0005
$10^9\delta(D_{22})_V$[c]	0.0033	0.0007	0.0010	0.0015

[a] Units of $\langle\bar{C}_i\rangle$ are mol·dm^{-3} and of $10^9\delta(D_{ij})_V$ are m^2·s^{-1}. The quantity z_1 is the solute molarity fraction of NaCl in the mixed-electrolyte solutions. [b] The first set of errors was obtained with propagation of error equations using the variance−covariance matrix of the least-squares parameters from the fits for all four experiments at each overall composition. [c] The second set of errors was obtained by the subset method. Reported uncertainties are $n - 1$ standard deviations.

This comparison suggests that realistic estimates for the uncertainties of the $(D_{11})_V$ and $(D_{12})_V$ coefficients are $\leq 0.01 \times 10^{-9}$ m^2·s^{-1}, of $(D_{22})_V$ are $\leq 0.003 \times 10^{-9}$ m^2·s^{-1}, and of $(D_{21})_V$ are $\leq 0.004 \times 10^{-9}$ m^2·s^{-1}.

Discussion

Coupled diffusion significantly enhances the rate of diffusion of NaCl but makes only fairly minor contributions to that of Na$_2$SO$_4$ in these solutions. The magnitude of the NaCl cross-term diffusion coefficient $(D_{12})_V$ increases as $\langle\bar{C}_T\rangle$

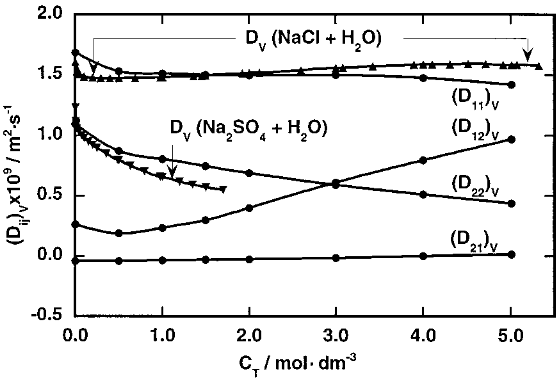

Figure 1. Values of the volume-fixed mutual diffusion coefficients $(D_{ij})_V$ at 298.15 K for NaCl + Na_2SO_4 + H_2O solutions at total concentrations of $\langle \bar{C}_T \rangle$ = (0.5000, 1.0002$_5$, 1.4990, 2.0000, 3.0003, 4.0010, and 5.0071) mol·dm^{-3}, along with the corresponding values at infinite dilution ($\langle \bar{C}_T \rangle$ = 0) from the Nernst−Hartley equation, at constant solute molarity fractions of z_1 = 0.9000 of NaCl. Also plotted are values of D_V for the limiting binary solutions NaCl(aq)[13,23−25] (z_1 = 1) and Na_2SO_4(aq)[14,23−25] (z_1 = 0). Symbols: ●, main-term and cross-term diffusion coefficients (D_{ij}); ▲, D_V of NaCl(aq); ▼, D_V of Na_2SO_4(aq).

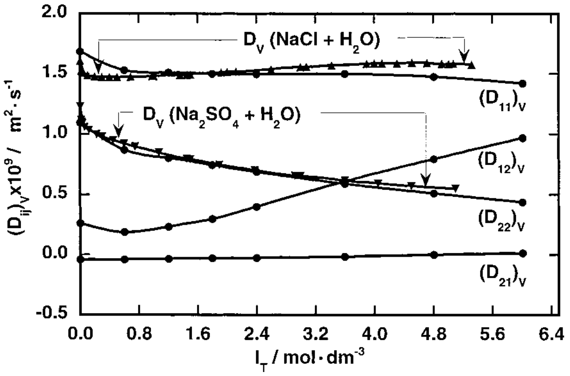

Figure 2. Values of the volume-fixed mutual diffusion coefficients $(D_{ij})_V$ at 298.15 K for NaCl + Na_2SO_4 + H_2O solutions as a function of the total volumetric ionic strengths I_T where I_T = 1.2000$\langle \bar{C}_T \rangle$, along with the corresponding values at infinite dilution (I_T = 0) from the Nernst−Hartley equation, at constant solute molarity fractions of z_1 = 0.9000 of NaCl. Also plotted are values of D_V for the limiting binary solutions NaCl(aq)[13,23−25] (z_1 = 1) and Na_2SO_4(aq)[14,23−25] (z_1 = 0). Symbols: ●, main-term and cross-term diffusion coefficients (D_{ij}); ▲, D_V of NaCl(aq); ▼, D_V of Na_2SO_4(aq).

increases, and becomes more than twice as large as the value of the Na_2SO_4 main-term diffusion coefficient $(D_{22})_V$ at the highest concentration studied. That large ratio of $(D_{12})_V$ to $(D_{22})_V$ at $\langle \bar{C}_T \rangle$ = 5.0071 mol·dm^{-3} indicates that any given concentration gradient of Na_2SO_4 will cause the cotransport of much more NaCl than of itself. In addition, although the cotransport of Na_2SO_4 resulting from any given concentration gradient of NaCl is very much smaller than that of NaCl, the flow of Na_2SO_4 will be decreased by coupled diffusion for concentrations with $\langle \bar{C}_T \rangle \leq 4.0$ mol·dm^{-3} because $(D_{21})_V$ is negative, but will be enhanced at higher concentrations where $(D_{21})_V$ becomes positive. However, we note that if comparisons are made using the solvent-fixed $(D_{ij})_0$ instead, then the changeover in sign from negative to positive values of D_{21} is shifted to lower concentrations.

Figure 1 contains plots of the $(D_{ij})_V$ at 298.15 K for z_1 = 0.9000 with $\langle \bar{C}_T \rangle$ = (0, 0.5000, 1.0002$_5$, 1.4990, 2.0000, 3.0003, 4.0010, and 5.0071) mol·dm^{-3}. The $(D_{ij})_V$ values at $\langle \bar{C}_T \rangle$ = 0 (infinite dilution) were calculated from the limiting ionic electrical conductances[32] and various fundamental constants, using the ternary solution analogue of the Nernst−Hartley equation.[8] The observed opposite signs for $(D_{12})_V$ and $(D_{21})_V$ when $\langle \bar{C}_T \rangle \leq 4.0$ mol·dm^{-3} are predicted qualitatively by the Nernst−Hartley equation, which is Coulombically based. The switch of $(D_{21})_V$ from negative to positive values with increasing concentration is, of course, not predicted by the Nernst−Hartley ternary solution equation, because the Nernst−Hartley values of D_{ij} are infinite dilution values and are thus constant at any fixed value of z_1.

In Figure 1, the diffusion coefficients of the limiting binary solutions NaCl(aq) and Na_2SO_4(aq) are also plotted to compare them with the main-term coefficients of the mixtures. The values of $(D_{11})_V$, the NaCl main-term coefficient, are higher than those of the NaCl(aq) binary solution diffusion coefficient D_V at low molarities, but the reverse is true when $\langle \bar{C}_T \rangle > 1.6$ mol·dm^{-3}. In contrast, the values of $(D_{22})_V$, the Na_2SO_4 main-term coefficient, are higher than those of the Na_2SO_4(aq) binary solution diffusion coefficient D_V at all experimental concentrations. However, the Nernst−Hartley values imply that $D_V > D_{22}$ at infinite dilution, so there must be a crossover at very low concentrations.

There are some sizable quantitative differences between the experimental $(D_{ij})_V$ and the Nernst−Hartley values, especially for $(D_{12})_V$ and $(D_{22})_V$, as can be seen in Figure 1. At z_1 = 0.9000, the Nernst−Hartley D_{22} values are significantly higher than the experimental $(D_{22})_V$ values by (0.224 to 0.658) × 10^{-9} m^2·s^{-1}, which is an overall decrease of 60% between infinite dilution and $\langle \bar{C}_T \rangle$ = 5.0071 mol·dm^{-3}. The values of $(D_{11})_V$ also exhibit a decrease with increasing concentration, with the Nernst−Hartley D_{11} being higher than the experimental $(D_{11})_V$ by (0.156 to 0.266) × 10^{-9} m^2·s^{-1}, which is an overall decrease of 16% between infinite dilution and $\langle \bar{C}_T \rangle$ = 5.0071 mol·dm^{-3}. The much larger decreases for the value of the Na_2SO_4 main-term coefficient $(D_{22})_V$ than for the NaCl main-term coefficient $(D_{11})_V$ parallel the concentration dependences of the diffusion coefficients of the limiting binary solutions Na_2SO_4(aq) and NaCl(aq). The smaller differences between D_V for NaCl(aq) and $(D_{11})_V$ in the ternary solutions, respectively, were anticipated, since NaCl is the predominant electrolyte component of our solutions. However, larger differences between D_V and $(D_{22})_V$ might have been expected for Na_2SO_4, since it was present as the minority electrolyte constituent.

The values of $(D_{12})_V$ change even more dramatically than the other three $(D_{ij})_V$ values with changes of $\langle \bar{C}_T \rangle$ for solutions with z_1 = 0.9000. The experimental values of $(D_{12})_V$ differ from the Nernst−Hartley cross-term D_{12} (a constant) by −0.077 × 10^{-9} m^2·s^{-1} at $\langle \bar{C}_T \rangle$ = 0.5000 mol·dm^{-3} to +0.705 × 10^{-9} m^2·s^{-1} at $\langle \bar{C}_T \rangle$ = 5.0071 mol·dm^{-3}. This is an overall increase of 267% between infinite dilution and $\langle \bar{C}_T \rangle$ = 5.0071 mol·dm^{-3}! For D_{21}, the Nernst−Hartley value is much closer to the experimental $(D_{21})_V$; its value is more negative than the experimental $(D_{21})_V$ results by ≤0.053 × 10^{-9} m^2·s^{-1}.

Figure 2 gives a plot of the $(D_{ij})_V$ diffusion coefficients at z_1 = 0.9000 and the D_V of the limiting binary solutions as a function of the total volumetric ionic strength I_T. The curves for the NaCl diffusion coefficients D_V and $(D_{11})_V$ are fairly similar to the corresponding curves of Figure 1, which is not surprising, since the ionic strength of the mixtures is only 20% greater than the value of $\langle \bar{C}_T \rangle$ and ionic strength and molarity are identical for NaCl(aq). Larger differences are expected for the Na_2SO_4 diffusion coefficients. Figure 2 indicates that D_V of Na_2SO_4 is higher than

$(D_{22})_V$ at all ionic strengths, which is the opposite of the order observed in Figure 1. Even more surprising, the values of D_V and $(D_{22})_V$ of Na_2SO_4 are very near the same at higher ionic strengths, even though the ionic strength fraction of Na_2SO_4 in the mixtures is only 25%. We did not expect this remarkable similarity.

It is obvious that simple empirical corrections, such as dividing the Nernst–Hartley D_{ij} values by the ratio of the viscosity of the solution to that of the solvent, will not bring their values into conformity with the experimental $(D_{ij})_V$ or with the $(D_{ij})_0$, because the cross-term diffusion coefficients increase with increasing concentration whereas the main-term diffusion coefficients both decrease. Similarly, dividing the Nernst–Hartley D_{ij} by the appropriate chemical potential derivatives generally brings the corrected Nernst–Hartley values into better agreement with the experimental values at lower concentrations. However, at high concentrations the resulting predicted D_{ij} values may be considerably different than the experimental values even for relatively simple strong electrolyte mixtures such as $NaCl + SrCl_2 + H_2O$ at 298.15 K.[29] Factors that directly affect the variation of the ionic mobilities with changing concentration, such as the electrophoretic effect and relaxation of the ionic atmosphere,[32] are neglected in these oversimplified models.

There is no rigorous theoretical relationship between the D_{ij} coefficients and the ratio of the viscosity of the solutions to that of the solvent, even for a binary solution diffusion coefficient D_V, and thus any viscosity "correction" must be considered to be a purely empirical term.[7,55] However, as discussed by Robinson and Stokes,[32] including an adjustable hydration number, along with the viscosity and chemical potential derivative terms, yielded a much-improved representation of the concentration dependence of D_V for several soluble strong electrolytes. The improved quality of the representation of the diffusion coefficients using all of the above factors suggests that the adjustable hydration number is compensating to a certain extent for some of the deficiencies of the model, including the approximate nature of the viscosity correction. However, since hydration of the sodium, chloride, and sulfate ions is not particularly strong, the importance of hydration in influencing the diffusion coefficients of the $NaCl + Na_2SO_4 + H_2O$ system is probably not as great as that for systems containing divalent or multivalent cations.

Leaist and Al-Dhaher[30] and Leaist and Kanakos[31] have generalized this model for common-ion mixed electrolyte solutions, and applied it to published diffusion coefficients at 298.15 K for the $NaCl + SrCl_2 + H_2O$ and $NaCl + MgCl_2 + H_2O$ systems, and to their own measurements for the $LiCl + KCl + H_2O$ system. They were able to represent all of the qualitative features of the dependences of the $(D_{ij})_V$ upon $\langle \bar{C}_T \rangle$ and z_i. In certain composition regions the agreement between their model and experiment was fairly good up to $\langle \bar{C}_T \rangle = 1.0\ mol\cdot dm^{-3}$ or even higher concentrations for most of the $(D_{ij})_V$, based on use of hydration parameters evaluated from the binary solution diffusion coefficients only. This agreement implies that their approach will be useful for estimating diffusion coefficients of mixed electrolyte solutions. However, their approach has not yet been applied to any common ion sodium salt mixtures such as $NaCl + Na_2SO_4 + H_2O$.

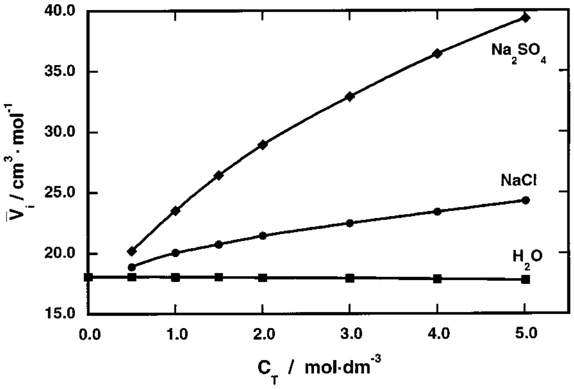

Figure 3. Values of the partial molar volumes at 298.15 K of NaCl, $\bar{V}_1$, of Na_2SO_4, $\bar{V}_2$, and of H_2O, $\bar{V}_0$, for $NaCl + Na_2SO_4 + H_2O$ solutions at total concentrations of $\langle \bar{C}_T \rangle = (0.5000, 1.0002_5, 1.4990, 2.0000, 3.0003, 4.0010, \text{and } 5.0071)\ mol\cdot dm^{-3}$, at constant solute molarity fractions of $z_1 = 0.9000$ of NaCl. Symbols: ●, $\bar{V}_1$; ◆, $\bar{V}_2$; ■, $\bar{V}_0$.

Figure 3 is a plot of the partial molar volumes of NaCl ($\bar{V}_1$), Na_2SO_4 ($\bar{V}_2$), and H_2O ($\bar{V}_0$). Although the values of $\bar{V}_0$, $\bar{V}_1$, and $\bar{V}_2$ are comparable in size at low concentrations, the values of $\bar{V}_1$ and $\bar{V}_2$ both increase with increasing concentration whereas values of $\bar{V}_0$ decrease. In addition, $\bar{V}_2$ increases more rapidly than $\bar{V}_1$, and at $\langle \bar{C}_T \rangle = 5.0\ mol\cdot dm^{-3}$, their ratio is $(\bar{V}_2/\bar{V}_1) = 1.6$.

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