Mutual Diffusion Coefficients and Densities at 298.15 K of Aqueous Mixtures of NaCl and Na_2SO_4 for Six Different Solute Fractions at a Total Molarity of 1.500 $mol·dm^{-3}$ and of Aqueous Na_2SO_4

Onofrio Annunziata,[†] **Joseh A. Rard,***[||] **John G. Albright,**[‡] **Luigi Paduano,**[§] **and Donald G. Miller**[⊥]

Chemistry Department, Texas Christian University, Fort Worth, Texas 76129, and Geosciences and Environmental Technologies, Earth and Environmental Sciences Directorate, Lawrence Livermore National Laboratory, University of California, Livermore, California 94550

Isothermal mutual diffusion coefficients (interdiffusion coefficients) were measured for ternary aqueous mixtures of NaCl and Na_2SO_4 at a constant total molarity of 1.500 $mol·dm^{-3}$ at 298.15 K, using Rayleigh interferometry with computerized data acquisition. The experiments were performed at NaCl molarity fractions of $z_1 = 1$, 0.90, 0.75, 0.50, 0.25, and 0. These measurements supplement our earlier results at total molarities of 0.500 and 1.000 $mol·dm^{-3}$. Diffusion coefficients were also measured at three additional concentrations of $Na_2SO_4(aq)$. Densities of all solutions were measured with a vibrating tube densimeter. At all ternary solution compositions, one cross-term diffusion coefficient has small negative values whereas the other has larger positive values. Comparing the results at 0.500, 1.000, and 1.500 $mol·dm^{-3}$ shows that both main-term diffusion coefficients decrease with increasing total concentration at any fixed value of z_1, whereas both cross-term coefficients are shifted in a positive direction. At 1.500 $mol·dm^{-3}$ both the NaCl main-term and cross-term diffusion coefficients have a maximum as a function of z_1, whereas the Na_2SO_4 cross-term coefficient has a minimum. Trace diffusion coefficients $D^*(Cl^-) = (1.14_5 \pm 0.02) \times 10^{-9}$ $m^2·s^{-1}$ and $D^*(SO_4^{2-}) = (0.80_5 \pm 0.01_5) \times 10^{-9}$ $m^2·s^{-1}$ were extrapolated from these results for the $Cl^-(aq)$ ion in 1.500 $mol·dm^{-3}$ $Na_2SO_4(aq)$ and for the $SO_4^{2-}(aq)$ ion in 1.500 $mol·dm^{-3}$ NaCl(aq). Values of $D^*(Cl^-)$ in $Na_2SO_4(aq)$ and in NaCl(aq) were found to be essentially identical, as were $D^*(SO_4^{2-})$ in these same two electrolytes, provided the comparisons are made at the same volumetric ionic strengths.

Introduction

Diffusive transport occurs in many chemical, geochemical, and industrial processes,[1−4] and diffusion coefficients are needed for calculation of various types of generalized transport coefficients.[5−9]

Aqueous salt solutions are often used to solubilize proteins, and increasing the salt concentration will sometimes cause salting-out of protein crystals. Various salts, including NaCl and Na_2SO_4, can produce this salting-out effect. Diffusion data for these salts and their mixtures will complement ongoing work at Texas Christian University to determine diffusion coefficients of ternary and quaternary aqueous solutions containing lysozyme. That work will provide fundamental data for modeling liquid-phase transport during protein crystal growth.

There is also a long-standing program at Lawrence Livermore National Laboratory of studying the thermodynamic and transport properties of aqueous solutions of the various salts present in seawater and natural brines and their mixtures. The present report is a continuation of our collaboration to characterize the diffusion coefficients of systems of mutual interest.

Felmy and Weare[2] have described a method of estimating diffusion coefficients based on Miller's estimation methods[6] and using Onsager's phenomenological coefficients, with the chemical potential derivatives being calculated using Pitzer's ion interaction model.[10] Felmy and Weare 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 the ternary solution subsystems, with most of the available diffusion data being for common-ion chloride salt mixtures.

Mutual diffusion coefficients have been reported from dilute solution to near saturation at 298.15 K for binary aqueous solutions of many of the major and minor salts present in seawater and other natural waters, and those experimental studies are summarized elsewhere.[11] Mutual diffusion data are also available at 298.15 K for several common-anion ternary aqueous solution compositions relevant to natural waters. These are mostly chloride salt mixtures[12−25] but include one composition of the system $NaHCO_3 + KHCO_3 + H_2O$.[26] Hao and Leaist[27] studied the noncommon-ion mixtures of $NaCl + MgSO_4 + H_2O$.

Relatively few diffusion studies have been reported for common-cation aqueous mixtures. Diffusion data have been reported for mixtures of $NaOH + Na_2SO_3 + H_2O$ and mixtures of $MgCl_2 + MgSO_4 + H_2O$ by Leaist and coworkers,[28,29] and for eight compositions of $NaCl + Na_2SO_4 + H_2O$ at total molarities of 0.500 and 1.000 $mol·dm^{-3}$.[11,18,30]

Except at low molarities of solute, the binary or ternary solution diffusion coefficients D and D_{ij} cannot be predicted quantitatively by the Nernst−Hartley equations,[5,6,11,16,17,24] which are based on an infinite dilution model, even when activity coefficient derivative corrections and other factors are included in the calculations.[17] Consequently, we are

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[†] Texas Christian University. E-mail: oannunziata@gamma.is.tcu.edu.

[||] Lawrence Livermore National Laboratory. E-mail: rard1@llnl.gov.

[‡] Texas Christian University. E-mail: albright@gamma.is.tcu.edu.

[§] Permanent address: Dipartimento di Chimica, Università di Napoli, 80134 Napoli, Italy. E-mail: padu@chemna.dichi.unina.it.

[⊥] Lawrence Livermore National Laboratory. E-mail: dmiller@llnl.gov.

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determining accurate D_{ij} values for a few representative ternary and quaternary aqueous salt systems to characterize experimentally the dependences of these coefficients on total concentration and on the solute mole ratio. These experimental D_{ij} can then be used as a "test bed" for developing and refining methods to estimate multicomponent solution D_{ij} for arbitrary mixtures at higher concentrations.

Since experimental D_{ij} for common-cation mixtures are quite limited, including those with sodium salts, in 1995 we began a systematic investigation of the D_{ij} for the system $NaCl + Na_2SO_4 + H_2O$ at 298.15 K but interrupted that study because of an interruption in funding. However, we now have support that allows our previous results[11,30] at 0.500 and 1.000 $mol \cdot dm^{-3}$ to be extended to 1.500 $mol \cdot dm^{-3}$. Because of solubility limitations resulting from the precipitation of $Na_2SO_4 \cdot 10H_2O(cr)$, 1.500 $mol \cdot dm^{-3}$ is close to the maximum concentration for which diffusion coefficient measurements can be made over the full range of z_1. The present study was undertaken in part to determine whether the cross-term diffusion coefficients D_{12} and D_{21} remain positive and negative, respectively, as the total concentration of the solution is increased to 1.500 $mol \cdot dm^{-3}$. Although this was found to be true at 1.500 $mol \cdot dm^{-3}$, there were major changes in several of the diffusion coefficients, particularly for D_{11}.

Since this report continues our earlier work, and because most details of the experimental measurements and data processing are identical to those reported in the earlier studies, we refer the readers to a previous paper[11] for more of these details.

Experimental Section

All experiments were performed at Texas Christian University.

Diffusion Coefficient Measurements. Diffusion experiments were performed by Rayleigh interferometry at $(298.15 \pm 0.00_5)$ K with free-diffusion boundary conditions, using the high-quality Gosting diffusiometer[31] with automated data recording. Miller et al.[24] and Miller and Albright[32] have described the Rayleigh method in considerable detail, including experimental and computational procedures. The molarity fractions z_1 of NaCl in these $\{z_1 NaCl + (1 - z_1)Na_2SO_4\}(aq)$ mixtures are 1, 0.900 00, 0.749 93, 0.500 00, 0.250 00, and 0 at a total molarity of 1.500 $mol \cdot dm^{-3}$. These z_1 values are very nearly the same as those used at 0.500 and 1.000 $mol \cdot dm^{-3}$,[11,30] which facilitates comparisons with our previous diffusion data. The values $z_1 = 1$ and $z_1 = 0$ denote the limiting binary solutions NaCl(aq) and Na_2SO_4(aq), respectively.

For each ternary solution composition, four diffusion experiments were performed at essentially the same average concentrations of each solute, $\bar{C}_1$ and $\bar{C}_2$. However, these four experiments involved different values of the ratio $\Delta C_1/(\Delta C_1 + \Delta C_2)$, where the ΔC_i are the differences between the concentrations of electrolyte i between the bottom and top sides of the initial diffusion boundary. The subscript 1 denotes NaCl, and the subscript 2 denotes Na_2SO_4. These ratios were selected to correspond to the refractive index fractions $\alpha_i \approx 0$, 0.2, 0.8, and 1, as recommended by Dunlop[12] and O'Donnell and Gosting.[14] The α_i are given by

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

where J is the total number of Rayleigh interference fringes (which is generally not an integer) and R_i is the refractive index increment of J with respect to the concentration 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 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 by the equation $\Delta n = R_1^* \Delta C_1 + R_2^* \Delta C_2$. These Δn are directly related to J by $\Delta n = \lambda J/a$, where $\lambda = 543.3655$ 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. Consequently, $R_1 = aR_1^*/\lambda$ and $R_2 = aR_2^*/\lambda$. We report the R_i because J is the directly observed experimental quantity. (The R_i^* are not known as precisely because they contain an additional uncertainty arising from the determination of a.) Extraction of the D_{ij} from the fringe position data only requires the ratio $R_i/R_j = R_i^*/R_j^*$, so it is immaterial which type of refractive index increment is reported.

All diffusion experiments were performed in cell C-1235-H-11, for which $a = 2.5057$ cm and which has a magnification factor of 1.7607_0 at the focal plane of our diffusiometer. This magnification factor was obtained by placing a transparent, precisely ruled scale in the center-of-cell position in the thermostated water bath and then comparing the observed scale line separations at the photodiode array[11] to the corresponding separations of those same lines on the original ruled scale as measured with a microcomparator. The reported value of the magnification factor is the average of several separate determinations and is precise to better than 0.03%.

A computer-controlled photodiode array was used for the "real time" recording of positions of the Rayleigh fringe patterns during the diffusion experiments. This photodiode array and its operation, the cell-filling techniques, the recording of the baseline patterns and the Rayleigh fringe patterns, and so forth are essentially the same as those described by Rard et al.[11] However, the original 66 MHz 486 DX computer was replaced with a 166 MHz Pentium computer to increase the speed of acquiring and processing the experimental information.

One computer code is used for interpolation of the experimental fringe position information recorded by the photodiode array to reconstruct the positions of 100 symmetrically paired fringes for each temporal scan, of which 96 of the fringe pairs are used in subsequent calculations. This code generates a file for each individual diffusion experiment that contains the J values, the 96 interpolated symmetrically paired Rayleigh fringe positions for each of the 50 scans for an individual experiment, and the times at which the Rayleigh patterns were recorded. For each set of four experiments at a given overall composition (fixed z_1), a second computer program TFIT combines the corresponding files and the concentration differences ΔC_i of each solute across the initial diffusion boundary. This computer program calculates the diffusion coefficients, their standard errors, and other pertinent quantities as described previously.[11,24,33]

Solution Preparation and Density Measurements. Solutions were prepared by mass from samples of NaCl(cr) that had previously been dried in air at 723 K,[34] from samples of stock solutions of Na_2SO_4(aq), and from purified water. The water purification was described previously.[11] The 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.

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)	Na_2SO_4(aq) [b]	Na_2SO_4(aq) [c]	Na_2SO_4(aq) [c]	Na_2SO_4(aq) [c]	Na_2SO_4(aq)[c]
$\bar{C}$	1.500 02	1.500 07	0.500 00	0.999 99	1.200 01	1.500 01
ΔC	0.200 40	0.101 79	0.102 84	0.102 40	0.102 23	0.100 09
ρ(top)	1.052 483	1.164 908	1.051 994	1.109 687	1.132 022	1.164 933
ρ(bottom)	1.060 146	1.175 893	1.064 114	1.121 151	1.143 297	1.175 775
$m(\bar{C})$	1.548 57	1.567 00	0.506 55	1.027 34	1.240 70	1.566 93
J	84.501	70.114	86.626	77.260	74.213	68.534
$10^{-2}R_i$	4.2167	6.8880	8.4235	7.5449	7.2594	6.8472
Δt	7.8	7.6	8.9	6.8	9.1	10.8
$10^9 D_V$	1.497_8	0.571_2	0.793_7	0.654_5	0.616_3	0.570_6
$10^9 M$	1.445	0.943	1.278	1.129	1.056	0.942

[a] Units of $\bar{C}$ and ΔC are mol·dm^{-3}, of m($\bar{C}$) are mol·kg^{-1}, of 10^{-2} R_i are mol^{-1}·dm^3, of ρ are g·cm^{-3}, of Δt are s, and 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-1235-H-11 was used for the diffusion measurements; for this cell the path length inside the cell is $a = 2.5057$ cm and the magnification factor is 1.7607_0. [b] The stock solution was prepared using Baker "Analyzed" Na_2SO_4(s) and purified water and was filtered through a 0.2 μm Corning "Low Extractable" Membrane Filtering Unit before being used for making solutions for diffusion experiments. [c] The stock solution was prepared using recrystallized Baker "Analyzed" Na_2SO_4 that was separated from the mother liquor by centrifugal draining, and purified water, and was then filtered through a 0.2 μm Corning "Low Extractable" Membrane Filtering Unit before being used for making solutions for diffusion experiments.

All apparent masses were converted to masses by using buoyancy corrections.

Ternary solutions with molarity fractions of $z_1 = 0.900\ 00$, 0.500 00, and 0.250 00 were prepared using dried OmniPur NaCl, whereas for the binary solution experiment and for the ternary solutions with $z_1 = 0.749\ 93$ we used dried Mallinckrodt Analytical Reagent NaCl.

Two stock solutions of Na_2SO_4(aq) were prepared directly from anhydrous Baker "Analyzed" Na_2SO_4(s) and purified water. An additional stock solution was used for four of the binary solution measurements and was prepared similarly from Na_2SO_4·$10H_2O$(cr). That Na_2SO_4·$10H_2O$(cr) was obtained by recrystallization of Baker "Analyzed" Na_2SO_4(s) followed by centrifugal draining. All of these Na_2SO_4(aq) stock solutions were filtered through a prewashed 0.2 μm Corning "Low Extractable" Membrane Filtering Unit before use.

The densities of all Na_2SO_4(aq) stock solutions were measured at $(298.15 \pm 0.00_5)$ K using a Mettler-Parr DMA/40 vibrating tube densimeter which was interfaced to an Apple computer for signal averaging and increased precision. The molar concentration of each Na_2SO_4(aq) stock solution was calculated from its measured density using eq 6 of Rard et al.[11] That equation is valid up to 2.6292 mol·dm^{-3}, which is well into the supersaturated region. We estimate that the stock solution molarities and molalities derived from density measurements are accurate to 0.02% or better and that the consistency of concentrations for solutions prepared from different Na_2SO_4(aq) stock solutions is better than 0.01%. However, since all eight solutions for any particular ternary solution composition were prepared from the same stock solution, they are internally more consistent than this. The densities of all solutions used for diffusion experiments were also measured with this vibrating tube densimeter.

At each given z_1, the eight densities from the four solution pairs were represented by the linear Taylor series expansion,[12,13]

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

using the method of least-squares. 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 $\bar{C}_1$ 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 solution with molar concentrations corresponding to $\langle \bar{C}_1 \rangle$ and $\langle \bar{C}_2 \rangle$. These H_1 and H_2 parameters were used for calculating the partial molar volumes $\bar{V}_i$ of the two solutes and water,[11,13] given in Table 3, which in turn were used to convert the experimentally based volume-fixed diffusion coefficients $(D_{ij})_V$ to solvent-fixed ones $(D_{ij})_0$. The appropriate equation 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. This equation is a generalization of the separate equations used previously[11] to calculate the partial molar volumes of the solutes and 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.[6,35] The main-term diffusion coefficients D_{ii} describe the flow of solute i due to its own concentration gradient, and the cross-term diffusion coefficients D_{ij} $(i \neq j)$ describe the flow of solute i due to a gradient of solute j. Under our experimental conditions of relatively small ΔC_i, these D_{ij} are in the *volume-fixed reference frame*[36] and are denoted as $(D_{ij})_V$.

Experimental values of the $(D_{ij})_V$ and H_i coefficients of eq 2 were used to test the static and dynamic stability of all our ternary solution diffusion boundaries.[37-39] All of the diffusion boundaries were stable.

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 the same type of information for the ternary solution experiments. Quantities reported (some are defined in the Experimental Section) are the $\bar{C}_i$ for both solutes; 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.[24,40] The ternary solution diffusion coefficients

Table 2. Compositions and Results for Ternary Solution Diffusion Experiments for $\{z_1\text{NaCl} + (1 - z_1)\text{Na}_2\text{SO}_4\}$(aq) Solutions at 298.15 K and at $\langle \bar{C}_T \rangle = 1.500$ mol·dm^{-3} Measured with Rayleigh Interferometry[a]

	$z_1 = 0.900\ 00$				$z_1 = 0.749\ 93$			
quantity	expt 1	expt 2	expt 3	expt 4	expt 1	expt 2	expt 3	expt 4
$\bar{C}_1$	1.349 086	1.349 124	1.349 164	1.349 058	1.124 472	1.124 475	1.124 462	1.124 476
$\bar{C}_2$	0.149 898	0.149 905	0.149 909	0.149 894	0.374 968	0.374 973	0.374 970	0.374 974
ΔC_1	−0.000 110	0.195 434	0.039 155	0.156 426	0.000 146	0.199 908	0.040 078	0.159 929
ΔC_2	0.098 435	0.000 011	0.078 770	0.019 706	0.102 602	−0.000 006	0.082 078	0.020 514
J(exptl)	79.366_5	80.767	79.916	80.728	80.529	80.295	80.545	80.397
J(calcd)	79.461	80.863	79.822	80.632	80.565	80.329	80.508	80.364
α_1	−0.000 57	0.999 89	0.202 94	0.802 60	0.000 73	1.000 06	0.200 05	0.799 71
Δt	9.9	11.2	9.1	12.8	8.2	8.0	11.3	8.7
$10^9 D_A$(exptl)	0.8465	1.4155	0.9320	1.2644	0.7795	1.3123	0.8553	1.1653
$10^9 D_A$(calcd)	0.8468	1.4147	0.9305	1.2646	0.7786	1.3094	0.8548_5	1.1664
ρ(top)	1.062 313	1.064 326	1.062 706	1.063 924	1.079 600	1.081 782	1.080 050	1.081 349
ρ(bottom)	1.073 676	1.071 699	1.073 310	1.072 092	1.091 316	1.089 166	1.090 886	1.089 599

	$z_1 = 0.500\ 00$				$z_1 = 0.250\ 00$			
quantity	expt 1	expt 2	expt 3	expt 4	expt 1	expt 2	expt 3	expt 4
$\bar{C}_1$	0.749 908	0.749 967	0.749 972	0.749 966	0.375 052	0.375 064	0.375 045	0.375 038
$\bar{C}_2$	0.749 918	0.749 967	0.749 986	0.749 975	1.125 151	1.125 192	1.125 174	1.125 119
ΔC_1	−0.000 080	0.209 461	0.041 897	0.167 639	−0.000 030	0.212 432	0.042 482	0.169 932
ΔC_2	0.107 914	0.000 062	0.086 414	0.021 728	0.112 585	0.000 043	0.090 186	0.022 479
J(exptl)	80.775	80.616	80.783	80.582	80.753	78.437	80.301	78.831
J(calcd)	80.751	80.535	80.787	80.683	80.718	78.428	80.345	78.831
α_1	−0.000 38	0.999 43	0.199 29	0.798 41	−0.000 14	0.999 61	0.195 13	0.795 53
Δt	7.9	10.3	7.6	11.1	10.3	9.7	10.6	10.3
$10^9 D_A$(exptl)	0.6894	1.1665	0.7583	1.0370	0.6210	1.0630	0.6824	0.9400
$10^9 D_A$(calcd)	0.6889	1.1656	0.7572	1.0364	0.6208	1.0629	0.6822	0.9407
ρ(top)	1.108 134	1.110 418	1.108 598	1.109 930	1.136 306	1.138 781	1.136 798	1.138 300
ρ(bottom)	1.120 188	1.117 927	1.119 742	1.118 392	1.148 641	1.146 190	1.148 177	1.146 655

[a] Units of $\bar{C}_i$ and ΔC_i are mol·dm^{-3}, of Δt are s, of $10^9 D_A$ are m^2·s^{-1}, and of ρ are g·cm^{-3}. Densities were measured using a Mettler-Parr DMA/40 vibrating tube densimeter. Cell C-1235-H-11 was used; the path length inside this cell is $a = 2.5057$ cm, and the magnification factor is 1.7607_0.

Table 3. Results from Ternary Solution Mutual Diffusion Coefficient and Density Measurements for $\{z_1\text{NaCl} + (1 - z_1)\text{Na}_2\text{SO}_4\}$(aq) Solutions at $\langle \bar{C}_T \rangle = 1.500$ mol·dm^{-3} and 298.15 K Using Rayleigh Interferometry[a]

quantity	$z_1 = 0.900\ 00$	$z_1 = 0.749\ 93$	$z_1 = 0.500\ 00$	$z_1 = 0.250\ 00$
$\langle \bar{C}_T \rangle$	$1.499\ 009_5$	1.499 442	1.499 915	1.500 209
$\langle \bar{C}_1 \rangle$	1.349 108	1.124 471	0.749 953	0.375 050
$\langle \bar{C}_2 \rangle$	$0.149\ 901_5$	0.374 971	$0.749\ 961_5$	1.125 159
$\langle \bar{C}_0 \rangle$	53.7248	53.6483	53.4998	53.3295
$m_1(\langle \bar{C}_1 \rangle, \langle \bar{C}_2 \rangle)$	1.393 896	1.163 458	0.778 110	0.390 373
$m_2(\langle \bar{C}_1 \rangle, \langle \bar{C}_2 \rangle)$	0.154 878	0.387 972	0.778 118	1.171 128
$10^{-2} R_1$	4.137 14	4.018 53	3.842 65	3.690 45
$10^{-2} R_2$	8.077 06	7.846 47	7.485 78	7.170 48
$\bar{\rho}$	1.068 006	1.085 468	1.114 166	1.142 481
H_1	37.707 ± 0.065	36.939 ± 0.049	35.880 ± 0.055	34.777 ± 0.053
H_2	115.625 ± 0.129	114.081 ± 0.095	111.687 ± 0.107	109.633 ± 0.101
$s(\rho)$	0.000 011	0.000 009	0.000 012	0.000 011
$s(\bar{\rho})$	0.000 004	0.000 003	0.000 004	0.000 004
$\bar{V}_1$	20.740	21.479	22.485	23.523
$\bar{V}_2$	26.417	27.923_5	30.244	32.208
$\bar{V}_0$	18.019	17.994_5	17.952_5	17.906
$10^{-9}\sigma_+$	0.671 33	0.679 59	0.715 36	$0.781\ 53_5$
$10^{-9}\sigma_-$	1.321 69	1.431 38	1.589 46	1.696 33
$10^{-2} S_A$	−77.74	−82.08	−88.12	−94.65
$10^9 (D_{11})_V$	1.5018 ± 0.0007	1.4964 ± 0.0012	1.4278 ± 0.0012	1.2953 ± 0.0008
$10^9 (D_{12})_V$	0.2970 ± 0.0011	0.3039 ± 0.0017	0.2603 ± 0.0017	0.1372 ± 0.0011
$10^9 (D_{21})_V$	−0.0305 ± 0.0003	−0.0655 ± 0.0005	−0.0917 ± 0.0005	−0.0809 ± 0.0003
$10^9 (D_{22})_V$	0.7444 ± 0.0004	0.6737 ± 0.0007	0.5993 ± 0.0006	0.5738 ± 0.0004
$10^9 (D_{11})_0$	1.5441	1.5317	1.4507	1.3062
$10^9 (D_{12})_0$	0.3330	0.3334	0.2790	0.1457
$10^9 (D_{21})_0$	−0.0258	−0.0537	−0.0688	−0.0481
$10^9 (D_{22})_0$	0.7484	0.6835	0.6180	0.5994

[a] Units of $\langle \bar{C}_i \rangle$ are mol·dm^{-3}, of $m_i(\langle \bar{C}_1 \rangle, \langle \bar{C}_2 \rangle)$ are mol·kg^{-1}, of $10^{-2} R_i$ are mol^{-1}·dm^3, of $\bar{\rho}$, $s(\rho)$, and $s(\bar{\rho})$ are g·cm^{-3}, of H_i are g·mol^{-1}, of $\bar{V}_i$ are cm^3·mol^{-1}, of $10^{-9}\sigma_+$ and $10^{-9}\sigma_-$ are m^{-2}·s, of $10^{-2} S_A$ are m^{-1}·s$^{1/2}$, and of $10^9 (D_{ij})_V$ and $10^9 (D_{ij})_0$ are m^2·s^{-1}. Here $s(\rho)$ 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. 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.

$(D_{ij})_V$ were obtained using TFIT exactly as described in Section 3 of ref 11.

Experimental and calculated J values are both reported in Table 2. These J(calcd) were obtained from the ΔC_i and the least-squares parameters R_i, using the second equality of eq 1. Calculation of the D_A(exptl) values was performed as described on page 4193 of ref 11.

The D_A(calcd) for each experiment was obtained as described elsewhere[11,24] 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 11 and are the reciprocals of the eigenvalues 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 24.

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, $|D_A(\text{exptl}) - D_A(\text{calcd})| \leq 0.0015 \times 10^{-9}\ \mathrm{m^2{\cdot}s^{-1}}$, except for the second experiment for the composition with $z_1 = 0.749\,93$, where the difference is somewhat larger.

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 the 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 given is the thermodynamic diffusion coefficient $M = D_V/\{d(m\phi)/dm\}$, 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).[41,42] Newer and much more accurate extended Pitzer equations[10] are available for the thermodynamic properties of both NaCl(aq) and Na_2SO_4(aq) as functions of temperature,[43,44] which will allow more accurate values of the chemical potential derivatives $\{d(m\phi)/dm\}$ to be calculated at 298.15 K. However, we used the older empirical isothermal activity equations to facilitate comparison of our present values of M with previous results from our two laboratories.[11,30,45,46]

Rard and Miller[45] 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. The original large-scale plot for their Figure 1 yields $D_V = (1.496_7 \pm 0.002) \times 10^{-9}\ \mathrm{m^2{\cdot}s^{-1}}$ at $\bar{C} = 1.5000\ \mathrm{mol{\cdot}dm^{-3}}$. Our experimental value of $D_V = 1.497_8 \times 10^{-9}\ \mathrm{m^2{\cdot}s^{-1}}$ at $\bar{C} = 1.500\,02\ \mathrm{mol{\cdot}dm^{-3}}$ agrees well within the uncertainty of the published values.

Our diffusion measurements for Na_2SO_4(aq) at $\bar{C} = 1.500\,07\ \mathrm{mol{\cdot}dm^{-3}}$, using Rayleigh interferometry, gave $D_V = 0.571_2 \times 10^{-9}\ \mathrm{m^2{\cdot}s^{-1}}$. A value of $D_V \approx (0.568 \pm 0.001) \times 10^{-9}\ \mathrm{m^2{\cdot}s^{-1}}$ at $1.500\ \mathrm{mol{\cdot}dm^{-3}}$ was estimated by graphical interpolation of a large-scale plot of the Rayleigh interferometric values of Rard and Miller,[46] which were measured at Lawrence Livermore National Laboratory using a less precise diffusiometer. These two values disagree by $0.003 \times 10^{-9}\ \mathrm{m^2{\cdot}s^{-1}}$ (0.5%), although no significant differences were observed at lower molarities.[11,30] The present measurements were made using a stock solution of Na_2SO_4(aq) prepared from anhydrous Na_2SO_4(s) and purified water, whereas, in the earlier study,[46] the Na_2SO_4 was recrystallized before use. Rard and Miller[46] reported the pHs of their air-saturated solutions graphically, and their solution pHs were slightly alkaline (pH $\leq$ 8.2) except at fairly low molalities where the pHs are determined mainly by the slight acidity of carbonic acid. Solutions of Na_2SO_4(aq) are expected to be very slightly alkaline due to a small amount of hydrolysis of the SO_4^{2-} ion. In contrast, the stock solution of Na_2SO_4(aq) and the solutions prepared from it for the present diffusion study were found to be slightly acidic with pHs $\sim$ 6.

We recrystallized a sample of our Baker "Analyzed" Na_2SO_4(s) and used it to prepare a new stock solution for some additional diffusion measurements for Na_2SO_4(aq) solutions. The solutions prepared from the recrystallized material had pHs nearly identical to those of solutions prepared from the unrecrystallized material. A diffusion experiment using samples prepared from the new stock solution, at $\bar{C} = 1.500\,01\ \mathrm{mol{\cdot}dm^{-3}}$, gave $D_V = 0.570_6 \times 10^{-9}\ \mathrm{m^2{\cdot}s^{-1}}$, which is lower than our first value of $D_V = 0.571_2 \times 10^{-9}\ \mathrm{m^2{\cdot}s^{-1}}$ by 0.1%, but the difference between this value and that from the earlier experiment is not large. This agreement suggests that acidic impurities are probably not responsible for the moderate disagreement between our diffusion coefficients at $\bar{C} = 1.5000\ \mathrm{mol{\cdot}dm^{-3}}$ and those reported by Rard and Miller.[46] We note that at pH $\sim$ 6 and pH $\sim$ 8 the molalities of hydrogen ion or hydroxide ion, respectively, are only about $10^{-6}\ \mathrm{mol{\cdot}dm^{-3}}$, which are much too low for these ions to be altering the measured diffusion coefficients of Na_2SO_4(aq) at the concentration of interest.

Some additional check experiments were made at three lower concentrations of Na_2SO_4(aq), where a comparison is also possible. Our new experimental measurement at $\bar{C} = 0.500\,00\ \mathrm{mol{\cdot}dm^{-3}}$ gives $D_V = 0.793_7 \times 10^{-9}\ \mathrm{m^2{\cdot}s^{-1}}$, Rard et al.[11] obtained $D_V = 0.793_2 \times 10^{-9}\ \mathrm{m^2{\cdot}s^{-1}}$ at $\bar{C} = 0.500\,00\ \mathrm{mol{\cdot}dm^{-3}}$, Wendt[47] obtained $D_V = 0.792_5 \times 10^{-9}\ \mathrm{m^2{\cdot}s^{-1}}$ at $\bar{C} = 0.499\,53\ \mathrm{mol{\cdot}dm^{-3}}$, and interpolation of the values of Rard and Miller[46] to $\bar{C} = 0.5000\ \mathrm{mol{\cdot}dm^{-3}}$ gave[11] $D_V = (0.791 \text{ to } 0.792) \times 10^{-9}\ \mathrm{m^2{\cdot}s^{-1}}$. Similarly, our new measurement at $\bar{C} = 0.999\,99\ \mathrm{mol{\cdot}dm^{-3}}$ gives $D_V = 0.654_5 \times 10^{-9}\ \mathrm{m^2{\cdot}s^{-1}}$, Albright et al.[30] obtained $D_V = 0.654_6 \times 10^{-9}\ \mathrm{m^2{\cdot}s^{-1}}$ at $\bar{C} = 1.000\,02\ \mathrm{mol{\cdot}dm^{-3}}$, Wendt[47] obtained $D_V = 0.653_9 \times 10^{-9}\ \mathrm{m^2{\cdot}s^{-1}}$ at $\bar{C} = 0.99954\ \mathrm{mol{\cdot}dm^{-3}}$, and interpolation[30] of the values of Rard and Miller[46] to $\bar{C} = 1.0000\ \mathrm{mol{\cdot}dm^{-3}}$ gave $D_V = (0.654 \pm 0.001) \times 10^{-9}\ \mathrm{m^2{\cdot}s^{-1}}$. All of these experimental values at both compositions are in very good agreement. At $\bar{C} = 1.200\,01\ \mathrm{mol{\cdot}dm^{-3}}$ our new measurement gives $D_V = 0.616_3 \times 10^{-9}\ \mathrm{m^2{\cdot}s^{-1}}$, which is slightly higher than the value of $D_V \sim 0.614 \times 10^{-9}\ \mathrm{m^2{\cdot}s^{-1}}$ estimated by interpolation of the results of Rard and Miller to $\bar{C} = 1.2000\ \mathrm{mol{\cdot}dm^{-3}}$.

On the basis of previous experience with the Gosting diffusiometer, experimental D_V are reproducible to about 0.03 to 0.05% for binary solutions, whereas the diffusiometer used by Rard and Miller[46] was capable of a precision of 0.1−0.2%. There is thus a slight disagreement between the present results for Na_2SO_4(aq) and those of Rard and Miller at concentrations $>1.0000\ \mathrm{mol{\cdot}dm^{-3}}$, which slightly exceeds the reported errors. In contrast, our two values measured with the Gosting diffusiometer agree very well at lower concentrations. Rard and Miller 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 cell above room temperature before filling it, which could have given rise to slight systematic distortions in the baseline corrections. In our opinion, the combined measurements from this laboratory, those of Rard and Miller,[46] and those of Wendt[47] are the most accurate diffusion coefficients for Na_2SO_4(aq) at 298.15 K for concentrations up to $1.0000\ \mathrm{mol{\cdot}dm^{-3}}$ Na_2SO_4(aq), but at higher concentrations our new measurements reported in Table 1 are to

Table 4. Comparison of Calculated Errors of the Ternary Solution $(D_{ij})_V$ for $\{z_1NaCl + (1 - z_1)Na_2SO_4\}(aq)$ Solutions at $\langle \bar{C}_T \rangle = 1.500$ mol·dm^{-3} and 298.15 K[a]

quantity	$z_1 = 0.900\ 00$	$z_1 = 0.749\ 93$	$z_1 = 0.500\ 00$	$z_1 = 0.250\ 00$
$\langle \bar{C}_T \rangle$	$1.499\ 009_5$	1.499 442	1.499 915	1.500 209
$\langle \bar{C}_1 \rangle$	1.349 108	1.124 471	0.749 953	0.375 050
$\langle \bar{C}_2 \rangle$	$0.149\ 901_5$	0.374 971	$0.749\ 961_5$	1.125 159
$10^9\delta(D_{11})_V$[b]	0.0007	0.0012	0.0012	0.0008
$10^9\delta(D_{12})_V$[b]	0.0011	0.0017	0.0017	0.0011
$10^9\delta(D_{21})_V$[b]	0.0003	0.0005	0.0005	0.0003
$10^9\delta(D_{22})_V$[b]	0.0004	0.0007	0.0006	0.0004
$10^9\delta(D_{11})_V$[c]	0.0033	0.0008	0.0047	0.0002
$10^9\delta(D_{12})_V$[c]	0.0029	0.0047	0.0125	0.0058
$10^9\delta(D_{21})_V$[c]	0.0010	0.0011	0.0015	0.0002
$10^9\delta(D_{22})_V$[c]	0.0007	0.0014	0.0041	0.0017

[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.

be preferred. However, the presumed slight systematic errors in the four highest concentration diffusion coefficients of Rard and Miller[46] are only 0.2−0.5% of the D_V values.

Ternary Solutions. Table 3 contains all the derived quantities for the four ternary solution compositions of the system NaCl + Na$_2$SO$_4$ + H$_2$O at 298.15 K and $\langle \bar{C}_T \rangle = 1.500$ mol·dm^{-3}. 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.[13,36] The reverse transformation, of the $(D_{ij})_0$ to the $(D_{ij})_V$, can be made using eq 64 of Miller.[6] 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$_2$SO$_4$, respectively, corresponding to a solution having the molarities of both salts equal to the overall 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,[48] which can be related to already defined quantities by

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

If $|10^{-2}S_A|$ decreases below ~(20 to 25) m^{-1}·s$^{1/2}$, then the calculated standard errors of the D_{ij} generally have significantly larger values than usual.[24,49] Furthermore, if the σ_+ and σ_- values are nearly equal, the nonlinear least-squares analysis of the diffusion data may not converge. Fortunately, σ_+ and σ_- differ by about a factor of 2 for our experiments and the $|10^{-2}S_A|$ values range from (77.74 to 94.65) m^{-1}·s$^{1/2}$, and no such computational difficulties were encountered.

Reported uncertainties in the $(D_{ij})_V$ in Table 3 were obtained from the statistical analysis portion of TFIT using standard propagation of error methods. However, as discussed elsewhere, we believe the actual uncertainties are larger than these statistical uncertainties indicate.[16,24,25,49,50] A more realistic "rule of thumb" estimate is that the actual errors are about four times larger than the statistical errors.[20−24]

Realistic errors for the $(D_{ij})_V$ may also be obtained using the data from various subsets of the diffusion experiments.[50] These calculations were performed with the four possible three-experiment subsets of the α_1 for each overall ternary solution composition. The results of this analysis are reported in Table 4, where the values of $\delta(D_{ij})_V$ are "$n - 1$" standard deviations calculated from the four resulting subset values of each $(D_{ij})_V$.

The calculated uncertainties of two of the $(D_{ii})_V$ for the $z_1 = 0.500\ 00$ case are somewhat larger than those given by the four times the statistical errors rule of thumb, but for the other three mixture compositions, there is an approximate agreement between the two different methods of estimating errors for the $(D_{ij})_V$.

This comparison suggests that the actual uncertainties of the two main-term $(D_{ii})_V$ coefficients are $\leq 0.005 \times 10^{-9}$ m^2·s^{-1}, of $(D_{21})_V$ are $\leq 0.002 \times 10^{-9}$ m^2·s^{-1}, and of $(D_{12})_V$ are generally $\leq 0.006 \times 10^{-9}$ m^2·s^{-1}. The exception is for $(D_{12})_V$ for the composition with $z_1 = 0.500\ 00$, where the uncertainty may be as large as 0.013×10^{-9} m^2·s^{-1}.

Discussion

As $z_1 \to 1$, $(D_{11})_V \to D_V$ for NaCl(aq). Similarly, $(D_{22})_V \to D_V$ for Na$_2$SO$_4$(aq) as $z_1 \to 0$. Also, as $z_1 \to 1$, $(D_{21})_V \to 0$ because no Na$_2$SO$_4$(aq) is present to be transported by coupled diffusion, and $(D_{12})_V \to 0$ as $z_1 \to 0$ because no NaCl(aq) is present to be transported by coupled diffusion.

Extrapolation of some of the $(D_{ij})_V$ to $z_1 = 1$ or $z_1 = 0$ yields significant new information. As $z_1 \to 1$, $(D_{22})_V \to D^*(SO_4^{2-})$, and as $z_1 \to 0$, $(D_{11})_V \to D^*(Cl^-)$, where $D^*(SO_4^{2-})$ is the trace diffusion coefficient of the SO_4^{2-} ion in a solution of 1.500 mol·dm^{-3} NaCl(aq) and where $D^*(Cl^-)$ is the trace diffusion coefficient of the Cl^- ion in a solution with molarity 1.500 mol·dm^{-3} Na$_2$SO$_4$(aq). Unlike the other extrapolated values, $(D_{12})_V$ as $z_1 \to 1$ and $(D_{21})_V$ as $z_1 \to 0$ are simply limiting values.

The solid curves of Figures 1 and 2 show the trends in the main-term and cross-term $(D_{ij})_V$, respectively, as functions of z_1 at $\langle \bar{C}_T \rangle = (0, 0.500, 1.000,$ and $1.500)$ mol·dm^{-3}. Additional plots (not presented here), similar to Figures 1 and 2, were made at 1.500 mol·dm^{-3} with the molarity composition fraction replaced by the ionic strength fraction, the equivalent fraction, and the ratio of the ionic molarity (osmolarity) of NaCl to the total ionic molarity. Extrapolated values of the cross-term coefficients, and of $D^*(Cl^-)$ and of $D^*(SO_4^{2-})$, were obtained graphically from these four plots by two of us independently. Additional extrapolations were also used, as described below. The average of these and the D_V values for the limiting binary solutions at molarities of 1.500 mol·dm^{-3} are summarized in Table 5 and were used to extend the curves in Figures 1 and 2 to $z_1 = 0$ and 1.

The experimental values of $(D_{11})_V$ and $(D_{22})_V$ are very smooth and regular functions of z_1 and connect smoothly with the D_V for their limiting binary solutions NaCl(aq) and Na$_2$SO$_4$(aq), respectively. Our extrapolations of $(D_{22})_V$

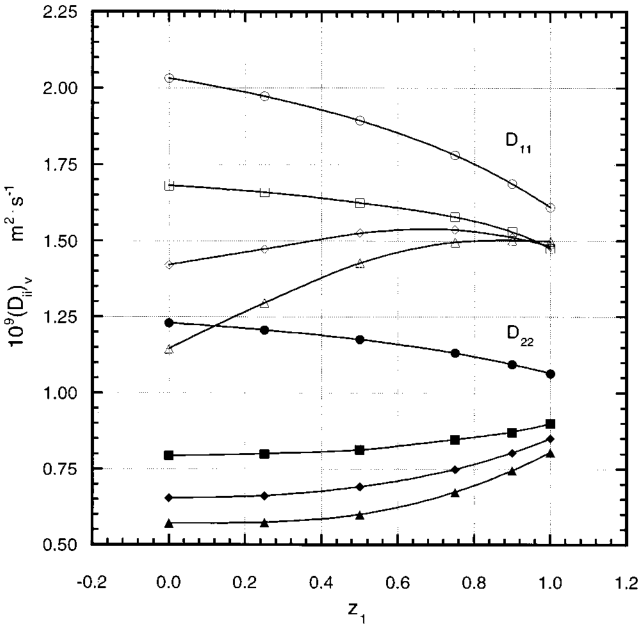

Figure 1. Values of the volume-fixed mutual diffusion main-term coefficients $(D_{ii})_{\rm V}$ at 298.15 K for NaCl + Na_2SO_4 + H_2O at total concentration $\langle \bar{C}_{\rm T} \rangle$ = (0.500, 1.000, and 1.500) mol·dm^{-3}, along with the corresponding values at infinite dilution ($\langle \bar{C}_{\rm T} \rangle = 0$) from the Nernst–Hartley equation, as a function of the solute molarity fraction z_1 of NaCl. Also plotted are values of $D_{\rm V}$ for the limiting binary solutions NaCl(aq) (at $z_1 = 1$) and Na_2SO_4(aq) (at $z_1 = 0$) and extrapolated values of the trace diffusion coefficients $D^*(Cl^-)$ and $D^*(SO_4^{2-})$. Symbols: ○, □, ◇, △, $(D_{11})_{\rm V}$ at (0, 0.500, 1.000, and 1.500) mol·dm^{-3}, respectively; ●, ■, ◆, ▲, $(D_{22})_{\rm V}$ at (0, 0.500, 1.000, and 1.500) mol·dm^{-3}, respectively.

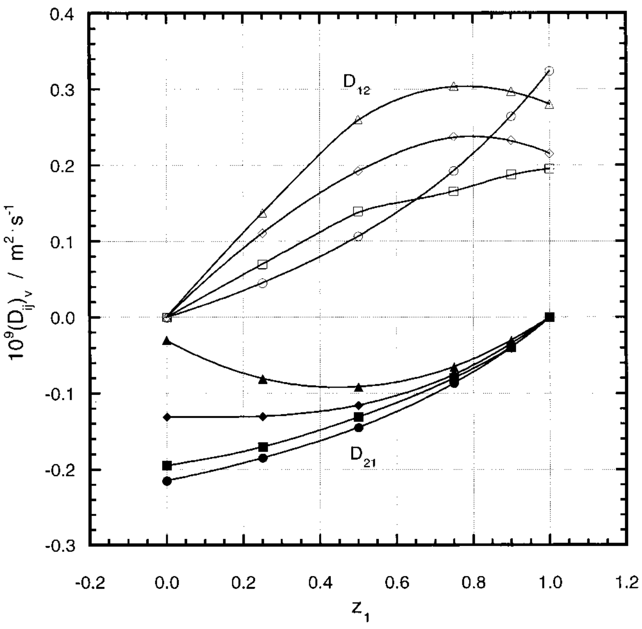

Figure 2. Values of the volume-fixed mutual diffusion cross-term coefficients $(D_{ij})_{\rm V}$ at 298.15 K for NaCl + Na_2SO_4 + H_2O at total concentration $\langle \bar{C}_{\rm T} \rangle$ = (0.500, 1.000, and 1.500) mol·dm^{-3}, along with the corresponding values at infinite dilution ($\langle \bar{C}_{\rm T} \rangle = 0$) from the Nernst–Hartley equation, as a function of the solute molarity fraction z_1 of NaCl. Symbols: ○, □, ◇, △, $(D_{12})_{\rm V}$ at (0, 0.500, 1.000, and 1.500) mol·dm^{-3}, respectively; ●, ■, ◆, ▲, $(D_{21})_{\rm V}$ at (0, 0.500, 1.000, and 1.500) mol·dm^{-3}, respectively. We revise our earlier estimate[30] of $(D_{12})_{\rm V}$ as $z_1 \rightarrow 1$ at concentration $\langle \bar{C}_{\rm T} \rangle$ = 1.000 mol·dm^{-3} from 0.204×10^{-9} m^2·s^{-1} to 0.215×10^{-9} m^2·s^{-1}, on the basis of an examination of the variations of $(D_{12})_{\rm V}$ with both $\langle \bar{C}_{\rm T} \rangle$ and z_1.

to obtain $D^*(SO_4^{2-})$ should be fairly accurate. However, extrapolation of $(D_{11})_{\rm V}$ to obtain $D^*(Cl^-)$ has larger uncertainties because of the steep decrease of $(D_{11})_{\rm V}$ as $z_1 \rightarrow 0$. We found that the difference $(D_{11})_{\rm V} - (D_{12})_{\rm V}$ showed much less variation with the composition fraction of NaCl, and this function was therefore used to obtain more precise extrapolated values of $D^*(Cl^-)$. Also, $(D_{12})_{\rm V}$ goes through a maximum at $z_1 \sim 0.8$ and $(D_{21})_{\rm V}$ has a minimum at $z_1 \sim 0.4$. Consequently, the direct extrapolation of $(D_{12})_{\rm V}$ as $z_1 \rightarrow 1$ and of $(D_{21})_{\rm V}$ as $z_1 \rightarrow 0$ would have greater uncertainties than our extrapolated values $D^*(SO_4^{2-})$, especially for $(D_{21})_{\rm V}$ where the trend is not completely defined at low values of z_1.

The Nernst–Hartley equations for ternary electrolyte solutions[6] predict that both D_{12}/e_1 and D_{21}/e_2 should be linear functions of e_1, where $e_1 = C_1/(C_1 + 2C_2)$ and $e_2 = 1 - e_1 = 2C_2/(C_1 + 2C_2)$ are the equivalent fractions of the corresponding solutes. Although this linear relationship does not hold at our concentrations of $\langle \bar{C}_{\rm T} \rangle$ = 1.500 mol·dm^{-3}, these two functions do not have the maxima or minima observed in the direct plots of $(D_{12})_{\rm V}$ and $(D_{21})_{\rm V}$ against z_1. Thus, the extrapolation of $(D_{21})_{\rm V}$ as $z_1 \rightarrow 0$ can be made more accurately using $(D_{21})_{\rm V}/e_2$, and our extrapolated value in Table 5 was based on this plot and related plots of $(D_{21})_{\rm V}/e_2$ against other composition fractions. However, the corresponding plots of $(D_{12})_{\rm V}/e_1$ were less useful for obtaining the extrapolated value as $z_1 \rightarrow 1$.

The $(D_{21})_{\rm V}$ values generally become more negative as $z_1 \rightarrow 0$, and $(D_{12})_{\rm V}$ usually becomes more positive as $z_1 \rightarrow 1$. Thus, coupled diffusion enhances the rate of diffusion of NaCl but reduces that of Na_2SO_4 in these solutions, and the magnitude of this coupling increases as the concentrations of the solutions are increased.

Our extrapolation technique, which uses mutual diffusion coefficients to determine trace diffusion coefficients, has the advantage over conventional methods that the solutions do not contain radioactive tracers or different isotopes. We are not aware of any direct determinations of $D^*(Cl^-)$ or $D^*(SO_4^{2-})$ by conventional methods for the same ionic media used here. However, some comparisons are possible.

A value of $D^*(SO_4^{2-}) = 0.816 \times 10^{-9}$ m^2·s^{-1} was recommended by Mills and Lobo[51] for solutions of Na_2SO_4(aq) at an ionic strength of I = 1.476 mol·dm^{-3}. This value was taken from the then unpublished study of Weingärtner et al.[52] Agreement with our extrapolated value $D^*(SO_4^{2-}) = (0.80_5 \pm 0.01_5) \times 10^{-9}$ m^2·s^{-1} is excellent despite the different electrolyte media.

Similarly, $D^*(Cl^-)$ for several electrolyte solutions were tabulated by Mills and Lobo.[51] Values of $D^*(Cl^-)$ at I = 4.5 mol·dm^{-3} are needed, since this is the total ionic strength of our solutions at $z_1 = 0$. Our extrapolated value is $D^*(Cl^-) = (1.14_5 \pm 0.02) \times 10^{-9}$ m^2·s^{-1}. The interpolated value of $D^*(Cl^-)$ in NaCl(aq) from Mills and Lobo at I = 4.5 mol·dm^{-3}, $(1.16 \pm 0.01) \times 10^{-9}$ m^2·s^{-1}, is essentially identical to our value in Na_2SO_4(aq).

The values of $D^*(Cl^-)$ are found to be virtually identical in solutions of NaCl(aq) and of Na_2SO_4(aq) at I = 4.500 mol·dm^{-3}, which also happens at I = 1.500 mol·dm^{-3} and at I = 3.000 mol·dm^{-3}.[11,30] This good agreement also holds for $D^*(SO_4^{2-})$ in solutions of NaCl(aq) and of Na_2SO_4(aq) at both I = 1.500 mol·dm^{-3} (present study) and I = 0.500 mol·dm^{-3} and I = 1.000 mol·dm^{-3}.[11,30] Such close agreement between $D^*(Cl^-)$ obtained in NaCl(aq) and Na_2SO_4(aq) solutions at the same stoichiometric ionic strengths, which occurs at all three ionic strengths from I = (1.500 to

Table 5. Values of $(D_{ij})_V$ for $\{z_1NaCl + (1 - z_1)Na_2SO_4\}$(aq) Solutions as $z_1 \rightarrow 0$ and $z_1 \rightarrow 1$ at $\langle \bar{C}_T \rangle = 1.500$ mol·dm^{-3} and 298.15 K[a]

quantity	$10^9(D_{ij})_V$	interpretation
$(D_{11})_V$ as $z_1 \rightarrow 1$	$1.497_8 \pm 0.001$	D_V(NaCl) at $C_1 = 1.500$ mol·dm^{-3}
$(D_{12})_V$ as $z_1 \rightarrow 1$	0.28 ± 0.02	extrapolated value at $I = 1.500$ mol·dm^{-3}
$(D_{21})_V$ as $z_1 \rightarrow 1$	0	by definition
$(D_{22})_V$ as $z_1 \rightarrow 1$	$0.80_5 \pm 0.01_5$	$D^*(SO_4^{2-})$ at $I = 1.500$ mol·dm^{-3} (extrapolated)
$(D_{11})_V$ as $z_1 \rightarrow 0$	$1.14_5 \pm 0.02$	$D^*(Cl^-)$ at $I = 4.500$ mol·dm^{-3} (extrapolated)
$(D_{12})_V$ as $z_1 \rightarrow 0$	0	by definition
$(D_{21})_V$ as $z_1 \rightarrow 0$	-0.03 ± 0.02	extrapolated value at $I = 4.500$ mol·dm^{-3}
$(D_{22})_V$ as $z_1 \rightarrow 0$	0.570_9[b]	$D_V(Na_2SO_4)$ at $C_2 = 1.500$ mol·dm^{-3}

[a] Units of $10^9(D_{ij})_V$ are m^2·s^{-1}. [b] Average of our two experimental values given in Table 1.

4.500) mol·dm^{-3}, seems to imply that the ionic strengths of the Na_2SO_4(aq) solutions are not being reduced significantly by the formation of sodium sulfate ion pairs. This conclusion conflicts with some thermodynamic analyses[53] which claim that fairly extensive ion pair formation occurs in these solutions.

This good agreement may be more than coincidental and could imply that the trace diffusion coefficient of an anion X^{n-} in a solution of electrolyte M_aY_b(aq) can be reliably estimated from its value in the common cation solution of $M_{a'}X_{b'}$(aq) at the same ionic strength. However, mutual and isotope diffusion coefficient measurements for other ternary aqueous electrolyte systems are needed to test the generality of this observation.

We note that the $(D_{12})_V$ and $(D_{21})_V$ values are of opposite sign and the difference between their values is approximately constant, $(D_{12})_V - (D_{21})_V = (0.317 \pm 0.068) \times 10^{-9}$ m^2·s^{-1}, at $\langle \bar{C}_T \rangle = 1.500$ mol·dm^{-3} for the four values of z_1. However, the differences are significantly larger for the two intermediate mixtures (with $z_1 = 0.749\ 93$ and 0.500 00) than for the other two mixtures which are closer to the limiting binary compositions (with $z_1 = 0.900\ 00$ and 0.250 00). This difference at 1.500 mol·dm^{-3} is also somewhat larger than the difference found at 0.500 mol·dm^{-3}, $(0.246 \pm 0.018) \times 10^{-9}$ m^2·s^{-1},[11] or at 1.000 mol·dm^{-3}, $(0.282 \pm 0.034) \times 10^{-9}$ m^2·s^{-1}.[30] Cross-term diffusion coefficients calculated from the Nernst−Hartley equation[11] yield a comparable difference of $(D_{12})_V - (D_{21})_V = (0.266 \pm 0.032) \times 10^{-9}$ m^2·s^{-1} at infinite dilution. For $\langle \bar{C}_T \rangle = (0.500$, 1.000, and 1.500) mol·dm^{-3}, $(D_{12})_V - (D_{21})_V$ has a small maximum at intermediate values of z_1, in contrast to the monotonic increase with z_1 at infinite dilution that is predicted by the Nernst−Hartley equation.

Figures 1 and 2 contain plots of the main-term ($i = j$) and the cross-term $(D_{ij})_V$ ($i \neq j$), respectively, as functions of z_1 at $\langle \bar{C}_T \rangle = (0$, 0.500, 1.000, and 1.500) mol·dm^{-3} and 298.15 K. The $(D_{ij})_V$ at $\langle \bar{C}_T \rangle = 0$ (infinite dilution) were calculated using the ternary solution analogue of the Nernst−Hartley equation.[6] The observed opposite signs for $(D_{12})_V$ and $(D_{21})_V$ at (0.500, 1.000, and 1.500) mol·dm^{-3}, see Figure 2, are predicted qualitatively by the Nernst−Hartley equation, which is Coulombically based.

However, there are some sizable quantitative differences between the experimental $(D_{ij})_V$ and the Nernst−Hartley values, especially for the main-term $(D_{ii})_V$, as can be seen in Figure 1. At $\langle \bar{C}_T \rangle = 1.500$ mol·dm^{-3}, the Nernst−Hartley D_{11} are significantly higher than the experimental $(D_{11})_V$ by (0.186 to 0.678) × 10^{-9} m^2·s^{-1}, and the Nernst−Hartley D_{22} are significantly higher than the experimental $(D_{22})_V$ by (0.351 to 0.633) × 10^{-9} m^2·s^{-1}. In addition, there are significant *qualitative* differences. At infinite dilution, both D_{11} and D_{22} *decrease monotonically* with increasing z_1. In contrast, $(D_{22})_V$ *increases monotonically* with increasing z_1 at all three experimental concentrations of $\langle \bar{C}_T \rangle = (0.500$ to 1.500) mol·dm^{-3}. Although $(D_{11})_V$ values at both $\langle \bar{C}_T \rangle =$ (0 and 0.500) mol·dm^{-3} have similar qualitative trends with z_1, at $\langle \bar{C}_T \rangle = 1.000$ mol·dm^{-3} its values increase from $z_1 = 0$ to ∼ 0.7 and then decrease at higher z_1, and at $\langle \bar{C}_T \rangle = 1.500$ mol·dm^{-3} this maximum shifts to $z_1 \sim 0.8$.

Also in contrast, at $\langle \bar{C}_T \rangle = 1.500$ mol·dm^{-3} the Nernst−Hartley cross-term D_{ij} ($i \neq j$) are closer to the experimental $(D_{ij})_V$ but are always smaller rather than larger. For D_{12}, the Nernst−Hartley values are smaller than the experimental ones by (0.033 to 0.154) × 10^{-9} m^2·s^{-1}. For D_{21}, the Nernst−Hartley values are smaller (more negative) than the experimental $(D_{21})_V$ by (0.010 to 0.104) × 10^{-9} m^2·s^{-1}. However, at $\langle \bar{C}_T \rangle = (0.500$ and 1.000) mol·dm^{-3}, some of the experimental cross-term $(D_{12})_V$ are larger than the Nernst−Hartley values, whereas others are smaller.

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 the $(D_{ij})_0$. 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 systems such as NaCl + $SrCl_2$ + H_2O at 298.15 K.[17]

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 this viscosity "correction" must be considered to be a purely empirical term.[5,54] However, as discussed by Robinson and Stokes,[55] including an adjustable hydration number into the model (that formally represents the number of waters bound to the ions), 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 success of the model 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.

Leaist and Al-Dhaher[56] have generalized this model to common-ion mixed electrolyte solutions and applied it to analyze published diffusion coefficients for the NaCl + $SrCl_2$ + H_2O and NaCl + $MgCl_2$ + H_2O systems at 298.15 K.[16,17,20−24] 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 is quite good up to $\langle \bar{C}_T \rangle = 1.0$ mol·dm^{-3} or even to higher concentrations, which implies that their model will be useful for predicting diffusion coefficients of mixed electrolyte solutions. However, this approach has not yet been applied to any common ion sodium salt mixtures such as $NaCl + Na_2SO_4 + H_2O$.

Three of the diffusion coefficients for $NaCl + Na_2SO_4 + H_2O$, $(D_{11})_V$, $(D_{22})_V$, and $(D_{21})_V$, form families of curves that vary slowly and systematically with increasing $\langle \bar{C}_T \rangle$. Thus, it should be possible to accurately estimate values of their diffusion coefficients at intermediate concentrations by interpolation. In contrast, the Nernst–Hartley infinite dilution values of D_{12} have a significantly different qualitative behavior than the experimental $(D_{12})_V$. The Nernst–Hartley curve does not predict the observed maximum and crosses all of the experimental $(D_{12})_V$ curves. Therefore, interpolation to intermediate concentrations could yield more uncertain results for $(D_{12})_V$ in certain regions of z_1 for $\langle \bar{C}_T \rangle < 1.000$ mol·dm^{-3}.

There are some significant changes with concentration in the variation of the $(D_{12})_V$ with z_1 at constant $\langle \bar{C}_T \rangle$. At infinite dilution the Nernst–Hartley values of both $(D_{12})_V$ and $(D_{21})_V$ increase monotonically with increasing values of z_1. However, at $\langle \bar{C}_T \rangle = 0.500$ mol·dm^{-3} the values of $(D_{12})_V$ approach a maximum at $z_1 \sim 0.5$, at $\langle \bar{C}_T \rangle = 1.000$ mol·dm^{-3} the maximum is at $z_1 \sim 0.7$, and this maximum shifts to $z_1 \sim 0.8$ at $\langle \bar{C}_T \rangle = 1.500$ mol·dm^{-3}. Neither this maximum nor its shift with increasing concentration is predicted by the Nernst–Hartley equations.

At infinite dilution the values of $(D_{21})_V$ also increase monotonically as z_1 increases. However, at finite concentrations the values of $(D_{21})_V$ at any fixed low z_1 begin to increase with increasing $\langle \bar{C}_T \rangle$, but by $\langle \bar{C}_T \rangle = 1.000$ mol·dm^{-3} values of $(D_{21})_V$ are essentially constant from $z_1 = 0$ to ~ 0.25. In contrast, at $\langle \bar{C}_T \rangle = 1.500$ mol·dm^{-3} the values of $(D_{21})_V$ go through a minimum at $z_1 \sim 0.4$ and then increase at larger values of z_1. It is not possible to accurately assess how rapidly $(D_{21})_V$ increases at lower values of z_1, since there is only a single composition point to characterize this region, but the presence of the upturn suggests that values of $(D_{21})_V$ at low z_1 will switch from negative to positive somewhere between $\langle \bar{C}_T \rangle = 2$ and 3 mol·dm^{-3}. However, because of solubility limitations for the precipitation of $Na_2SO_4 \cdot 10H_2O(cr)$, it will probably not be possible to investigate this composition region using presently available experimental techniques.

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