

# Ternary Solution Mutual Diffusion Coefficients and Densities of Aqueous Mixtures of NaCl and Na<sub>2</sub>SO<sub>4</sub> at 298.15 K for Six Different Solute Fractions at a Total Molarity of 1.000 mol·dm<sup>-3</sup>

John G. Albright\* and Seth M. Gillespie†

Chemistry Department, Texas Christian University, Fort Worth, Texas 76129

Joseph A. Rard and Donald G. Miller

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<sub>2</sub>SO<sub>4</sub> at a constant total molarity of 1.000 mol·dm<sup>-3</sup> and 298.15 K. Measurements were performed using Rayleigh interferometry with computerized data acquisition at NaCl molarity fractions of  $z_1 = 1, 0.90, 0.75, 0.50, 0.25,$  and 0. Densities of the solutions were measured with a vibrating tube densimeter. At all ternary solution compositions, one cross-term diffusion coefficient has negative values whereas the other has positive values. These measurements supplement our earlier results at 0.500 mol·dm<sup>-3</sup>. Both main-term diffusion coefficients are significantly smaller at 1.000 mol·dm<sup>-3</sup> than at 0.500 mol·dm<sup>-3</sup> at any fixed value of  $z_1$ , whereas both cross-term coefficients are shifted in a positive direction. Trace diffusion coefficients  $D^*(\text{Cl}^-)$  and  $D^*(\text{SO}_4^{2-})$  were extrapolated from these results for the Cl<sup>-</sup>(aq) ion in 1.0 mol·dm<sup>-3</sup> Na<sub>2</sub>SO<sub>4</sub>(aq) and for the SO<sub>4</sub><sup>2-</sup>(aq) ion in 1.0 mol·dm<sup>-3</sup> NaCl(aq). Values of  $D^*(\text{Cl}^-)$  in Na<sub>2</sub>SO<sub>4</sub>(aq) and in NaCl(aq) were found to be essentially identical, as were  $D^*(\text{SO}_4^{2-})$  in these same two electrolytes, provided the comparisons were made at the same volumetric ionic strengths.

---

## Introduction

Many chemical, geochemical, and industrial processes involve diffusive transport of aqueous electrolytes (Anderson and Graf, 1978; Felmy and Weare, 1991; Noulty and Leaist, 1987; Steefel and Lichtner, 1994). Diffusion coefficients are also part of the transport data required for calculation of various types of generalized transport coefficients (Miller, 1966, 1967a,b, 1981; Zhong and Friedman, 1988).

Aqueous NaCl solutions are often used to dissolve proteins, and increasing the NaCl concentration will cause salting-out of protein crystals in some cases. Sulfate salts such as Na<sub>2</sub>SO<sub>4</sub> also can cause salting-out of proteins. 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 under both microgravity conditions and normal gravity conditions.

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 (see Rard et al., 1996). 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 (Albright et al., 1989; Dunlop, 1959; Dunlop and Gosting, 1959; Kim, 1982; Leaist, 1988;

Mathew et al., 1989, 1990; Miller et al., 1986, 1993, 1996; O'Donnell and Gosting, 1959; Paduano et al., 1989; Rard and Miller, 1987, 1988), as well as one composition of the system NaHCO<sub>3</sub> + KHCO<sub>3</sub> + H<sub>2</sub>O (Albright et al., 1987). Noncommon ion mixtures of NaCl + MgSO<sub>4</sub> + H<sub>2</sub>O have also been studied (Hao and Leaist, 1995).

However, fewer diffusion studies have been reported for common-cation aqueous mixtures. These include six mixtures of NaOH + Na<sub>2</sub>SO<sub>3</sub> + H<sub>2</sub>O (Leaist, 1985), several mixtures of MgCl<sub>2</sub> + MgSO<sub>4</sub> + H<sub>2</sub>O (Deng and Leaist, 1991), four mixtures of NaCl + Na<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O at a total molarity of 0.500 mol·dm<sup>-3</sup> (Rard et al., 1996), and one at 1.000 mol·dm<sup>-3</sup> (Miller et al., 1986).

Except at low molarities of solute, the binary or ternary solution diffusion coefficients  $D$  and  $D_{ij}$  cannot be predicted accurately by the Nernst–Hartley equations (Miller, 1966, 1967a; Miller et al., 1993; Rard et al., 1996; Rard and Miller, 1987, 1988), which are based on an infinite dilution model. Consequently, we are determining accurate  $D_{ij}$  values for a few selected 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, we report a systematic investigation of the  $D_{ij}$  for the system NaCl + Na<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O at 298.15 K at a constant total molarity of 1.000 mol·dm<sup>-3</sup>. This is a ternary subsystem of the seawater salts and extends our previous results (Rard et

† Student at the Texas Academy of Mathematics and Science, University of North Texas, Denton, TX 76203.

al., 1996) at  $0.500 \text{ mol}\cdot\text{dm}^{-3}$  to a higher molarity. 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 at  $0.500 \text{ mol}\cdot\text{dm}^{-3}$ .

To conserve space here, we refer the readers to our previous paper (Rard et al., 1996) for some definitions of quantities reported, equations, and more detailed descriptions and the experiments and data analysis methods.

## Experimental Section

All experiments were performed at Texas Christian University.

**Diffusion Coefficient Measurements.** Diffusion experiments were performed by Rayleigh interferometry at  $(298.15 \pm 0.00_5) \text{ K}$  using the high-quality Gosting diffusimeter (Gosting et al., 1973), with automated data recording and with free-diffusion boundary conditions inside the diffusion cell. Solute molarity fractions  $z_1$  of NaCl in these  $\{z_1\text{NaCl} + (1 - z_1)\text{Na}_2\text{SO}_4\}(\text{aq})$  mixtures were 1, 0.900 03, 0.750 43, 0.500 02, 0.250 00, and 0 at a total molarity of  $1.000 \text{ mol}\cdot\text{dm}^{-3}$ . To facilitate comparison, these  $z_1$  values are very nearly the same as those used at  $0.500 \text{ mol}\cdot\text{dm}^{-3}$  (Rard et al., 1996). The values  $z_1 = 1$  and  $z_1 = 0$  correspond to the limiting binary solutions NaCl(aq) and  $\text{Na}_2\text{SO}_4(\text{aq})$ , respectively.

Miller et al. (1993) have described the Rayleigh method in considerable detail, including experimental and computational procedures. Also see the article by Miller and Albright (1991).

For each ternary solution composition, four diffusion experiments were performed at essentially the same average concentrations of each solute,  $\bar{C}_1$  and  $\bar{C}_2$ , but at different values of the ratio  $\Delta C_1/\Delta C_2$ , where the  $\Delta C_i$  are the differences in the concentration of electrolyte  $i$  between the bottom and top of the initial diffusion boundary. Subscript 1 denotes NaCl and subscript 2  $\text{Na}_2\text{SO}_4$ . These ratios correspond to refractive index fractions of  $\alpha_i \approx 0, 0.2, 0.8,$  and  $1$  (Dunlop, 1959; O'Donnell and Gosting, 1959). The  $\alpha_i$  are related to the concentration differences, their ratios, and the refractive index increment  $R_i$  for solute  $i$  by

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

where  $J$  is the total number of Rayleigh interference fringes (not necessarily an integer). The  $\alpha_i$  and  $R_i$  are obtained by the method of least squares from the set of experimental  $J$  and  $\Delta C_i$  values, provided all four experiments are performed in the same cell.

An alternative type of refractive index increment  $R_i^*$  can be defined directly by  $\Delta n = R_1^* \Delta C_1 + R_2^* \Delta C_2$ , where  $\Delta n$  is the difference in refractive index between the top and bottom solutions forming the diffusion boundary. These  $\Delta n$  are calculated from  $\Delta n = \lambda J \mathbf{a}$ , where  $\lambda = 543.3655 \text{ nm}$  is the wavelength in air of the helium-argon laser green line used by our interferometer and  $\mathbf{a}$  is the path length of the light inside the diffusion cell. Consequently,  $R_1 = \mathbf{a} R_1^* / \lambda$  and  $R_2 = \mathbf{a} R_2^* / \lambda$ . We report the  $R_i$ , since  $J$  is a directly observable experimental quantity. However, the  $R_i^*$  formalism is necessary for comparing refractive indexes from experiments in different cells.

Two different cells were used for the experiments. All experiments with  $z_1 = 0.900 03$  and for the limiting binary solutions were performed in cell C-1334-H-11 for which  $\mathbf{a} = 2.4960 \text{ cm}$ , whereas the experiments for the other three ternary solution compositions were performed in cell C-1235-H-11 for which  $\mathbf{a} = 2.5051 \text{ cm}$ .

A computer-controlled photodiode array was used for the "real time" recording of positions of the Rayleigh fringe patterns during the diffusion experiments. The computer-controlled photodiode array and its operation, the cell filling techniques, the recording of the baseline patterns and of the Rayleigh fringe patterns, etc., have been described (Rard et al., 1996). 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.

A computer program TFIT combines the interpolated symmetrically paired Rayleigh fringe positions, the  $J$  values, the times at which the Rayleigh patterns were recorded, and the concentration differences  $\Delta C_i$  of each solute across the initial diffusion boundary for each set of four experiments at a given overall composition (fixed  $z_1$ ). TFIT yields the diffusion coefficients, their standard errors, and other pertinent quantities described in Rard et al. (1996), Miller (1988), and Miller et al. (1993).

**Solution Preparations and Density Measurements.** Solutions were prepared by mass from samples of oven-dried NaCl(cr), from samples of stock solutions of  $\text{Na}_2\text{SO}_4(\text{aq})$ , and from purified water. The water purification and drying of the NaCl(cr) were described previously (Rard et al., 1996). Assumed molar masses are  $58.443 \text{ g}\cdot\text{mol}^{-1}$  for NaCl,  $142.037 \text{ g}\cdot\text{mol}^{-1}$  for  $\text{Na}_2\text{SO}_4$ , and  $18.0153 \text{ g}\cdot\text{mol}^{-1}$  for  $\text{H}_2\text{O}$ . All apparent masses were converted to masses using buoyancy corrections.

Three stock solutions of  $\text{Na}_2\text{SO}_4(\text{aq})$  were prepared directly from anhydrous Baker "Analyzed"  $\text{Na}_2\text{SO}_4(\text{s})$  and purified water. Two additional stock solutions were prepared similarly from  $\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}(\text{cr})$ , which was obtained by recrystallization of  $\text{Na}_2\text{SO}_4(\text{s})$  followed by centrifugal draining.

The densities of all five  $\text{Na}_2\text{SO}_4(\text{aq})$  stock solutions were determined in duplicate at  $(298.15 \pm 0.00_5) \text{ K}$  using a Mettler-Parr DMA/40 vibrating tube densimeter, which was interfaced to a computer for signal averaging and increased precision. The molar concentration of each  $\text{Na}_2\text{SO}_4(\text{aq})$  stock solution was calculated from its measured density using eq 6 of Rard et al. (1996). That equation is valid to  $2.6092 \text{ mol}\cdot\text{dm}^{-3}$ , which is well into the supersaturated region. We estimate that these stock solution molarities and molalities are accurate to 0.02 % or better. 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.

Densities of solutions used for diffusion experiments were similarly measured in duplicate with the vibrating tube densimeter. The  $\bar{C}_i$  and  $\Delta C_i$  values reported in Tables 1 and 2 were based on the average of the density measurements.

At each given  $z_1$ , the eight densities from the four solution pairs were represented by the linear Taylor series expansion (Dunlop, 1959; Dunlop and Gosting, 1959)

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

using the method of least squares. The  $C_1$  and  $C_2$  are the concentrations of NaCl and  $\text{Na}_2\text{SO}_4$ , respectively, for each individual solution,  $\bar{C}_1$  and  $\bar{C}_2$  are the corresponding concentration averages for all four solution pairs,  $H_i$  are least-squares parameters, and  $\bar{\rho}$  is a least-squares parameter representing the density of a solution with molar concentrations corresponding to  $\bar{C}_1$  and  $\bar{C}_2$ .

The  $H_1$  and  $H_2$  parameters of eq 2 are required for calculating the partial molar volumes  $\bar{V}_i$  (Dunlop and Gosting, 1959), given in Table 3, which are in turn used to

**Table 1. Results from Binary Solution Mutual Diffusion Coefficient and Density Measurements for NaCl(aq) and Na<sub>2</sub>SO<sub>4</sub>(aq) Solutions at 298.15 K with Rayleigh Interferometry and Vibrating Tube Densimetry<sup>a</sup>**

quantity	NaCl(aq)	Na <sub>2</sub> SO <sub>4</sub> (aq)
$\bar{C}$	1.001 38	1.000 02
$\Delta C$	0.190 29	0.089 99
$\rho(\text{top})$	1.033 383	1.110 370
$\rho(\text{bottom})$	1.040 798	1.120 456
$m(\bar{C})$	1.023 31	1.027 36 <sub>5</sub>
$J(\text{exptl})$	82.707	68.003
$10^{-2} \times R_i$	4.346 3	7.556 7
$\Delta t$	13	9
$10^9 \times D_V$	1.482 2	0.654 6
$10^9 \times M$	1.518	1.129

<sup>a</sup> Units for  $\bar{C}$  and  $\Delta C$  are mol·dm<sup>-3</sup>, of  $m(\bar{C})$  are mol·kg<sup>-1</sup>, of  $10^{-2} \times R_i$  are mol<sup>-1</sup>·dm<sup>3</sup>, of  $\rho$  are g·cm<sup>-3</sup>, of  $\Delta t$  are s, and of  $10^9 \times D_V$  and  $10^9 \times M$  are m<sup>2</sup>·s<sup>-1</sup>. The density values are the average of duplicate determinations with a Mettler–Parr DMA/40 vibrating tube densimeter. These experiments were performed by Onofrio Annunziata using cell C-1334-H-11.

convert the experimentally based volume-fixed diffusion coefficients ( $D_{ij}$ )<sub>V</sub> to solvent-fixed ones ( $D_{ij}$ )<sub>0</sub>. See eqs 8 and 9 of Rard et al. (1996).

### Calculations for Ternary Solutions

Diffusion of solutes in a ternary solution under isothermal and isobaric conditions requires four diffusion coefficients  $D_{ij}$ , where  $i$  and  $j = 1$  or  $2$  (Miller, 1967a). 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  $\Delta C_i$ , these  $D_{ij}$  are in the *volume-fixed reference frame* and are denoted by ( $D_{ij}$ )<sub>V</sub>.

Experimental values of the ( $D_{ij}$ )<sub>V</sub> and  $H_i$  coefficients of eq 2 were used to test the static and dynamic stabilities of

all our ternary solution diffusion boundaries (Miller and Vitagliano, 1986; Vitagliano et al., 1984, 1986). Calculations and experiments indicate all boundaries were stable.

Tables 1 and 2 contain all concentration information for solutions used in our diffusion experiments, along with the densities and other experimental information. Quantities reported (besides those defined in the Experimental Section) are  $\bar{C}_i$ , the average concentration of electrolyte  $i$  of the top and bottom solutions used for that particular diffusion experiment;  $\Delta t$ , the starting time correction that is added to the recorded “clock” times to correct them to the times corresponding to diffusion from an infinitely sharp boundary; and  $D_A$ , the reduced height–area ratio (Miller et al., 1993). The ternary solution diffusion coefficients ( $D_{ij}$ )<sub>V</sub> were obtained using TFIT exactly as described in Section 3 of Rard et al. (1996).

Experimental and calculated  $J$  values are both reported in Table 2. These  $J(\text{calcd})$  were obtained from the least-squares parameters  $R_i$  and  $\Delta C_i$ , using the reciprocal of the second equality of eq 1.

Calculation of the  $D_A(\text{exptl})$  values was performed as described on page 4193 of Rard et al. (1996), with the cutoff conditions  $0.84 > f(J-j) > 0.28$  (Miller et al., 1993). Here  $f(J-j) = -f(j) = (J-2j)/J$  and  $j$  is the number of any particular Rayleigh fringe.

The  $D_A(\text{calcd})$  for each experiment were obtained as described elsewhere (Miller et al., 1993; Rard et al., 1996) with the  $\alpha_1$  of that experiment and the four least-squares Rayleigh parameters appropriate to that overall composition. These four parameters are  $a$ ,  $b$ ,  $s_1$ , and  $s_2$ , where  $s_1 = \sqrt{\sigma_+}$  and  $s_2 = \sqrt{\sigma_-}$ . The quantities  $\sigma_+$  and  $\sigma_-$  are defined in terms of the  $D_{ij}$  by eqs 12 and 13 of Rard et al. (1996), and  $a$  and  $b$  are defined in terms of the  $D_{ij}$  and  $R_i$  by eqs 8 and 9 of Miller et al. (1993). 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 be-

**Table 2. Compositions and Results for Ternary Solution Diffusion Experiments for {z<sub>1</sub>NaCl + (1 - z<sub>1</sub>)Na<sub>2</sub>SO<sub>4</sub>} (aq) Solutions at 298.15 K and at  $\bar{C}_T = 1.000$  mol·dm<sup>-3</sup> with Rayleigh Interferometry<sup>a</sup>**

quantity	expt. 1	expt. 2	expt. 3	expt. 4	expt. 1	expt. 2	expt. 3	expt. 4
	<b>z<sub>1</sub> = 0.900 03</b>				<b>z<sub>1</sub> = 0.750 43</b>			
$\bar{C}_1$	0.900 986	0.900 010	0.900 223	0.899 802	0.749 988	0.749 868	0.750 016	0.749 729
$\bar{C}_2$	0.100 000	0.100 000	0.100 006	0.099 974	0.249 438	0.249 414	0.249 394	0.249 53
$\Delta C_1$	0.001 946	0.189 959	0.037 347	0.150 411	0.000 027	0.1878 87	0.037 589	0.152 386
$\Delta C_2$	0.092 012	-0.000 001	0.070 006	0.019 043	0.091 795	-0.000 015	0.073 785	0.018 292
$J(\text{exptl})$	79.467	81.246	75.787	80.690	76.954	79.104	77.658	79.381
$J(\text{calcd})$	79.463	81.285	75.806	80.636	76.942	79.033	77.651	79.440
$\alpha_1$	0.010 48	1.000 01	0.210 82	0.798 19	0.000 15	1.000 16	0.203 65	0.807 02
$\Delta t$	13	13	14	15	9	13	11	9
$10^9 \times D_A(\text{exptl})$	0.888 9	1.412 9 <sub>5</sub>	0.968 3	1.275 0	0.831 9	1.324 8	0.906 4	1.202 0
$10^9 \times D_A(\text{calcd})$	0.888 4	1.413 4	0.967 9	1.274 0	0.832 4	1.325 2	0.907 4	1.200 7 <sub>5</sub>
$\rho(\text{top})$	1.039 620	1.041 420	1.040 233	1.041 014	1.051 576	1.053 368	1.051 864	1.052 976
$\rho(\text{bottom})$	1.050 601	1.048 719	1.049 970	1.049 045	1.062 358	1.060 530	1.061 957	1.060 898 <sub>5</sub>
	<b>z<sub>1</sub> = 0.500 02</b>				<b>z<sub>1</sub> = 0.250 00</b>			
$\bar{C}_1$	0.499 978	0.500 048	0.500 006	0.499 938	0.250 020	0.250 026	0.250 006	0.249 948
$\bar{C}_2$	0.499 936	0.500 042	0.499 950	0.499 922	0.749 948	0.749 970	0.749 990	0.750 014
$\Delta C_1$	-0.000 032	0.186 973	0.039 009	0.153 002	0.000 036	0.169 974	0.155 001	0.039 996
$\Delta C_2$	0.090 954	-0.000 112	0.073 003	0.018 302	0.092 038	0.000 900	0.018 280	0.076 026
$J(\text{exptl})$	73.508	75.722	74.762 <sub>5</sub>	76.727	71.999	67.570	75.185	75.372
$J(\text{calcd})$	73.474	75.670	74.790	76.783	72.082	67.533	75.255	75.255
$\alpha_1$	-0.000 18	1.001 20	0.211 34	0.807 41	0.000 20	0.989 56	0.809 80	0.208 96
$\Delta t$	10	21	9	12	16	21	12	17
$10^9 \times D_A(\text{exptl})$	0.758 9	1.203 8	0.830 0	1.092 6	0.701 0	1.104 1	1.008 4	0.765 4
$10^9 \times D_A(\text{calcd})$	0.759 2 <sub>5</sub>	1.204 2	0.829 9	1.091 9	0.701 1	1.104 5	1.008 8	0.765 4
$\rho(\text{top})$	1.071 424	1.073 306	1.071 720	1.072 759	1.090 913	1.092 983	1.092 302	1.091 142
$\rho(\text{bottom})$	1.081 932	1.080 196	1.081 630	1.080 513	1.101 374	1.099 232	1.099 988	1.101 229

<sup>a</sup> Units of  $\bar{C}_i$  and  $\Delta C_i$  are mol·dm<sup>-3</sup>, of  $\Delta t$  are s, of  $10^9 \times D_A$  are m<sup>2</sup>·s<sup>-1</sup>, and of  $\rho$  are g·cm<sup>-3</sup>. Density values are the average of duplicate measurements (done on separate days) using the Mettler–Parr DMA/40 vibrating tube densimeter. Cell C-1334-H-11 was used for experiments with  $z_1 = 0.900 03$  and cell C-1235-H-11 for experiments with the other three values of  $z_1$ .

**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  $\bar{C}_T = 1.000 \text{ mol}\cdot\text{dm}^{-3}$  and 298.15 K<sup>a</sup>**

quantity	$z_1$			
	0.900 03	0.750 43	0.500 02	0.250 00
$\bar{C}_T$	1.000 250	0.999 301	0.999 955	0.999 981
$\bar{C}_1$	0.900 255	0.749 901	0.499 993	0.250 000
$\bar{C}_2$	0.099 995	0.249 400	0.499 962	0.749 981
$\bar{C}_0$	54.301 7	54.270 0	54.201 2	54.121 2
$m_1(\bar{C}_1, \bar{C}_2)$	0.920 260	0.767 013	0.512 051	0.256 408
$m_2(\bar{C}_1, \bar{C}_2)$	0.102 217	0.255 091	0.512 020	0.769 204
$10^{-2} \times R_1$	4.279 12	4.207 08	4.051 96	3.931 68
$10^{-2} \times R_2$	8.545 70	8.380 69	8.079 62	7.830 23
$\bar{\rho}$	1.045 078	1.056 941	1.076 685	1.096 145
$H_1$	38.412 ± 0.139	38.036 ± 0.158	36.902 ± 0.266	36.172 ± 0.211
$H_2$	118.549 ± 0.290	117.405 ± 0.325	115.723 ± 0.551	113.649 ± 0.407
$s(\rho \text{ fit})$	0.000 024	0.000 027	0.000 045	0.000 034
$s(\bar{\rho})$	0.000 008	0.000 010	0.000 016	0.000 012
$\bar{V}_1$	20.058	20.426	21.533	22.229
$\bar{V}_2$	23.519	24.653	26.304	28.335
$\bar{V}_0$	18.040	18.031	18.009	17.982
$10^{-9} \times \sigma_+$	0.666 64	0.660 60	0.667 40	0.687 58
$10^{-9} \times \sigma_-$	1.227 30	1.295 08	1.391 46	1.470 99
$10^{-2} \times S_A$	-70.25	-71.91	-74.65	-77.60
$10^9 \times (D_{11})_V$	1.5117 ± 0.0005	1.5373 ± 0.0034	1.5259 ± 0.0005	1.4726 ± 0.0011
$10^9 \times (D_{12})_V$	0.2324 ± 0.0008	0.2372 ± 0.0051	0.1922 ± 0.0007	0.1107 ± 0.0016
$10^9 \times (D_{21})_V$	-0.0349 ± 0.0002	-0.0758 ± 0.0014	-0.1158 ± 0.0002	-0.1305 ± 0.0005
$10^9 \times (D_{22})_V$	0.8032 ± 0.0003	0.7486 ± 0.0020	0.6911 ± 0.0003	0.6616 ± 0.0006
$10^9 \times (D_{11})_0$	1.538 8	1.559 9	1.541 2	1.480 1
$10^9 \times (D_{12})_0$	0.254 0	0.255 1	0.203 6	0.116 2
$10^9 \times (D_{21})_0$	-0.031 9	-0.068 3	-0.100 5	-0.108 1
$10^9 \times (D_{22})_0$	0.805 6	0.754 5	0.702 5	0.677 9

<sup>a</sup> Units for  $\bar{C}_i$  are  $\text{mol}\cdot\text{dm}^{-3}$ ; of  $m_i(\bar{C}_1, \bar{C}_2)$  are  $\text{mol}\cdot\text{kg}^{-1}$ , of  $10^{-2} \times R_i$  are  $\text{mol}^{-1}\cdot\text{dm}^3$ , of  $\bar{\rho}$ ,  $s(\bar{\rho})$ , and  $s(\rho)$  are  $\text{g}\cdot\text{cm}^{-3}$ , of  $H_i$  are  $\text{g}\cdot\text{mol}^{-1}$ , of  $\bar{V}_i$  are  $\text{cm}^3\cdot\text{mol}^{-1}$ , of  $10^{-9} \times \sigma_+$  and  $10^{-9} \times \sigma_-$  are  $\text{m}^{-2}\cdot\text{s}$ , of  $10^{-2} \times S_A$  are  $\text{m}^{-1}\cdot\text{s}^{1/2}$ , and of  $10^9 \times (D_{ij})_V$  and  $10^9 \times (D_{ij})_0$  are  $\text{m}^2\cdot\text{s}^{-1}$ . The quantity  $z_1$  is the solute molarity fraction of NaCl, and the total solute molarity is  $\bar{C}_T = \bar{C}_1 + \bar{C}_2$ . To obtain densities from eq 2 in units of  $\text{g}\cdot\text{cm}^{-3}$  when  $C_i$  and  $\bar{C}_i$  are in units of  $\text{mol}\cdot\text{dm}^{-3}$ , divide the listed values of  $H_i$  by  $10^3$ . The "±" value given immediately to the right of each  $D_{ij}$  value is its standard error as calculated from the data reduction algorithm.

tween  $D_A(\text{exptl})$  and  $D_A(\text{calcd})$  is exceptionally good for our experiments at  $z_1 = 0.250 00$ .

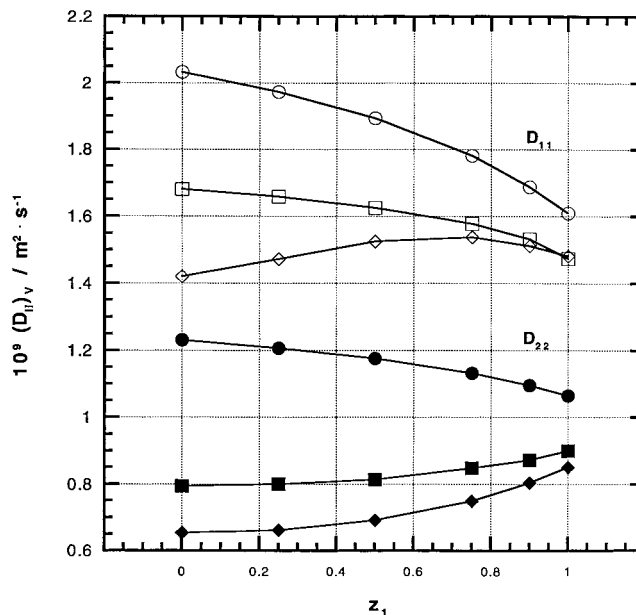
## Results

**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  $\text{Na}_2\text{SO}_4(\text{aq})$  ( $z_1 = 0$ ) at 298.15 K. Also given is the thermodynamic diffusion coefficient  $M = D_V / \{d(m\phi)/dm\}$ , where  $\phi$  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  $\phi$  of  $\text{Na}_2\text{SO}_4(\text{aq})$  (Rard and Miller, 1981) and  $\text{NaCl}(\text{aq})$  (Hamer and Wu, 1972).

Rard and Miller (1979a) 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  $D_V = (1.481_9 \pm 0.002) \times 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$  at  $\bar{C} = 1.0014 \text{ mol}\cdot\text{dm}^{-3}$ . Our experimental value of  $D_V = 1.482_2 \times 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$  at  $\bar{C} = 1.001 38 \text{ mol}\cdot\text{dm}^{-3}$  is in excellent agreement.

Wendt (1962) reported  $D_V = 0.653_9 \times 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$  for  $\text{Na}_2\text{SO}_4(\text{aq})$  at  $\bar{C} = 0.999 54 \text{ mol}\cdot\text{dm}^{-3}$  and 298.15 K from Gouy interferometry, which is in excellent agreement with our value of  $0.654_6 \times 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$  at  $\bar{C} = 1.000 02 \text{ mol}\cdot\text{dm}^{-3}$  from Rayleigh interferometry. A value of  $D_V \approx (0.654 \pm 0.001) \times 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$  at  $1.000 \text{ mol}\cdot\text{dm}^{-3}$  was obtained by graphical interpolation of a large-scale plot of the Rayleigh interferometric values of Rard and Miller (1979b), which were measured with a less precise diffusimeter. All three values agree within 0.11%.

On the basis of previous experience with the Gosting diffusimeter, experimental  $D_V$  values are reproducible to



**Figure 1.** Values of the volume-fixed mutual diffusion main-term coefficients  $(D_{ij})_V$  at 298.15 K for NaCl +  $\text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$  at total concentration  $\bar{C}_T = (0.500 \text{ and } 1.000) \text{ mol}\cdot\text{dm}^{-3}$ , along with the corresponding values at infinite dilution from the Nernst-Hartley equation, as a function of the solute molarity fraction  $z_1$  of NaCl. Also plotted are values of  $D_V$  for the limiting binary solutions NaCl(aq) (at  $z_1 = 1$ ) and  $\text{Na}_2\text{SO}_4(\text{aq})$  (at  $z_1 = 0$ ) and extrapolated values of  $D^*(\text{Cl}^-)$  and  $D^*(\text{SO}_4^{2-})$ . Symbols:  $\circ, \square, \diamond$ ,  $(D_{11})_V$  at (0, 0.500, and 1.000)  $\text{mol}\cdot\text{dm}^{-3}$ , respectively;  $\bullet, \blacksquare, \blacklozenge$ ,  $(D_{22})_V$  at (0, 0.500, and 1.000)  $\text{mol}\cdot\text{dm}^{-3}$ , respectively.

about 0.03 to 0.05% for binary solutions, but there is an additional uncertainty of about 0.03% because of uncer-

tainty in the value of the magnification factor MF for the diffusion cells in the Gosting diffusometer (Rard et al., 1996).

**Ternary Solutions.** Table 3 contains all the derived quantities for the four ternary solution compositions of the system NaCl + Na<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O at 298.15 K and  $\bar{C}_T = 1.000 \text{ mol}\cdot\text{dm}^{-3}$ . Most reported quantities were defined elsewhere (Rard et al., 1996) or in the experimental or calculations sections. We report both the experimental volume-fixed ( $D_{ij}$ )<sub>v</sub> and the derived solvent-fixed ( $D_{ij}$ )<sub>0</sub>, which are related by eq 64 of Miller (1967a). The quantities  $m_1(\bar{C}_1, \bar{C}_2)$  and  $m_2(\bar{C}_1, \bar{C}_2)$  are the molalities of NaCl and Na<sub>2</sub>SO<sub>4</sub>, respectively, corresponding to a solution having the molarities of both salts equal to the overall averages  $\bar{C}_1$  and  $\bar{C}_2$  of all four experiments at that overall composition. Another quantity reported in Table 3 is  $S_A$  (Fujita and Gosting, 1956), which can be related to quantities defined here or in Rard et al. (1996) by

$$S_A = [D_{22} - D_{11} + (R_1/R_2)D_{12} - (R_2/R_1)D_{21}]/[(D_{11}D_{22} - D_{12}D_{21})(\sqrt{\sigma_+} + \sqrt{\sigma_-})] \\ = b(\sqrt{\sigma_+} - \sqrt{\sigma_-}) \quad (3)$$

If  $|10^{-2}S_A|$  decreases below  $\sim(20 \text{ to } 25) \text{ m}^{-1}\cdot\text{s}^{1/2}$ , then the standard errors of the  $D_{ij}$  generally become significantly larger than when  $|10^{-2}S_A|$  has larger values (Miller et al., 1993; Rard and Miller, 1990). Furthermore, if the  $\sigma_+$  and  $\sigma_-$  values are nearly equal, the nonlinear least-squares analysis of the diffusion data may not converge. Fortunately,  $\sigma_+$  and  $\sigma_-$  differ by about a factor of 2 for our experiments and  $|10^{-2}S_A|$  ranges from (70.25 to 77.60)  $\text{m}^{-1}\cdot\text{s}^{1/2}$ , and no such difficulties were encountered.

Reported uncertainties in the ( $D_{ij}$ )<sub>v</sub> in Table 3 were obtained from the statistical analysis portion of TFIT using standard propagation of error methods. However, we believe the actual uncertainties are larger than these statistical uncertainties (Miller et al., 1994, 1996; Rard and Miller, 1987, 1990). A rough "rule of thumb" for some systems is that the actual errors are about four times larger than the statistical errors (Albright et al., 1989; Mathew et al., 1989, 1990; Miller et al., 1993; Paduano et al., 1989).

An alternative method for estimating realistic errors for the ( $D_{ij}$ )<sub>v</sub> is by using the data from various subsets of the diffusion experiments (Miller et al., 1994). These calculations were performed with the four possible three-experiment subsets of  $\alpha_1$ . The results 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 ( $D_{ij}$ )<sub>v</sub>.

The calculated sets of statistical errors and the errors obtained by the subset analysis are approximately equal at  $z_1 = 0.50002$ , and both of these error sets are smallest at this composition. This agreement implies all four experiments with  $z_1 = 0.50002$  are of unusually high quality and exceptionally consistent.

Errors from the subset analysis and the propagation of error calculations are generally not completely consistent for the various ( $D_{ij}$ )<sub>v</sub>. However, the comparison suggests that the actual uncertainties of the main-term ( $D_{ii}$ )<sub>v</sub> are  $\leq 0.004 \times 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$  and of the cross-term ( $D_{ij}$ )<sub>v</sub> are  $\leq 0.01 \times 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$ .

Miller et al. (1986) reported Rayleigh interferometric values of the ( $D_{ij}$ )<sub>v</sub> for NaCl + Na<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O at  $\bar{C}_T = 1.000 \text{ mol}\cdot\text{dm}^{-3}$  and  $z_1 = 0.50000_5$  at 298.15 K, which is essentially identical to one of our compositions. However, we later discovered that the computer program used in that

**Table 4. Comparison of Calculated Errors of Ternary Solution ( $D_{ij}$ )<sub>v</sub> for  $\{z_1\text{NaCl} + (1 - z_1)\text{Na}_2\text{SO}_4\}$ (aq) Solutions at  $\bar{C}_T = 1.000 \text{ mol}\cdot\text{dm}^{-3}$  and 298.15 K<sup>a</sup>**

quantity	$z_1$			
	0.900 03	0.750 43	0.500 02	0.250 00
$\bar{C}_T$	1.000 250	0.999 301	0.999 955	0.999 981
$\bar{C}_1$	0.900 255	0.749 901	0.499 993	0.250 000
$\bar{C}_2$	0.099 995	0.249 400	0.499 962	0.749 981
$10^9 \times \delta(D_{11})_v^b$	0.000 5	0.003 4	0.000 5	0.001 1
$10^9 \times \delta(D_{12})_v^b$	0.000 8	0.005 1	0.000 7	0.001 6
$10^9 \times \delta(D_{21})_v^b$	0.000 2	0.001 4	0.000 2	0.000 5
$10^9 \times \delta(D_{22})_v^b$	0.000 3	0.002 0	0.000 3	0.000 6
$10^9 \times \delta(D_{11})_v^c$	0.003 3	0.000 6	0.001 2	0.000 3
$10^9 \times \delta(D_{12})_v^c$	0.002 2	0.000 5	0.000 5	0.007 0
$10^9 \times \delta(D_{21})_v^c$	0.001 3	0.011 2	0.000 2	0.000 3
$10^9 \times \delta(D_{22})_v^c$	0.000 7	0.004 0	0.000 2	0.001 9

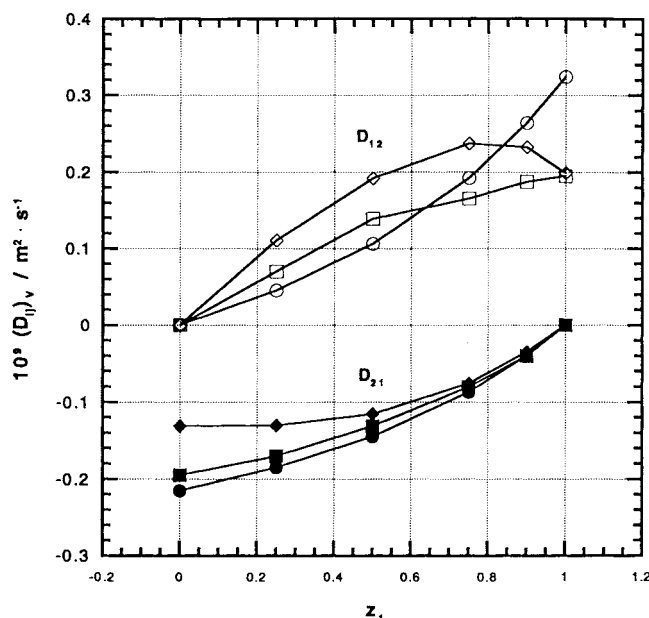
<sup>a</sup> Units for  $\bar{C}_i$  are  $\text{mol}\cdot\text{dm}^{-3}$  and of  $10^9 \times \delta(D_{ij})_v$  are  $\text{m}^2\cdot\text{s}^{-1}$ . The quantity  $z_1$  is the solute molarity fraction of NaCl in the mixed-electrolyte solutions. <sup>b</sup> The first set of errors was obtained with propagation of error equations using the variance-covariance matrix of the least-squares parameters. <sup>c</sup> The second set of errors was obtained by the subset method. Reported uncertainties are  $n - 1$  standard deviations.

1986 report correctly calculated the ( $D_{ij}$ )<sub>v</sub> but gave erroneously large values for their statistical uncertainties. This error was detected by checking the uncertainty expressions using the computer algebra program ALJABR. After properly recalculating the uncertainties, that study yields ( $D_{11}$ )<sub>v</sub> =  $(1.5040 \pm 0.0023) \times 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$ , ( $D_{12}$ )<sub>v</sub> =  $(0.1797 \pm 0.0032) \times 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$ , ( $D_{21}$ )<sub>v</sub> =  $-(0.1086 \pm 0.0009) \times 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$ , and ( $D_{22}$ )<sub>v</sub> =  $(0.6941 \pm 0.0012) \times 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$ . In addition, they performed only three experiments rather than our usual four, and a less precise diffusometer was used. Consequently, we believe their actual errors are several times larger than these statistical ones. Despite this, these earlier ( $D_{ij}$ )<sub>v</sub> agree fairly well with our more precise results in Table 3. The differences of  $0.022 \times 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$  for ( $D_{11}$ )<sub>v</sub>, of  $0.013 \times 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$  for ( $D_{12}$ )<sub>v</sub>, of  $0.007 \times 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$  for ( $D_{21}$ )<sub>v</sub>, and of  $0.003 \times 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$  for ( $D_{22}$ )<sub>v</sub> are smaller than the probable uncertainties of the earlier study.

## Discussion

Extrapolation of some of the ( $D_{ij}$ )<sub>v</sub> to  $z_1 = 1$  and  $z_1 = 0$  yields significant new information. As  $z_1 \rightarrow 1$ , ( $D_{11}$ )<sub>v</sub>  $\rightarrow D_V$  for NaCl(aq). Similarly, ( $D_{22}$ )<sub>v</sub>  $\rightarrow D_V$  for Na<sub>2</sub>SO<sub>4</sub>(aq) as  $z_1 \rightarrow 0$ . Also, as  $z_1 \rightarrow 1$ , ( $D_{21}$ )<sub>v</sub>  $\rightarrow 0$  because no Na<sub>2</sub>SO<sub>4</sub>(aq) is present to be transported by coupled diffusion. Similarly ( $D_{12}$ )<sub>v</sub>  $\rightarrow 0$  as  $z_1 \rightarrow 0$  because no NaCl(aq) is present to be transported by coupled diffusion. As  $z_1 \rightarrow 1$ , ( $D_{22}$ )<sub>v</sub>  $\rightarrow D^*(\text{SO}_4^{2-})$ , and as  $z_1 \rightarrow 0$ , ( $D_{11}$ )<sub>v</sub>  $\rightarrow D^*(\text{Cl}^-)$ , where  $D^*(\text{Cl}^-)$  is the trace diffusion coefficient of Cl<sup>-</sup> in a solution with molarity  $1.000 \text{ mol}\cdot\text{dm}^{-3}$  Na<sub>2</sub>SO<sub>4</sub>(aq) and  $D^*(\text{SO}_4^{2-})$  is the trace diffusion coefficient of SO<sub>4</sub><sup>2-</sup> in a solution of  $1.000 \text{ mol}\cdot\text{dm}^{-3}$  NaCl(aq). Unlike the other extrapolated values of the ( $D_{ij}$ )<sub>v</sub>, ( $D_{11}$ )<sub>v</sub> as  $z_1 \rightarrow 1$  and ( $D_{21}$ )<sub>v</sub> as  $z_1 \rightarrow 0$  are simply limiting values.

The solid curves of Figures 1 and 2 show the trends in the main-term and cross-term ( $D_{ij}$ )<sub>v</sub>, respectively, as functions of  $z_1$  at  $\bar{C}_T = (0, 0.500, \text{ and } 1.000) \text{ mol}\cdot\text{dm}^{-3}$ . Additional plots (not presented here), similar to Figures 1 and 2, were made at  $1.000 \text{ mol}\cdot\text{dm}^{-3}$  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, of  $D^*(\text{Cl}^-)$ , and of  $D^*(\text{SO}_4^{2-})$  were obtained graphically from these four



**Figure 2.** Values of the volume-fixed mutual diffusion cross-term coefficients  $(D_{ij})_V$  at 298.15 K for NaCl + Na<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O at total concentration  $\bar{C}_T = (0.500 \text{ and } 1.000) \text{ mol}\cdot\text{dm}^{-3}$ , along with the corresponding values at infinite dilution from the Nernst–Hartley equation, as a function of the solute molarity fraction  $z_1$  of NaCl. Symbols:  $\circ, \square, \diamond$ ,  $(D_{12})_V$  at (0, 0.500, and 1.000) mol·dm<sup>-3</sup>, respectively;  $\bullet, \blacksquare, \blacklozenge$ ,  $(D_{21})_V$  at (0, 0.500, and 1.000) mol·dm<sup>-3</sup>, respectively. Lines connecting the experimental values of the  $(D_{ij})_V$  at  $\bar{C}_T = (0.500 \text{ and } 1.000) \text{ mol}\cdot\text{dm}^{-3}$  are only to guide the eye, since some of the plots are not smooth to this scale.

**Table 5.** Values of  $(D_{ij})_V$  for  $\{z_1\text{NaCl} + (1 - z_1)\text{Na}_2\text{SO}_4\}$  (aq) Solutions as  $z_1 \rightarrow 0$  and  $z_1 \rightarrow 1$  at  $\bar{C}_T = 1.000 \text{ mol}\cdot\text{dm}^{-3}$  and 298.15 K

quantity	$10^9 \times (D_{ij})_V$	interpretation
$(D_{11})_V$ as $z_1 \rightarrow 1$	$1.482 \pm 0.002$	$D_V(\text{NaCl})$ at $C_1 = 1.000 \text{ mol}\cdot\text{dm}^{-3}$
$(D_{12})_V$ as $z_1 \rightarrow 1$	$0.204 \pm 0.011$	extrapolated value
$(D_{21})_V$ as $z_1 \rightarrow 1$	0	by definition
$(D_{22})_V$ as $z_1 \rightarrow 1$	$0.850 \pm 0.011$	$D^*(\text{SO}_4^{2-})$ at $I = 1.000 \text{ mol}\cdot\text{dm}^{-3}$ (extrapolated)
$(D_{11})_V$ as $z_1 \rightarrow 0$	$1.421 \pm 0.027$	$D^*(\text{Cl}^-)$ at $I = 3.000 \text{ mol}\cdot\text{dm}^{-3}$ (extrapolated)
$(D_{12})_V$ as $z_1 \rightarrow 0$	0	by definition
$(D_{21})_V$ as $z_1 \rightarrow 0$	$-0.131 \pm 0.021$	extrapolated value
$(D_{22})_V$ as $z_1 \rightarrow 0$	$0.654 \pm 0.001$	$D_V(\text{Na}_2\text{SO}_4)$ at $C_2 = 1.000 \text{ mol}\cdot\text{dm}^{-3}$

<sup>a</sup> Units for  $10^9 \times (D_{ij})_V$  are  $\text{m}^2\cdot\text{s}^{-1}$ .

plots by two of us independently. The average of these and the  $D_V$  values for the limiting binary solutions at 1.000 mol·dm<sup>-3</sup> are summarized in Table 5 and were used to extend the curves in Figures 1 and 2 to  $z_1 = 0$  and 1.

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<sub>2</sub>SO<sub>4</sub>(aq), respectively. Thus our extrapolations of  $(D_{11})_V$  to obtain  $D^*(\text{Cl}^-)$  and of  $(D_{22})_V$  to obtain  $D^*(\text{SO}_4^{2-})$  should be accurate. However, the small cross-term  $(D_{ij})_V$  values have significant uncertainties compared to their variation with  $z_1$ . Thus it is possible that the extrapolated values of  $(D_{12})_V$  as  $z_1 \rightarrow 1$  and of  $(D_{21})_V$  as  $z_1 \rightarrow 0$  could have larger uncertainties than our estimates.

We do note that the  $(D_{12})_V$  and  $(D_{21})_V$  curves are roughly parallel, and thus their difference is approximately constant at  $(D_{12})_V - (D_{21})_V = (0.282 \pm 0.034) \times 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$  at  $\bar{C}_T = 1.000 \text{ mol}\cdot\text{dm}^{-3}$  for the four values of  $z_1$ . This

difference is only slightly larger than that at 0.500 mol·dm<sup>-3</sup>,  $(0.246 \pm 0.018) \times 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$  (Rard et al., 1996). Cross-term diffusion coefficients calculated from the Nernst–Hartley equation (Rard et al., 1996) yield a comparable difference of  $(D_{12})_V - (D_{21})_V = (0.266 \pm 0.032) \times 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$  at infinite dilution. For both  $\bar{C}_T = (0.500 \text{ and } 1.000) \text{ mol}\cdot\text{dm}^{-3}$ ,  $(D_{12})_V - (D_{21})_V$  has a small maximum around  $z_1 \sim 0.5$  to 0.6, in contrast to the monotonic increase with  $z_1$  that occurs at infinite dilution.

The  $(D_{21})_V$  value becomes more negative as  $z_1 \rightarrow 0$ , and  $(D_{12})_V$  usually becomes more positive as  $z_1 \rightarrow 1$ . Thus, coupled diffusion enhances the diffusion of NaCl but reduces that of Na<sub>2</sub>SO<sub>4</sub> in these solutions.

Our extrapolation technique, which uses mutual diffusion coefficients to determine trace diffusion coefficients, has the advantage over conventional methods in that the solutions do not contain radioactive tracers or different isotopes. We are not aware of any direct determinations of  $D^*(\text{Cl}^-)$  or  $D^*(\text{SO}_4^{2-})$  by conventional methods for the same ionic media used here. However, some comparisons are possible.

A value of  $D^*(\text{SO}_4^{2-}) = 0.87 \times 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$  was obtained by interpolation of the results recommended by Mills and Lobo (1989) for solutions of Na<sub>2</sub>SO<sub>4</sub>(aq) at an ionic strength of  $I = 1.0 \text{ mol}\cdot\text{dm}^{-3}$ . Their values were based on the then unpublished study of Weingärtner et al. (1993). Agreement with our  $D^*(\text{SO}_4^{2-}) = (0.85_0 \pm 0.01_1) \times 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$  is quite good, given the different electrolyte media.

Similarly,  $D^*(\text{Cl}^-)$  for several electrolyte solutions were tabulated by Mills and Lobo (1989). Values of  $D^*(\text{Cl}^-)$  at  $I = 3.0 \text{ mol}\cdot\text{dm}^{-3}$  are needed since this is the total ionic strength of our solutions at  $z_1 = 0$ . The  $D^*(\text{Cl}^-)$  for MgCl<sub>2</sub>(aq), BaCl<sub>2</sub>(aq), and NiCl<sub>2</sub>(aq) range from  $(1.10 \text{ to } 1.52) \times 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$  and indicate that  $D^*(\text{Cl}^-)$  depends strongly on the divalent cation present. Our extrapolated value,  $D^*(\text{Cl}^-) = (1.42_1 \pm 0.02_7) \times 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$ , is near the upper end of this range. In addition, the  $D^*(\text{Cl}^-)$  of the alkali metal chloride solutions show even greater differences and, except for NaCl(aq), tend to be larger than our value. In contrast,  $D^*(\text{Cl}^-)$  in NaCl(aq) at  $I = 3.0 \text{ mol}\cdot\text{dm}^{-3}$ ,  $1.45 \times 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$ , is quite close to our value in Na<sub>2</sub>SO<sub>4</sub>(aq).

The values of  $D^*(\text{Cl}^-)$  are found to be virtually identical in solutions of NaCl(aq) (Mills and Lobo, 1989) and of Na<sub>2</sub>SO<sub>4</sub>(aq) at  $I = 3.000 \text{ mol}\cdot\text{dm}^{-3}$ . The same happens at  $I = 1.500 \text{ mol}\cdot\text{dm}^{-3}$  (Rard et al., 1996). This is also true for  $D^*(\text{SO}_4^{2-})$  in solutions of NaCl(aq) and of Na<sub>2</sub>SO<sub>4</sub>(aq) at both  $I = 1.000 \text{ mol}\cdot\text{dm}^{-3}$  (present study) and at  $I = 0.500 \text{ mol}\cdot\text{dm}^{-3}$  (Rard et al., 1996). 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  $M_aX_b$ (aq) at the same ionic strength. However,  $(D_{ij})_V$  measurements are needed for additional  $\bar{C}_T$  values for aqueous mixtures of NaCl and Na<sub>2</sub>SO<sub>4</sub>, as well as mutual and isotope diffusion coefficient measurements for other ternary systems, to test the generality of this observation.

Figures 1 and 2 contain plots of the main-term and the cross-term  $D_{ij}$ , respectively, as functions of  $z_1$  at  $\bar{C}_T = (0, 0.500, \text{ and } 1.000) \text{ mol}\cdot\text{dm}^{-3}$  and 298.15 K. The  $D_{ij}$  at  $\bar{C}_T = 0$  (infinite dilution) were calculated using the ternary solution analogue of the Nernst–Hartley equation (Miller, 1967a). The observed opposite signs for  $(D_{12})_V$  and  $(D_{21})_V$  at (0.500 and 1.000) mol·dm<sup>-3</sup>, see Figure 2, are probably largely Coulombic in origin because they 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  $(D_{ij})_V$  as can be seen in Figure 1. At  $\bar{C}_T = 1.000 \text{ mol}\cdot\text{dm}^{-3}$ , the Nernst–Hartley  $D_{11}$  are significantly higher than the experimental  $(D_{11})_V$  by  $(0.176 \text{ to } 0.500) \times 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$ , and the Nernst–Hartley  $D_{22}$  are significantly higher than the experimental  $(D_{22})_V$  by  $(0.292 \text{ to } 0.545) \times 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$ . 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 both  $\bar{C}_T = (0.500 \text{ and } 1.000) \text{ mol}\cdot\text{dm}^{-3}$ . Although  $(D_{11})_V$  values at both  $\bar{C}_T = (0 \text{ and } 0.500) \text{ mol}\cdot\text{dm}^{-3}$  have similar qualitative trends with  $z_1$ , at  $\bar{C}_T = 1.000 \text{ mol}\cdot\text{dm}^{-3}$  its values increase from  $z_1 = 0$  to  $\sim 0.7$  and then decrease at higher  $z_1$ .

In contrast, at  $\bar{C}_T = 1.000 \text{ mol}\cdot\text{dm}^{-3}$  the Nernst–Hartley cross-term  $D_{ij}$  are closer to the experimental  $(D_{ij})_V$ . For  $D_{12}$ , Nernst–Hartley values are larger than experimental  $(D_{12})_V$  by  $0.032 \times 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$  at  $z_1 = 0.900$  but are smaller than experimental ones by  $(0.045 \text{ to } 0.086) \times 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$  at the other values of  $z_1$ . For  $D_{21}$ , the Nernst–Hartley values are more negative than the experimental  $(D_{21})_V$  by  $(0.005 \text{ to } 0.054_5) \times 10^{-9} \text{ m}^2\cdot\text{s}^{-1}$ . However, at  $\bar{C}_T = 0.500 \text{ mol}\cdot\text{dm}^{-3}$  the  $(D_{12})_V$  at  $z_1 \approx 0.75$  is smaller than the Nernst–Hartley value, rather than being larger.

Three of these diffusion coefficients,  $(D_{11})_V$ ,  $(D_{22})_V$ , and  $(D_{21})_V$ , form families of curves that vary slowly and systematically with increasing  $\bar{C}_T$ . Thus it should be possible to accurately estimate 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 both sets of experimental  $(D_{12})_V$ . The Nernst–Hartley curve does not predict the observed maximum and crosses the experimental curves. Therefore, interpolation to intermediate concentrations would yield uncertain results for  $(D_{12})_V$ , particularly when  $z_1 > 0.5$ .

It is obvious that simple empirical corrections, such as dividing the Nernst–Hartley  $D_{ij}$  values by the relative viscosity of the solutions, cannot bring them *all* into conformity with the experimental  $(D_{ij})_V$  or the  $(D_{ij})_0$ .

We note that the cross-term  $(D_{12})_V$  values at any fixed value of  $z_1 \leq 0.6$  become larger as  $\bar{C}_T$  increases from  $(0.500 \text{ to } 1.000) \text{ mol}\cdot\text{dm}^{-3}$ , and that  $(D_{21})_V$  seem to be shifting from more negative to less negative values. It is probable that  $(D_{21})_V$  will become positive if  $\bar{C}_T$  is increased much further. However, because of the more limited solubility of  $\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}(\text{cr})$ , this sign change may not occur below the solubility limit for solutions rich in  $\text{Na}_2\text{SO}_4(\text{aq})$ .

We also note that there is a subtle difference in the dependence of the  $(D_{12})_V$  upon  $z_1$  at constant  $\bar{C}_T = 1.000 \text{ mol}\cdot\text{dm}^{-3}$  that was not present at  $\bar{C}_T = 0.500 \text{ mol}\cdot\text{dm}^{-3}$  or at infinite dilution. See Figure 2. The  $(D_{12})_V$  exhibit a slight maximum at  $z_1 \sim 0.7$  when  $\bar{C}_T = 1.000 \text{ mol}\cdot\text{dm}^{-3}$ , whereas at  $\bar{C}_T = 0.500 \text{ mol}\cdot\text{dm}^{-3}$  and infinite dilution (Rard et al., 1996) they monotonically increase as  $z_1$  increases.

## Acknowledgment

We thank Onofrio Annunziata (Texas Christian University) for performing the two diffusion experiments for the limiting binary solutions  $\text{NaCl}(\text{aq})$  and  $\text{Na}_2\text{SO}_4(\text{aq})$ , and Joanne L. Levatin (Lawrence Livermore National Laboratory) for adapting some of our older computer programs to meet our current requirements. E-mail addresses of the authors are albright@gamma.is.tcu.edu (J.G.A.), rard1@llnl.gov (J.A.R.), and dmiller@llnl.gov (D.G.M.).

## Literature Cited

- Albright, J. G.; Mathew, R.; Miller, D. G. Measurement of Binary and Ternary Mutual Diffusion Coefficients of Aqueous Sodium and Potassium Bicarbonate Solutions at 25 °C. *J. Phys. Chem.* **1987**, *91*, 210–215.
- Albright, J. G.; Mathew, R.; Miller, D. G.; Rard, J. A. Isothermal Diffusion Coefficients for  $\text{NaCl}\text{--}\text{MgCl}_2\text{--}\text{H}_2\text{O}$  at 25 °C. 1. Solute Concentration Ratio of 3:1. *J. Phys. Chem.* **1989**, *93*, 2176–2180.
- Anderson, D. E.; Graf, D. L. Ionic Diffusion in Naturally-Occurring Aqueous Solutions: Use of Activity Coefficients in Transition-State Models. *Geochim. Cosmochim. Acta* **1978**, *42*, 251–262.
- Deng, Z.; Leaist, D. G. Ternary Mutual Diffusion Coefficients of  $\text{MgCl}_2 + \text{MgSO}_4 + \text{H}_2\text{O}$  and  $\text{Na}_2\text{SO}_4 + \text{MgSO}_4 + \text{H}_2\text{O}$  from Taylor Dispersion Profiles. *Can. J. Chem.* **1991**, *69*, 1548–1553.
- Dunlop, P. J. Data for Diffusion in a Concentrated Solution of the System  $\text{NaCl}\text{--}\text{KCl}\text{--}\text{H}_2\text{O}$  at 25°. A Test of the Onsager Reciprocal Relation for this Composition. *J. Phys. Chem.* **1959**, *63*, 612–615.
- Dunlop, P. J.; Gosting, L. J. Use of Diffusion and Thermodynamic Data to Test the Onsager Reciprocal Relation for Isothermal Diffusion in the System  $\text{NaCl}\text{--}\text{KCl}\text{--}\text{H}_2\text{O}$  at 25°. *J. Phys. Chem.* **1959**, *63*, 86–93.
- Felmy, A. R.; Weare, J. H. Calculation of Multicomponent Ionic Diffusion from Zero to High Concentration: I. The System  $\text{Na}\text{--}\text{K}\text{--}\text{Ca}\text{--}\text{Mg}\text{--}\text{Cl}\text{--}\text{SO}_4\text{--}\text{H}_2\text{O}$  at 25 °C. *Geochim. Cosmochim. Acta* **1991**, *55*, 113–131.
- Fujita, H.; Gosting, L. J. An Exact Solution of the Equations for Free Diffusion in Three-Component Systems with Interacting Flows, and Its Use in Evaluation of the Diffusion Coefficients. *J. Am. Chem. Soc.* **1956**, *78*, 1099–1106.
- Gosting, L. J.; Kim, H.; Loewenstein, M. A.; Reinfelds, G.; Revzin, A. A Versatile Optical Diffusometer Including a Large Optical Bench of New Design. *Rev. Sci. Instrum.* **1973**, *44*, 1602–1609.
- Hamer, W. J.; Wu, Y.-C. Osmotic Coefficients and Mean Activity Coefficients of Uni-Univalent Electrolytes in Water at 25 °C. *J. Phys. Chem. Ref. Data* **1972**, *1*, 1047–1099.
- Hao, L.; Leaist, D. G. Interdiffusion Without a Common Ion in Aqueous  $\text{NaCl}\text{--}\text{MgSO}_4$  and  $\text{LiCl}\text{--}\text{NaOH}$  Mixed Electrolytes. *J. Solution Chem.* **1995**, *24*, 523–535.
- Kim, H. Diffusion Coefficients for One Composition of the System  $\text{H}_2\text{O}\text{--}\text{NaCl}\text{--}\text{KCl}$ . *J. Chem. Eng. Data* **1982**, *27*, 255–256.
- Leaist, D. G. Moments Analysis of Restricted Ternary Diffusion: Sodium Sulfite + Sodium Hydroxide + Water. *Can. J. Chem.* **1985**, *63*, 2933–2939.
- Leaist, D. G. Ternary Diffusion in Aqueous  $\text{NaCl} + \text{MgCl}_2$  Solutions at 25 °C. *Electrochim. Acta* **1988**, *33*, 795–799.
- Mathew, R.; Paduano, L.; Albright, J. G.; Miller, D. G.; Rard, J. A. Isothermal Diffusion Coefficients for  $\text{NaCl}\text{--}\text{MgCl}_2\text{--}\text{H}_2\text{O}$  at 25 °C. 3. Low  $\text{MgCl}_2$  Concentrations with a Wide Range of  $\text{NaCl}$  Concentrations. *J. Phys. Chem.* **1989**, *93*, 4370–4374.
- Mathew, R.; Albright, J. G.; Miller, D. G.; Rard, J. A. Isothermal Diffusion Coefficients for  $\text{NaCl}\text{--}\text{MgCl}_2\text{--}\text{H}_2\text{O}$  at 25 °C. 4. Solute Concentration Ratio of 1:3. *J. Phys. Chem.* **1990**, *94*, 6875–6878.
- Miller, D. G. Application of Irreversible Thermodynamics to Electrolyte Solutions. I. Determination of Ionic Transport Coefficients  $l_{ij}$  for Isothermal Vector Transport Processes in Binary Electrolyte Systems. *J. Phys. Chem.* **1966**, *70*, 2639–2659.
- Miller, D. G. Application of Irreversible Thermodynamics to Electrolyte Solutions. II. Ionic Transport Coefficients  $l_{ij}$  for Isothermal Vector Transport Processes in Ternary Systems. *J. Phys. Chem.* **1967a**, *71*, 616–632.
- Miller, D. G. Application of Irreversible Thermodynamics to Electrolyte Solutions. III. Equations for Isothermal Vector Transport Processes in  $n$ -Component Systems. *J. Phys. Chem.* **1967b**, *71*, 3588–3592.
- Miller, D. G. Explicit Relations of Velocity Correlation Coefficients to Onsager  $l_{ij}$ s, to Experimental Quantities, and to Infinite Dilution Limiting Laws for Binary Electrolyte Solutions. *J. Phys. Chem.* **1981**, *85*, 1137–1146. The terms  $v_1^2 c'(10^3 \rho^2)$  and  $v_2^2 c'(10^3 \rho^2)$  should be in front of the left-hand square brackets of eq A1 and eq A2, respectively, and the term in front of the square bracket of eq A3 should be  $\alpha_2^2/(10^3 \rho^2)$ .
- Miller, D. G. A Method for Obtaining Multicomponent Diffusion Coefficients Directly from Rayleigh and Gouy Fringe Position Data. *J. Phys. Chem.* **1988**, *92*, 4222–4226.
- Miller, D. G.; Vitagliano, V. Experimental Test of McDougall's Theory for the Onset of Convective Instabilities in Isothermal Ternary Systems. *J. Phys. Chem.* **1986**, *90*, 1706–1717.
- Miller, D. G.; Albright, J. G. Optical Methods. In *Measurement of the Transport Properties of Fluids*; Wakeham, W. A., Nagashima, A., Sengers, J. V., Eds.; Experimental Thermodynamics, Vol. III; Blackwell Scientific Publications: Oxford, 1991; pp 272–294 (references on pp 316–320).
- Miller, D. G.; Ting, A. W.; Rard, J. A.; Eppstein, L. B. Ternary Diffusion Coefficients of the Brine Systems  $\text{NaCl} (0.5 \text{ M})\text{--}\text{Na}_2\text{SO}_4 (0.5 \text{ M})\text{--}\text{H}_2\text{O}$  and  $\text{NaCl} (0.489 \text{ M})\text{--}\text{MgCl}_2 (0.051)\text{--}\text{H}_2\text{O}$  (Seawater Composition) at 25 °C. *Geochim. Cosmochim. Acta* **1986**, *50*, 2397–2403.
- Miller, D. G.; Albright, J. G.; Mathew, R.; Lee, C. M.; Rard, J. A.; Eppstein, L. B. Isothermal Diffusion Coefficients of  $\text{NaCl}\text{--}\text{MgCl}_2\text{--}$

- H<sub>2</sub>O at 25 °C. 5. Solute Concentration Ratio of 1:1 and Some Rayleigh Results. *J. Phys. Chem.* **1993**, *97*, 3885–3899.
- Miller, D. G.; Paduano, L.; Sartorio, R.; Albright, J. G. Analysis of Gouy Fringe Data and Comparison of Rayleigh and Gouy Optical Diffusion Measurements Using the System Raffinose (0.015 M)–KCl (0.5 M)–H<sub>2</sub>O at 25 °C. *J. Phys. Chem.* **1994**, *98*, 13745–13754.
- Miller, D. G.; Sartorio, R.; Paduano, L.; Rard, J. A.; Albright, J. G. Effects of Different Sized Concentration Differences Across Free Diffusion Boundaries and Comparison of Gouy and Rayleigh Diffusion Measurements Using NaCl–KCl–H<sub>2</sub>O. *J. Solution Chem.* **1996**, *25*, 1185–1211.
- Mills, R.; Lobo, V. M. M. *Self-Diffusion in Electrolyte Solutions*; Elsevier: Amsterdam, 1989.
- Noulty, R. A.; Leaist, D. G. Diffusion in Aqueous Copper Sulfate and Copper Sulfate–Sulfuric Acid Solutions. *J. Solution Chem.* **1987**, *16*, 813–825.
- O'Donnell, I. J.; Gosting, L. J. The Concentration Dependence of the Four Diffusion Coefficients of the System NaCl–KCl–H<sub>2</sub>O at 25 °C. In *The Structure of Electrolytic Solutions*; Hamer, W. J., Ed.; John Wiley: New York, 1959; pp 160–182.
- Paduano, L.; Mathew, R.; Albright, J. G.; Miller, D. G.; Rard, J. A. Isothermal Diffusion Coefficients for NaCl–MgCl<sub>2</sub>–H<sub>2</sub>O at 25 °C. 2. Low Concentrations of NaCl with a Wide Range of MgCl<sub>2</sub> Concentrations. *J. Phys. Chem.* **1989**, *93*, 4366–4370.
- Rard, J. A. Isopiestic Determination of the Osmotic Coefficients of Lu<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>(aq) and H<sub>2</sub>SO<sub>4</sub>(aq) at the Temperature  $T = 298.15$  K, and Review and Revision of the Thermodynamic Properties of Lu<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>(aq) and Lu<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>·8H<sub>2</sub>O(cr). *J. Chem. Thermodyn.* **1996**, *28*, 83–110.
- Rard, J. A.; Miller, D. G. The Mutual Diffusion Coefficients of NaCl–H<sub>2</sub>O and CaCl<sub>2</sub>–H<sub>2</sub>O at 25 °C from Rayleigh Interferometry. *J. Solution Chem.* **1979a**, *8*, 701–716.
- Rard, J. A.; Miller, D. G. The Mutual Diffusion Coefficients of Na<sub>2</sub>SO<sub>4</sub>–H<sub>2</sub>O and MgSO<sub>4</sub>–H<sub>2</sub>O at 25 °C from Rayleigh Interferometry. *J. Solution Chem.* **1979b**, *8*, 755–766.
- Rard, J. A.; Miller, D. G. Isopiestic Determination of the Osmotic Coefficients of Aqueous Na<sub>2</sub>SO<sub>4</sub>, MgSO<sub>4</sub>, and Na<sub>2</sub>SO<sub>4</sub>–MgSO<sub>4</sub> at 25 °C. *J. Chem. Eng. Data* **1981**, *26*, 33–38.
- Rard, J. A.; Miller, D. G. Ternary Mutual Diffusion Coefficients of NaCl–SrCl<sub>2</sub>–H<sub>2</sub>O at 25 °C. 1. Total Concentrations of 0.5 and 1.0 mol·dm<sup>-3</sup>. *J. Phys. Chem.* **1987**, *91*, 4614–4620.
- Rard, J. A.; Miller, D. G. Ternary Mutual Diffusion Coefficients of NaCl–SrCl<sub>2</sub>–H<sub>2</sub>O at 25 °C. 2. Total Concentrations of 2.0 and 3.0 mol·dm<sup>-3</sup>. *J. Phys. Chem.* **1988**, *92*, 6133–6140.
- Rard, J. A.; Miller, D. G. Ternary Mutual Diffusion Coefficients of ZnCl<sub>2</sub>–KCl–H<sub>2</sub>O at 25 °C by Rayleigh Interferometry. *J. Solution Chem.* **1990**, *19*, 129–148.
- Rard, J. A.; Albright, J. G.; Miller, D. G.; Zeidler, M. E. Ternary Mutual Diffusion Coefficients and Densities of the System {z<sub>1</sub>NaCl + (1 – z<sub>1</sub>)Na<sub>2</sub>SO<sub>4</sub>}(aq) at 298.15 K and a Total Molarity of 0.5000 mol dm<sup>-3</sup>. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 4187–4197.
- Steeffel, C. I.; Lichtner, P. C. Diffusion and Reaction in Rock Matrix Bordering a Hyperalkaline Fluid-Filled Fracture. *Geochim. Cosmochim. Acta* **1994**, *58*, 3595–3612.
- Vitagliano, P. L.; Della Volpe, C.; Vitagliano, V. Gravitational Instabilities in Free Diffusion Boundaries. *J. Solution Chem.* **1984**, *13*, 549–562.
- Vitagliano, V.; Borriello, G.; Della Volpe, C.; Ortona, O. Instabilities in Free Diffusion Boundaries of NaCl–Sucrose–H<sub>2</sub>O Solutions at 25 °C. *J. Solution Chem.* **1986**, *15*, 811–826.
- Weingärtner, H.; Price, W. E.; Edge, A. V. J.; Mills, R. Transport Measurements in Aqueous Sodium Sulfate. Evidence for Like-Ion Pairs in Concentrated Solutions. *J. Phys. Chem.* **1993**, *97*, 6289–6291.
- Wendt, R. P. Studies of Isothermal Diffusion at 25° in the System Water–Sodium Sulfate–Sulfuric Acid and Tests of the Onsager Relation. *J. Phys. Chem.* **1962**, *66*, 1279–1288.
- Zhong, E. C.; Friedman, H. L. Self-Diffusion and Distinct Diffusion of Ions in Solution. *J. Phys. Chem.* **1988**, *92*, 1685–1692.

Received for review January 20, 1998. Accepted April 23, 1998. Support from the Chemistry Department of Texas Christian University and from NASA Grant NA68-1356 for J.G.A. and S.M.G. is gratefully acknowledged. The work of J.A.R. and D.G.M. was performed under the auspices of the Office of Basic Energy Sciences, Division of Geosciences, of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract No. W-7405-ENG-48.

JE9800196