Mutual Diffusion Coefficients and Densities at 298.15 K of Aqueous Mixtures of NaCl and Na_2SO_4 with NaCl Solute Fractions of 0.9500, Trace Diffusion Coefficients of SO_4^{2-} in NaCl(aq), and Trace Refractive Index Increments and Partial Molar Volumes of Na_2SO_4 and NaCl[†]

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Isothermal mutual diffusion coefficients (interdiffusion coefficients) and refractive index increments were measured for ternary aqueous mixtures of NaCl and Na_2SO_4 at constant NaCl molarity fraction $z_1 = 0.9500$ at 298.15 K, using high precision Rayleigh interferometry with computerized data acquisition. The densities of these solutions were measured using vibrating tube densimetry. The experiments were performed at seven total molarities ranging from (0.499 92 to 4.978 34) mol·dm^{-3}. These measurements supplement our earlier ones at other compositions and composition fractions. The Na_2SO_4 cross-term diffusion coefficient D_{21} is small and negative at nearly all of the ternary solution compositions, whereas the NaCl cross-term diffusion coefficient D_{12} is larger and positive. However, at $z_1 = 0.9500$, D_{21} changes sign as the total concentration exceeds 4.3 mol·dm^{-3}, and above 3.2 mol·dm^{-3} the value of D_{12} exceeds that of the corresponding Na_2SO_4 main-term diffusion coefficient D_{22}. Thus, at high concentrations, a concentration gradient of Na_2SO_4 causes the transport of more NaCl than of itself. At each fixed total concentration, extrapolation of Na_2SO_4 main-term diffusion coefficients from these and our earlier results, to zero concentration fraction of Na_2SO_4 (i.e., $z_1 \rightarrow 1$), yielded the trace diffusion coefficient of the SO_4^{2-} ion $D^{tr}(SO_4^{2-})$ in NaCl(aq). Comparing these $D^{tr}(SO_4^{2-})$ values in NaCl(aq) to published $D^{tr}(SO_4^{2-})$ values in Na_2SO_4(aq) shows agreement to 1−8%, when the comparisons are made at equal volumetric ionic strength. Similar extrapolations of the volumetric and refractive index increment results yielded the trace partial molar volume and trace refractive index increment, respectively. Densities of NaCl(aq) at 298.15 K were critically reanalyzed.

Introduction

The salt NaCl is the major electrolyte constituent of seawater and many natural brines, and Na_2SO_4 is also present in many brines at significant concentrations. Experimental values of the thermodynamic and transport properties of the aqueous solutions of these salts and their mixtures are thus required for understanding the formation and evolution of these natural waters. These properties are also needed for more efficient commercial extraction of the constituent salts or the desalination of seawater and brackish water. Diffusion data for these solutions also complement ongoing research at Texas Christian University to provide diffusion data for modeling liquid-phase transport during protein crystal growth and for understanding protein−salt interactions.[1,2]

We and our collaborators have been measuring properties of aqueous solutions of the various soluble salts present in seawater and natural brines.[3−19] In particular, we reported precise mutual diffusion coefficients of NaCl(aq) and mutual diffusion coefficients and osmotic coefficients of Na_2SO_4(aq) at 298.15 K,[3,6,7] and a thermodynamic equation of state for Na_2SO_4(aq) from freezing temperatures to 423.65 K.[5]

In 1995 we began a systematic investigation of the mutual diffusion coefficients and densities/partial molar volumes of $\{(z_1)\mathrm{NaCl} + (1 - z_1)\mathrm{Na_2SO_4}\}$(aq) at 298.15 K, and we have reported our results at total concentrations of (0.500, 1.000, and 1.500) mol·dm^{-3} over the NaCl composition fraction range $z_1 = 0.25$ to 0.90,[16−18] and at $z_1 = 0.90$ to a total concentration of 5.007 mol·dm^{-3}.[19] Because of solubility limitations at 298.15 K, 1.500 mol·dm^{-3} is very close to the maximum concentration for which diffusion coefficient measurements can be made over the full range of z_1 values.[20]

Such systematic measurements can be used to obtain trace diffusion coefficients. Consider a ternary common-ion electrolyte solution containing one solvent. Let mutual diffusion measurements be made at some constant total concentration (i.e., at a particular constant total molarity, constant total volumetric ionic strength, constant ionic molarity, constant total molality, etc.) but with different

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[†] We note with regret the recent death of Dr. Reginald Mills. Under his leadership, the Diffusion Research Unit at the Australian National University (Canberra) became the world's leading center for precise tracer diffusion coefficient measurements. This paper is dedicated to Dr. Mills.

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ratios of the two solutes. For the case of electrolytes M_xA and M_yB with a *common cation* but chemically distinct anions A and B, let the main-term diffusion coefficients be denoted as D_{11} and D_{22}, where 1 represents solute M_xA and 2 represents solute M_yB, and the subscripts x and y are the stoichiometric coefficients. As the mole ratio of M_xA to M_yB approaches zero (still at some type of fixed total concentration), the value of D_{11} approaches the trace diffusion coefficient of anion A, $D^{tr}(A)$, in the binary solution of M_yB(aq) at this same total concentration. In addition, the cross-term diffusion coefficient D_{12} approaches zero because there is no M_xA present to be transported by coupled diffusion.[21,22] Correspondingly, as the mole ratio of M_yB to M_xA approaches zero, the value of D_{22} approaches the trace diffusion coefficient of the other anion B, $D^{tr}(B)$, in the binary solution of M_xA(aq), and D_{21} approaches zero. Similarly, if the diffusion measurements are instead made for a ternary *common-anion* system containing two chemically distinct cations, these measurements may be analyzed to yield the corresponding trace diffusion coefficients of the cations.

Traditional methods for measuring trace diffusion coefficients require radioactive tracers. However, labeled versions of the anion or cation to be investigated may not be readily available for some structurally more complicated ions or for elements lacking radioactive isotopes with suitable half-lives. An important advantage of using mutual diffusion coefficients to obtain trace diffusion coefficients is that use of nonradioactive materials in the diffusion measurements simplifies laboratory precautions and waste disposal problems. A disadvantage is that a larger number of experiments is needed to extrapolate the results to zero concentrations of the noncommon ions. However, this disadvantage is offset because the mutual diffusion coefficients measured at various ratios of solute are interesting in their own right and provide a direct characterization of the mass transport of the individual electrolytes in the presence of concentration gradients. A second disadvantage is that trace diffusion coefficients of the common ion cannot be obtained by this method.

The driving forces for mutual diffusion are the gradients of the chemical potentials of the individual electrolytes,[23−25] whereas trace diffusion is driven by the entropy of mixing $\Delta_{mix}S_m$. Except for the trace diffusion coefficients at finite concentrations and the calculated trace values at infinite dilution, mutual diffusion and tracer diffusion coefficients are not directly related, and one cannot be calculated from the other.

Only a few mutual diffusion studies for ternary common-ion solutions have been made at a sufficient number of concentrations that allowed or would allow the extraction of trace diffusion coefficients. These studies include ours of the $\{(z_1)NaCl + (1 - z_1)MgCl_2\}$(aq) system using optical interferometry,[10−14] Leaist's at lower concentrations using the conductometric method,[26] and several studies by Leaist and co-workers using the Taylor dispersion method.[27,28] Extraction of trace diffusion coefficients from these mutual diffusion coefficients places such high demands on the quality of the experimental D_{ij} values that the resulting D^{tr} values in most cases are not likely to be more accurate than a few percent.

The diffusion coefficients of our first two compositions of $\{(z_1)NaCl + (1 - z_1)Na_2SO_4\}$(aq) were measured with traditional Gouy interferometry using the Gosting diffusiometer[29] with the interference patterns (typically about 10 to 12) being recorded on glass plates.[16] Shortly thereafter, computerized automation of data collection for the Rayleigh interferometry mode of this diffusiometer was completed.[16] Now, 50 temporal scans of the Rayleigh fringe patterns are normally made during a diffusion experiment, and much larger amounts of information are collected during each scan, which has resulted in a significant enhancement in the precision and accuracy of the derived diffusion coefficients. Diffusion data for our other 14 reported compositions of $\{(z_1)NaCl + (1 - z_1)Na_2SO_4\}$(aq) were measured using this automated Rayleigh mode.[16−19]

The measurements at constant total molarities of (0.5, 1.0, and 1.5) mol·dm^{-3} were used to derive $D^{tr}(SO_4^{2-})$ values in NaCl(aq) and $D^{tr}(Cl^-)$ values in Na_2SO_4(aq) at these three concentrations.[16−18] However, measurements at higher concentrations of (2.0 to 5.0) mol·dm^{-3} were limited to mixtures with $z_1 = 0.90$,[19] so trace diffusion coefficients could not be derived.

We now extend our earlier diffusion measurements to include mixtures with $z_1 = 0.95$, which are nearer to a "trace" concentration of Na_2SO_4 in NaCl(aq). These combined results are extrapolated here to the limit of $z_1 \rightarrow 1$ to yield $D^{tr}(SO_4^{2-})$ in (0.5, 1.0, 1.5, 2.0, 3.0, 4.0, and 5.0) mol·dm^{-3} NaCl(aq). At each total concentration of (0.5, 1.0, and 1.5) mol·dm^{-3}, we now have experimental diffusion data at five different values of z_1, along with the limiting binary solutions. These allow very accurate $D^{tr}(SO_4^{2-})$ values to be derived. We believe that these three new $D^{tr}(SO_4^{2-})$ values are as accurate, if not more accurate, than the best quality measurements possible using radioactive tracers with diaphragm cells, and are more accurate than those typically made with the open ended capillary method.[30]

Since our diffusion coefficients were measured using an optical interferometric method, they also yield refractive index increments, which were similarly extrapolated to yield their limiting trace values for the two electrolytes. Furthermore, densities were measured for all solutions used in the diffusion experiments, which we analyzed to yield the trace partial molar volumes of Na_2SO_4 in NaCl(aq) at all seven concentrations and of NaCl in (0.5, 1.0, and 1.5) mol·dm^{-3} Na_2SO_4(aq). We report these internally consistent trace properties of $\{(z_1)NaCl + (1 - z_1)Na_2SO_4\}$(aq) solutions at 298.15 K.

Easteal and Woolf[31] reported $D^{tr}(SO_4^{2-})$ values in (0.1000, 0.2001, 0.3000, 0.5001, 1.000, 2.000, and 3.000) mol·dm^{-3} NaCl(aq) at 298.15 K and in several other aqueous electrolytes that were determined with a diaphragm cell using ^{35}S-labeled sulfate ions. We compare these results with our derived values in the discussion below.

Experimental Section

All experimental measurements were made in the Diffusion Research Laboratory at Texas Christian University. Most details of the experimental measurements and data processing are identical to those reported in some of our earlier studies, and we refer the readers to a previous paper.[16]

Diffusion Coefficient and Refractive Index Increment Measurements. Diffusion experiments were performed using Rayleigh optical interferometry at (298.15 ± 0.00$_5$) K with free-diffusion boundary conditions inside the diffusion cell.[14,32] These diffusion measurements were made with the high-quality Gosting diffusiometer[29] and with automated "real time" recording of the fringe positions.[16−19] The movement of the photodiode array is now controlled with a 550 MHz Pentium 3 Dell Computer.[19]

At each overall solution composition (constant total molarity), diffusion experiments were performed with four solution pairs having essentially the same average concentrations of each solute, $\bar{C}_1$ and $\bar{C}_2$, but with different values of ΔC_1 and ΔC_2, where the ΔC_i values are the concentration differences of electrolyte i between the bottom and the top sides of the initial diffusion boundary. Subscript 1 denotes NaCl, and subscript 2, Na_2SO_4.

At most compositions, the ΔC_i values were selected to correspond to the refractive index fractions $\alpha_i \approx (0, 0.2, 0.8, \text{and } 1)$, as recommended by Dunlop[33] and O'Donnell and Gosting,[21] and α_i is defined by

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

where J is the total number of Rayleigh interference fringes and R_i is the refractive index increment of J with respect to the concentration increment of solute i. By eq 1, $\alpha_1 + \alpha_2 = 1$ for a two-solute system. The α_i and R_i values are obtained by least-squares analysis of the four sets of experimental J, ΔC_1, and ΔC_2 values at essentially the same $\bar{C}_1$ and $\bar{C}_2$ values. The overall solute concentration is given by $\langle \bar{C}_T \rangle = \langle \bar{C}_1 \rangle + \langle \bar{C}_2 \rangle$, where $\langle \bar{C}_1 \rangle$ and $\langle \bar{C}_2 \rangle$ are the averages of the four $\bar{C}_1$ and $\bar{C}_2$ values for these experiments.

A different type of refractive index increment R_i^* directly describes the difference in refractive index Δn between the two solutions forming the initial diffusion boundary, where $\Delta n = \lambda J/a = R_1^*\Delta C_1 + R_2^*\Delta C_2$, $\lambda = 543.366$ nm is the wavelength in air of the helium−neon laser green line used by our interferometer, and a is the path length of the light inside the diffusion cell. We usually report R_i values rather than R_i^* values, because J is directly observed experimentally whereas Δn is not. However, five different diffusion cells were used in this and our previous investigations of the $\{(z_1)\text{NaCl} + (1 - z_1)\text{Na}_2\text{SO}_4\}(\text{aq})$ system.[16−19] Each cell has a slightly different a value, although all of their a distances are fairly close to 2.5 cm. The J values are directly proportional to their corresponding cell's a distance, whereas Δn and R_i^* values are independent of a. Therefore, R_i^* will be used when comparing refractive index increments in the analysis below.

Solution Preparations and Density Measurements. Solutions were prepared by mass from samples of Mallinckrodt Analytical reagent NaCl(cr) that had previously been dried in air at 723 K,[34] from samples of stock solutions of Na_2SO_4(aq), and from purified water. The water purification, the purification of the Baker "Analyzed" Na_2SO_4, the determination of the molalities of the Na_2SO_4(aq) stock solutions, and the solution preparations were described previously.[16] Assumed molar masses are 58.443 g·mol^{-1} for NaCl, 142.037 g·mol^{-1} for Na_2SO_4, and 18.0153 g·mol^{-1} for H_2O.

The densities of the solutions used in our diffusion experiments were measured with a Mettler-Parr DMA/40 vibrating tube densimeter. At each investigated composition at constant $\langle \bar{C}_T \rangle$, the densities of the solutions from the four solution pairs were represented by the linear Taylor series expansion,[33,35]

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

using the method of least-squares. C_1 and C_2 are the molar concentrations of NaCl and Na_2SO_4, respectively, for each individual solution; the density increments H_i are least-squares parameters; and $\bar{\rho}$ is a least-squares parameter representing the density of a ternary solution having a concentration corresponding exactly to $\langle \bar{C}_1 \rangle$ and $\langle \bar{C}_2 \rangle$. As long as this density expansion is centered around the overall mean concentrations $\langle \bar{C}_1 \rangle$ and $\langle \bar{C}_2 \rangle$, then the value of $\bar{\rho}$ will be exactly equal to the average of all of the densities used in the evaluation. These H_1 and H_2 parameters are used for calculating the partial molar volumes $V_m(i)$ of the two solutes and water, and these $V_m(i)$ are required for converting the experimentally based volume-fixed diffusion coefficients $(D_{ij})_V$ to solvent-fixed ones $(D_{ij})_0$. The $V_m(i)$ values are related to the H_i values by the equation

$$V_m(i) = (M_i - H_i)/(\bar{\rho} - H_1<\bar{C}_1> - H_2<\bar{C}_2>) \qquad (3)$$

where M_i is the molar mass of component i and $H_0 = 0$ for the solvent.[18]

Examination of eq 3 indicates that the error in a $V_m(i)$ value is due mainly to the error in its corresponding H_i coefficient, because errors in the M_i values and in $\bar{\rho}$ are negligible by comparison. The values of the denominator of eq 3 are of the order of unity. At low concentrations, the standard error of a $V_m(i)$ value may thus be assumed equal to the standard error in its corresponding H_i coefficient, but at high concentrations the standard errors will be very slightly larger.

Diffusion Calculations

The complete description of diffusion of solutes in a ternary common-ion solution under isothermal and isobaric conditions requires four diffusion coefficients D_{ij}, where i and j = 1 or 2.[24,36] The generalized Fick's second-law equations for diffusive flow in one dimension are

$$-J_1 = D_{11}(\partial C_1/\partial x)_{T,p} + D_{12}(\partial C_2/\partial x)_{T,p} \qquad (4a)$$

and

$$-J_2 = D_{21}(\partial C_1/\partial x)_{T,p} + D_{22}(\partial C_2/\partial x)_{T,p} \qquad (4b)$$

where J_1 and J_2 are the flows of these two solutes and x is the vertically downward direction. The main-term diffusion coefficients D_{ii} describe the flow of each solute i due to its own concentration gradient, and the cross-term diffusion coefficients D_{ij} $(i \neq j)$ describe the coupled flow of solute i due to a gradient of the other solute j. Our experimental condition of relatively small ΔC_i values yields values of D_{ii} and D_{ij} in the volume-fixed reference frame,[22] which are denoted collectively as $(D_{ij})_V$.

Table 1 contains all quantities reported for each individual experiment. They are $\bar{C}_i$ and ΔC_i for both solutes; the densities of the top and bottom solutions forming the diffusion boundary, ρ(top) and ρ(bottom), respectively; J; α_1; the starting time correction, Δt, 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.[14,16,37] The extraction of diffusion coefficients and their standard errors was described previously.[14,16] All diffusion boundaries were found to be statically and dynamically stable.[38−40]

Both experimental and calculated (least-squares) J values are reported in Table 1, where the J(calcd) values were calculated using the second equality of eq 1.

The experimental D_A(exptl) were calculated as described on page 4193 of ref 16, as were the D_A(calcd) by a method described elsewhere.[14,16] Agreement between D_A(exptl) and D_A(calcd) values is generally very good, with $|D_A(\text{exptl}) - D_A(\text{calcd})| \leq 0.0018 \times 10^{-9}$ m^2·s^{-1}, except for the second experiment of the series of experiments with $\langle \bar{C}_T \rangle$ = 1.499 91 mol·dm^{-3}, the third experiment of the series with $\langle \bar{C}_T \rangle$ = 1.999 04 mol·dm^{-3}, and the fourth experiment of the series with $\langle \bar{C}_T \rangle$ = 4.978 34 mol·dm^{-3}. Even for the experiments with more discrepant D_A values, $10^2[\{|D_A(\text{exptl}) - D_A(\text{calcd})|\}/D_A(\text{exptl})]$ is only (0.2 to 0.3)%. Values

Table 1. Compositions and Results for $\{(z_1)NaCl + (1 - z_1)Na_2SO_4\}(aq)$ Ternary Solution Diffusion Experiments at z_1 = 0.9500 and 298.15 K[a]

	$\langle \bar{C}_T \rangle = 0.499\ 920\ mol \cdot dm^{-3}$				$\langle \bar{C}_T \rangle = 0.999\ 568\ mol \cdot dm^{-3}$			
quantity	expt 1	expt 2	expt 3	expt 4	expt 1	expt 2	expt 3	expt 4
$\bar{C}_1$	0.474 923$_5$	0.474 929	0.474 928	0.474 924	0.949 530$_5$	0.949 560	0.949 730$_5$	0.949 576
$\bar{C}_2$	0.024 993	0.024 995$_5$	0.024 993$_5$	0.024 995	0.049 954$_5$	0.049 977$_5$	0.049 968	0.049 976$_5$
ΔC_1	0.011 083	0.179 123	0.062 578	0.143 258	−0.000 829	0.186 802	0.037 315	0.149 278
ΔC_2	0.049 142	−0.000 001	0.045 865	0.017 472	0.093 476	−0.000 002	0.074 794	0.018 695
J(exptl)	50.122$_5$	80.115	70.132	80.107	80.375$_5$	80.586	80.632	80.480
J(calcd)	50.116	80.103	70.133	80.121	80.344	80.553	80.664	80.513
α_1	0.098 90	1.000 01	0.399 03	0.799 60	−0.004 45	1.000 02	0.199 49	0.799 54
Δt	13.2	7.0$_5$	6.6	9.0	10.4	8.0$_5$	6.0	6.7
$10^9 D_A$(exptl)	0.985 3	1.450 1	1.111 1	1.320 6	0.902 5	1.443 5	0.984 3	1.304 2
$10^9 D_A$(calcd)	0.984 8	1.448 4$_5$	1.110 8	1.320 5	0.902 2	1.445 3	0.984 3	1.303 4
ρ(top)	1.016 139	1.015 830	1.015 334	1.015 470	1.035 463	1.037 393	1.035 856	1.037 029
ρ(bottom)	1.022 631	1.022 954	1.023 456	1.023 310	1.046 403	1.044 652	1.046 203	1.045 037

	$\langle \bar{C}_T \rangle = 1.499\ 913\ mol \cdot dm^{-3}$				$\langle \bar{C}_T \rangle = 1.999\ 036\ mol \cdot dm^{-3}$			
quantity	expt 1	expt 2	expt 3	expt 4	expt 1	expt 2	expt 3	expt 4
$\bar{C}_1$	1.424 954	1.424 947	1.424 924$_5$	1.424 914$_5$	1.899 142$_5$	1.899 082	1.899 113$_5$	1.899 039
$\bar{C}_2$	0.074 974$_5$	0.074 996$_5$	0.074 946	0.074 995	0.099 930$_5$	0.099 951	0.099 938	0.099 948$_5$
ΔC_1	−0.001 315	0.186 804	0.036 341	0.149 211	−0.001 970	0.186 694	0.035 769	0.148 936
ΔC_2	0.093 493	−0.000 005	0.074 727	0.018 696	0.093 421	−0.000 007	0.074 735	0.018 676
J(exptl)	75.963$_5$	78.224	76.340	77.650	72.014	75.916	72.596	75.162
J(calcd)	75.943	78.159	76.346	77.730	71.921	75.928	72.725	75.114
α_1	−0.007 25	1.000 05	0.199 17	0.803 21	−0.011 14	1.000 07	0.200 05	0.806 45
Δt		8.1	6.7	11.1	10.9	11.9	10.0	6.7
$10^9 D_A$(exptl)	0.871 2	1.451 5	0.958 1$_5$	1.304 3	0.846 4	1.467 8	0.941 7	1.305 0
$10^9 D_A$(calcd)	0.872 8	1.455 3	0.959 4	1.302 8	0.847 1	1.467 2	0.938 9	1.304 5
ρ(top)	1.056 778	1.058 672	1.057 145	1.058 276	1.077 608	1.079 403	1.077 970	1.079 030
ρ(bottom)	1.067 568	1.065 747	1.067 212	1.066 116	1.088 173	1.086 360	1.087 816	1.086 696

	$\langle \bar{C}_T \rangle = 2.995\ 364\ mol \cdot dm^{-3}$				$\langle \bar{C}_T \rangle = 3.988\ 875\ mol \cdot dm^{-3}$			
quantity	expt 1	expt 2	expt 3	expt 4	expt 1	expt 2	expt 3	expt 4
$\bar{C}_1$	2.845 620$_5$	2.845 705$_5$	2.845 414	2.845 687	3.789 375	3.789 713	3.789 393$_5$	3.789 299
$\bar{C}_2$	0.149 739	0.149 773$_5$	0.149 743	0.149 771$_5$	0.199 405$_5$	0.199 459	0.199 419$_5$	0.199 436
ΔC_1	−0.003 709	0.186 358	0.034 779	0.148 476	−0.005 632	0.185 948	0.032 647	0.147 652
ΔC_2	0.093 228	−0.000 014	0.074 600	0.018 641	0.093 009	−0.000 024	0.074 403	0.018 584
J(exptl)	65.183$_5$	72.054	66.707	70.794$_5$	59.306	68.905	61.308	67.155
J(calcd)	65.162	72.081	66.744	70.752	59.356	68.984	61.268	67.067
α_1	−0.022 02	1.000 14	0.201 57	0.811 79	−0.035 21	1.000 23	0.197 73	0.816 94
Δt	5.3	9.9	8.5	7.0	6.5	6.2	5.7	4.3
$10^9 D_A$(exptl)	0.822 4	1.505 0	0.925 2	1.327 2	0.810 3	1.528 9	0.920 7	1.346 9
$10^9 D_A$(calcd)	0.822 5	1.503 3	0.924 9	1.325 8	0.811 3	1.529 8	0.920 4	1.346 1
ρ(top)	1.118 043	1.119 783	1.118 220[b]	1.119 416	1.157 230	1.158 950	1.157 569	1.158 504
ρ(bottom)	1.128 138	1.126 502	1.127 826	1.126 860	1.166 943	1.165 485	1.166 641$_5$	1.165 685

	$\langle \bar{C}_T \rangle = 4.978\ 342\ mol \cdot dm^{-3}$			
quantity	expt 1	expt 2	expt 3	expt 4
$\bar{C}_1$	4.729 536$_5$	4.729 320	4.729 432	4.729 475$_5$
$\bar{C}_2$	0.248 883	0.248 911	0.248 891$_5$	0.248 919
ΔC_1	−0.007 997	0.185 343	0.030 562	0.146 658
ΔC_2	0.092 743	−0.000 040	0.074 179	0.018 516
J(exptl)	53.861	66.353	56.354	63.817
J(calcd)	53.878	66.340	56.327	63.841
α_1	−0.053 15	1.000 37	0.194 28	0.822 55
Δt	4.9	3.5$_5$	5.6	9.2
$10^9 D_A$(exptl)	0.800 0$_5$	1.523 0	0.914 3	1.347 1
$10^9 D_A$(calcd)	0.800 9	1.522 0	0.915 2	1.344 7
ρ(top)	1.195 365	1.196 801	1.195 657	1.196 559
ρ(bottom)	1.204 671	1.203 176	1.204 347	1.203 516

[a] Units of $\bar{C}_i$ and ΔC_i are $mol \cdot dm^{-3}$, those of Δt are s, those of $10^9 D_A$ are $m^2 \cdot s^{-1}$, and those of ρ are $g \cdot cm^{-3}$. Densities were measured using the Mettler-Parr DMA/40 vibrating tube densimeter. Cell C-1335-H-11 was used for all of the diffusion experiments; the optical path length inside this cell is a = 2.4943 cm, and the magnification factor is 1.7580. [b] This density was given zero weight when the parameters of eq 2 were evaluated.

of D_A(exptl) obtained with Rayleigh interferometry are determined mainly by the position of the fringes closest to the center of the diffusion boundary, where the effects of measurement errors are largest.[14] Thus, the resulting D_A(exptl) values are not known as precisely as those determined more directly with Gouy interferometry. However, comparing D_A(exptl) with D_A(calc) provides a measure of the internal consistency of the four experiments at each fixed $\langle \bar{C}_T \rangle$ value.

Ternary Solution D_{ij}

Table 2 contains all the derived quantities for the NaCl + Na_2SO_4 + H_2O system at 298.15 K and z_1 = 0.9500. We report both the experimental volume-fixed $(D_{ij})_V$ values and

Table 2. Results from Ternary Solution Mutual Diffusion Coefficient and Density Measurements for {(z_1)NaCl + (1 − z_1)Na_2SO_4}(aq) Solutions at z_1 = 0.9500 and 298.15 K[a]

quantity	z_1 = 0.950 00	z_1 = 0.950 01	z_1 = 0.950 01	z_1 = 0.950 00$_5$
$\langle \bar{C}_T \rangle$	0.499 920	0.999 568	1.499 913	1.999 036
$\langle \bar{C}_1 \rangle$	0.474 926	0.949 599	1.424 935	1.899 094
$\langle \bar{C}_2 \rangle$	0.024 994	0.049 969	0.074 978	0.099 942
$\langle \bar{C}_0 \rangle$	54.846 9	54.309 9	53.746 7	53.160 2
$m_1(\langle \bar{C}_1 \rangle, \langle \bar{C}_2 \rangle)$	0.480 654	0.970 554	1.471 642	1.982 979
$m_2(\langle \bar{C}_1 \rangle, \langle \bar{C}_2 \rangle)$	0.025 296	0.051 071	0.077 436	0.104 356$_5$
$10^{-2}R_1$	4.472 01	4.312 31	4.184 24	4.067 28
$10^{-2}R_2$	9.189 64	8.633 36	8.181 73	7.784 36
$\bar{\rho}$	1.019 390	1.041 005	1.062 189	1.082 882
H_1	39.747 ± 0.036	38.912 ± 0.340	37.934 ± 0.106	37.240 ± 0.086
H_2	122.997 ± 0.124	117.978 ± 0.678	116.083 ± 0.213	113.883$_5$ ± 0.172
$s(\rho$ fit)	0.000 006	0.000 064	0.000 020	0.000 016
$s(\bar{\rho})$	0.000 002	0.000 020	0.000 006	0.000 005
V_m(NaCl)	18.744	19.567	20.521	21.187
$V_m(Na_2SO_4)$	19.089	24.103$_5$	25.968	28.132
$V_m(H_2O)$	18.062	18.048$_5$	18.025$_5$	18.001
$10^{-9}\sigma_+$	0.668 27$_5$	0.674 54	0.668 04	0.668 31
$10^{-9}\sigma_-$	1.120 27	1.197 60$_5$	1.277 52	1.367 21
$10^{-2}S_A$	−62.05	−69.58	−75.80	−81.60
$10^9(D_{11})_V$	1.5018 ± 0.0005	1.4873 ± 0.0004	1.5037 ± 0.0008	1.5021 ± 0.0013
$10^9(D_{12})_V$	0.1723 ± 0.0011	0.2114 ± 0.0006	0.2882$_5$ ± 0.0013	0.3676 ± 0.0020
$10^9(D_{21})_V$	−0.0190 ± 0.0002	−0.0148 ± 0.0001$_5$	−0.0170 ± 0.0003	−0.0122 ± 0.0005
$10^9(D_{22})_V$	0.8873 ± 0.0004	0.8302 ± 0.0002	0.7759$_5$ ± 0.0005	0.7256 ± 0.0007
$10^9(D_{11})_0$	1.5151	1.5152	1.5485	1.5646
$10^9(D_{12})_0$	0.1820	0.2348	0.3266	0.4235
$10^9(D_{21})_0$	−0.0183	−0.0134	−0.0147	−0.0089$_5$
$10^9(D_{22})_0$	0.8878	0.8315	0.7780	0.7285

quantity	z_1 = 0.950 00	z_1 = 0.950 00	z_1 = 0.950 00
$\langle \bar{C}_T \rangle$	2.995 364	3.988 875	4.978 342
$\langle \bar{C}_1 \rangle$	2.845 607	3.789 445	4.729 441
$\langle \bar{C}_2 \rangle$	0.149 757	0.199 430	0.248 901
$\langle \bar{C}_0 \rangle$	51.930 5	50.642 1	49.305 6
$m_1(\langle \bar{C}_1 \rangle, \langle \bar{C}_2 \rangle)$	3.041 664	4.153 577	5.324 414
$m_2(\langle \bar{C}_1 \rangle, \langle \bar{C}_2 \rangle)$	0.160 075	0.218 593	0.280 213
$10^{-2}R_1$	3.868 39	3.710 70	3.580 61
$10^{-2}R_2$	7.143 46	6.606 40	6.118 13
$\bar{\rho}$	1.123 120	1.162 126	1.200 011$_5$
H_1	36.175 ± 0.168	35.184 ± 0.348	34.405 ± 0.126
H_2	109.722 ± 0.376	106.546 ± 0.693	103.178 ± 0.251
$s(\rho$ fit)	0.000 032$_5$	0.000 065	0.000 024
$s(\bar{\rho})$	0.000 011	0.000 021	0.000 007
V_m(NaCl)	22.185	23.085	23.762
$V_m(Na_2SO_4)$	32.194	35.225	38.413
$V_m(H_2O)$	17.948	17.880	17.808$_5$
$10^{-9}\sigma_+$	0.656 94	0.651 54	0.660 86
$10^{-9}\sigma_-$	1.578 90	1.842 03	2.155 04
$10^{-2}S_A$	−88.80	−92.15	−92.09
$10^9(D_{11})_V$	1.5280 ± 0.0005	1.5370$_5$ ± 0.0007	1.5086 ± 0.0007
$10^9(D_{12})_V$	0.5999 ± 0.0008	0.8299 ± 0.0016$_5$	0.9941 ± 0.0009
$10^9(D_{21})_V$	−0.0087 ± 0.0002	−0.0026$_5$ ± 0.0003	0.0048 ± 0.0003
$10^9(D_{22})_V$	0.6275 ± 0.0002$_5$	0.5407 ± 0.0003	0.4686 ± 0.0003
$10^9(D_{11})_0$	1.6307	1.6851$_5$	1.7027
$10^9(D_{12})_0$	0.7023	0.9898	1.2183
$10^9(D_{21})_0$	−0.0033	0.0051	0.0150
$10^9(D_{22})_0$	0.6329	0.5491	0.4804

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

the derived solvent-fixed $(D_{ij})_0$ values, which can be interconverted using equations given elsewhere.[22,24,35] The quantities $m_1(\langle \bar{C}_1 \rangle, \langle \bar{C}_2 \rangle)$ and $m_2(\langle \bar{C}_1 \rangle, \langle \bar{C}_2 \rangle)$ are the molalities of NaCl and Na_2SO_4, respectively, corresponding to a solution having the molarities of both salts equal to the averages $\langle \bar{C}_1 \rangle$ and $\langle \bar{C}_2 \rangle$ of all four experiments at that overall composition.

Another quantity reported in Table 2 is S_A,[41] which is related to D_{ij}, R_i, and σ_+ and σ_- by

$$S_A = [D_{22} - D_{11} + (R_1/R_2)D_{12} - (R_2/R_1)D_{21}]/[(D_{11}D_{22} - D_{12}D_{21})(\sqrt{\sigma_+} + \sqrt{\sigma_-})] \quad (5)$$

where $\sigma_+ = s_1^2$ and $\sigma_- = s_2^2$ are the reciprocals of the two

Table 3. Comparison of Calculated Errors of Ternary Solution $(D_{ij})_V$ Values for $\{(z_1)\mathrm{NaCl} + (1 - z_1)\mathrm{Na_2SO_4}\}(\mathrm{aq})$ Solutions at $z_1 = 0.9500$ and 298.15 K[a]

quantity	value	value	value	value
$\langle \bar{C}_\mathrm{T} \rangle/\mathrm{mol \cdot dm^{-3}}$	0.499 920	0.999 568	1.499 913	1.999 036
$\langle \bar{C}_1 \rangle/\mathrm{mol \cdot dm^{-3}}$	0.474 926	0.949 599	1.424 935	1.899 094
$\langle \bar{C}_2 \rangle/\mathrm{mol \cdot dm^{-3}}$	0.024 994	0.049 969	0.074 978	0.099 942
z_1	0.950 00	0.950 01	0.950 01	$0.950\ 00_5$
$10^9\delta(D_{11})_V/\mathrm{m^2 \cdot s^{-1}}$ [b]	0.0005	0.0004	0.0008	0.0013
$10^9\delta(D_{12})_V/\mathrm{m^2 \cdot s^{-1}}$ [b]	0.0011	0.0006	0.0013	0.0020
$10^9\delta(D_{21})_V/\mathrm{m^2 \cdot s^{-1}}$ [b]	0.0002	0.0001_5	0.0003	0.0005
$10^9\delta(D_{22})_V/\mathrm{m^2 \cdot s^{-1}}$ [b]	0.0004	0.0002	0.0005	0.0007
$10^9\delta(D_{11})_V/\mathrm{m^2 \cdot s^{-1}}$ [c]	0.0021	0.0007	0.0010	0.0027
$10^9\delta(D_{12})_V/\mathrm{m^2 \cdot s^{-1}}$ [c]	0.0017	0.0014	0.0006	0.0014
$10^9\delta(D_{21})_V/\mathrm{m^2 \cdot s^{-1}}$ [c]	0.0007	0.0003	0.0007	0.0008
$10^9\delta(D_{22})_V/\mathrm{m^2 \cdot s^{-1}}$ [c]	0.0008	0.0006	0.0008	0.0011
$\langle \bar{C}_\mathrm{T} \rangle/\mathrm{mol \cdot dm^{-3}}$	2.995 364	3.988 875	4.978 342	
$\langle \bar{C}_1 \rangle/\mathrm{mol \cdot dm^{-3}}$	2.845 607	3.789 445	4.729 441	
$\langle \bar{C}_2 \rangle/\mathrm{mol \cdot dm^{-3}}$	0.149 757	0.199 430	0.248 901	
z_1	0.950 00	0.950 00	0.950 00	
$10^9\delta(D_{11})_V/\mathrm{m^2 \cdot s^{-1}}$ [b]	0.0005	0.0007	0.0007	
$10^9\delta(D_{12})_V/\mathrm{m^2 \cdot s^{-1}}$ [b]	0.0008	0.0016_5	0.0009	
$10^9\delta(D_{21})_V/\mathrm{m^2 \cdot s^{-1}}$ [b]	0.0002	0.0003	0.0003	
$10^9\delta(D_{22})_V/\mathrm{m^2 \cdot s^{-1}}$ [b]	0.0002_5	0.0003	0.0003	
$10^9\delta(D_{11})_V/\mathrm{m^2 \cdot s^{-1}}$ [c]	0.0021	0.0014	0.0039	
$10^9\delta(D_{12})_V/\mathrm{m^2 \cdot s^{-1}}$ [c]	0.0022	0.0010	0.0044	
$10^9\delta(D_{21})_V/\mathrm{m^2 \cdot s^{-1}}$ [c]	0.0006	0.0002	0.0014_5	
$10^9\delta(D_{22})_V/\mathrm{m^2 \cdot s^{-1}}$ [c]	0.0007	0.0006	0.0017	

[a] The quantity $z_1 = \langle \bar{C}_1 \rangle / \langle \bar{C}_\mathrm{T} \rangle$ is the solute molarity fraction of NaCl, and the total solute molarity is $\langle \bar{C}_\mathrm{T} \rangle = \langle \bar{C}_1 \rangle + \langle \bar{C}_2 \rangle$. [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 the $n - 1$ standard deviations.

eigenvalues of the diffusion coefficient matrix for a three-component system.[14,32]

If the σ_+ and σ_- values are nearly equal, or if $|10^{-2}S_A|$ is small, then the nonlinear least-squares analysis of the fringe position data may possibly not converge or the statistical errors of the D_{ij} values may be unusually large.[14] Since $\sigma_-/\sigma_+ = 1.7$ to 3.3 and $|10^{-2}S_A| = (62.05$ to $92.15)$ $\mathrm{m^{-1} \cdot s^{1/2}}$ for our experiments, no computational difficulties were encountered.

The reported uncertainties of the $(D_{ij})_V$ values given in Table 2 were estimated from the statistical analysis portion of the diffusion coefficient extraction program TFIT,[16] using standard propagation of error methods. However, as noted previously, we believe the true uncertainties are about four times larger than these statistical values.[10−19,42−44]

More realistic estimates of the $(D_{ij})_V$ errors may be made using various subsets of the diffusion experiments.[44] These error estimates use the $(D_{ij})_V$ values calculated from the four possible three-experiment subsets of the α_1 values at each constant $\langle \bar{C}_\mathrm{T} \rangle$ value. The results are reported in Table 3, where the values of $\delta(D_{ij})_V$ are the "$n - 1$" standard deviations that were derived by averaging the resulting values of each $(D_{ij})_V$ value from the four subset combinations.

The calculated uncertainties of most of the $(D_{ij})_V$ values from the subset analysis are generally two to five times their corresponding statistical errors, and are in general agreement with the four times "rule of thumb" estimate mentioned above. However, at $\langle \bar{C}_\mathrm{T} \rangle = 1.499\ 91\ \mathrm{mol \cdot dm^{-3}}$, the statistical and subset errors for the $(D_{ij})_V$ values are approximately equal, which indicates that the four diffusion experiments at this composition are particularly consistent internally.

These comparisons suggest that realistic estimates for the actual uncertainties of $(D_{11})_V$ and $(D_{12})_V$ for solutions with $z_1 = 0.9500$ are $\leq 0.004 \times 10^{-9}\ \mathrm{m^2 \cdot s^{-1}}$, and that those for the actual uncertainties of $(D_{22})_V$ and of $(D_{21})_V$ are $\leq 0.002 \times 10^{-9}\ \mathrm{m^2 \cdot s^{-1}}$. Except at the highest concentration of $\langle \bar{C}_\mathrm{T} \rangle = 4.978\ 32\ \mathrm{mol \cdot dm^{-3}}$, the derived uncertainties of most $(D_{ij})_V$ values are significantly smaller than those given by these upper limits. However, the $(D_{11})_V$ value at $\langle \bar{C}_\mathrm{T} \rangle = 0.999\ 57\ \mathrm{mol \cdot dm^{-3}}$ is probably low by $\approx 0.01 \times 10^{-9}\ \mathrm{m^2 \cdot s^{-1}}$, on the basis of plots of $(D_{ij})_V$ against $\langle \bar{C}_\mathrm{T} \rangle$ for the experiments with $z_1 = 0.9500$ and of plots of $(D_{ij})_V$ against z_1 for experiments at constant $\langle \bar{C}_\mathrm{T} \rangle$. These constant $\langle \bar{C}_\mathrm{T} \rangle$ plots are analogous to Figures 1 and 2 of ref 18, but with the new results for $z_1 = 0.9500$ added.

Discussion of the Dependence of the Values of $(D_{ij})_V$ on Solution Composition

Coupled diffusion significantly enhances the rate of diffusion of NaCl but makes only minor contributions to that of $\mathrm{Na_2SO_4}$ in these $\mathrm{NaCl + Na_2SO_4 + H_2O}$ solutions. The size of the NaCl cross-term diffusion coefficient increases as $\langle \bar{C}_\mathrm{T} \rangle$ increases for solutions with $z_1 = 0.9500$, becoming more than twice as large as the $\mathrm{Na_2SO_4}$ main-term diffusion coefficient at $\langle \bar{C}_\mathrm{T} \rangle = 4.978\ 34\ \mathrm{mol \cdot dm^{-3}}$, that is, $(D_{12})_V/(D_{22})_V = 2.12$. We similarly found that $(D_{12})_V/(D_{22})_V = 2.22$ for solutions with $z_1 = 0.9000$ when $\langle \bar{C}_\mathrm{T} \rangle = 5.007\ 09\ \mathrm{mol \cdot dm^{-3}}$.[19] At high $\langle \bar{C}_\mathrm{T} \rangle$, any given concentration gradient of $\mathrm{Na_2SO_4}$ will cause the flow of much more NaCl than of itself. In contrast, the $\mathrm{Na_2SO_4}$ flow resulting from any given concentration gradient of NaCl is very much smaller than the NaCl flow produced by the same gradient, and the $\mathrm{Na_2SO_4}$ flow will be decreased by coupled diffusion for concentrations $\langle \bar{C}_\mathrm{T} \rangle \leq 4.3\ \mathrm{mol \cdot dm^{-3}}$ when $z_1 = 0.9500$ because $(D_{21})_V$ is negative. However, it will be enhanced at higher concentrations where $(D_{21})_V$ becomes positive. We note that if comparisons are made using the solvent-fixed $(D_{ij})_0$ instead, then the switch in sign from negative to positive values of D_{21} is shifted to lower $\langle \bar{C}_\mathrm{T} \rangle$ values at both $z_1 = 0.9000$ and $z_1 = 0.9500$.

Measurements of the $(D_{ij})_V$ at $z_1 < 0.9$ are not available for $\langle \bar{C}_\mathrm{T} \rangle > 1.5\ \mathrm{mol \cdot dm^{-3}}$ and will probably not be possible at higher $\langle \bar{C}_\mathrm{T} \rangle$ for low values of z_1, owing to solubility limitations imposed by precipitation of $\mathrm{Na_2SO_4 \cdot 10H_2O(cr)}$.[20] However, examination of Figure 2 of Annunziata *et al.*,[18] which is a plot of $(D_{12})_V$ and $(D_{21})_V$ as a function of z_1 at constant $\langle \bar{C}_\mathrm{T} \rangle$, indicates that values of $(D_{21})_V$ should change from negative to positive at significantly lower concentrations of $\langle \bar{C}_\mathrm{T} \rangle$ ($\sim 2\ \mathrm{mol \cdot dm^{-3}}$) as $z_1 \rightarrow 0$.

Figure 1 contains plots of $(D_{ij})_V$ at 298.15 K for $z_1 = 0.9500$ with $\langle \bar{C}_\mathrm{T} \rangle = (0$ to $4.978\ 34)\ \mathrm{mol \cdot dm^{-3}}$. The $(D_{ij})_V$ values at $\langle \bar{C}_\mathrm{T} \rangle = 0$ (infinite dilution) were calculated from the limiting ionic electrical conductances[45] (after conversion of their values from international to absolute ohms), the equivalent concentration fractions, and various fundamental constants (Faraday's constant $F = 96\ 485\ \mathrm{C \cdot mol^{-1}}$ and the gas constant $R = 8.3145\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$) using the ternary solution analogues of the Nernst−Hartley equation.[24] These calculated Nernst−Hartley values are $D_{11} = 1.651_5 \times 10^{-9}\ \mathrm{m^2 \cdot s^{-1}}$, $D_{12} = 0.292_6 \times 10^{-9}\ \mathrm{m^2 \cdot s^{-1}}$, $D_{21} = -0.021_0 \times 10^{-9}\ \mathrm{m^2 \cdot s^{-1}}$, and $D_{22} = 1.081_4 \times 10^{-9}\ \mathrm{m^2 \cdot s^{-1}}$. (The Nernst−Hartley values are not subscripted for a reference frame because volume-fixed and solvent-fixed D_{ij} values become equal at infinite dilution.) The observed opposite signs for $(D_{12})_V$ and $(D_{21})_V$ when $\langle \bar{C}_\mathrm{T} \rangle \leq 4.3\ \mathrm{mol \cdot dm^{-3}}$ are predicted qualitatively by the Nernst−Hartley equation, which is Coulombically based. The switch of $(D_{21})_V$ from negative to positive values with increasing concentration at constant z_1 is not predicted because the Nernst−Hartley values of D_{ij} are concentration-independent infinite dilution

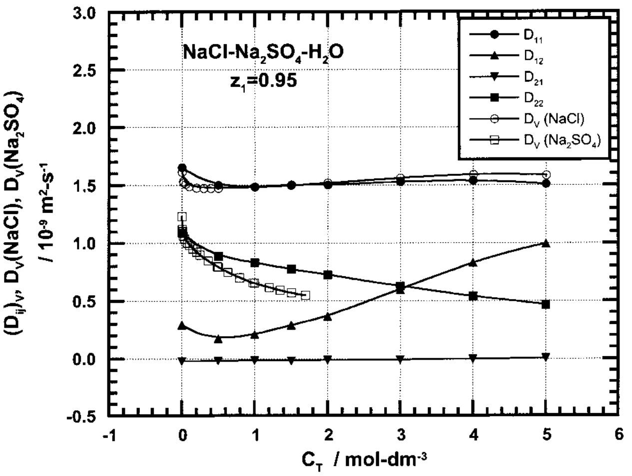

Figure 1. Plot of the volume-fixed mutual diffusion coefficients $(D_{ij})_V$ at 298.15 K for NaCl + Na_2SO_4 + H_2O solutions at total molarity concentrations of $\langle \bar{C}_T \rangle$ = (0.499 92 to 4.978 34) mol·dm^{-3}, along with the corresponding values at infinite dilution ($\langle \bar{C}_T \rangle = 0$) from the Nernst−Hartley equation, at constant NaCl molarity fractions of z_1 = 0.9500. Also plotted are values of D_V for the limiting binary solutions NaCl(aq),[16−19] including some of the points of Rard and Miller[6] at lower concentrations (z_1 = 1), and for Na_2SO_4(aq)[7,16−19,46] (z_1 = 0). In this and all subsequent figures, the smoothed curves are graphical smoothings generated internally by the plotting software KaleidaGraph, and they are only intended to guide the eye rather than being rigorous descriptions of the composition dependences of these properties.

values and would thus be horizontal straight lines in Figures 1 and 2.

In Figure 1, the diffusion coefficients of the limiting binary solutions NaCl(aq)[6,16−19] and Na_2SO_4(aq)[7,16−19,46] are compared with the main-term coefficients of the mixtures with z_1 = 0.9500. The $(D_{11})_V$ values are slightly higher than those of the NaCl(aq) binary solution diffusion coefficient D_V at lower molarities, but $D_V > (D_{11})_V$ when $\langle \bar{C}_T \rangle > 1.5$ mol·dm^{-3}. In contrast, the $(D_{22})_V$ values are higher than those of the Na_2SO_4(aq) D_V at all experimental concentrations. Furthermore, the $(D_{22})_V$ values for solutions with z_1 = 0.9500 are slightly higher than those with z_1 = 0.9000. However, the Nernst−Hartley equation values imply that $D_V > (D_{22})_V$ at infinite dilution for both z_1 = 0.9000 and z_1 = 0.9500, so there must be crossovers at some very low value of $\langle \bar{C}_T \rangle$.

There are sizable quantitative differences between the experimental $(D_{ij})_V$ values and the Nernst−Hartley values, especially for $(D_{12})_V$ and $(D_{22})_V$, as can be seen in Figure 1. At z_1 = 0.9500 the Nernst−Hartley D_{22} value is significantly higher than the experimental $(D_{22})_V$ value, by as much as 2.3 times at $\langle \bar{C}_T \rangle$ = 4.978 34 mol·dm^{-3}. In contrast, the $(D_{11})_V$ values have both a minimum and maximum as a function of $\langle \bar{C}_T \rangle$, which are also present for D_V of the limiting binary solution NaCl(aq). The $(D_{11})_V$ values thus exhibit more complicated behavior than the $(D_{22})_V$ values as a function of $\langle \bar{C}_T \rangle$, with the Nernst−Hartley D_{11} being higher than the experimental $(D_{11})_V$ by as much as 11% between infinite dilution and $\langle \bar{C}_T \rangle$ = 4.978 34 mol·dm^{-3}. However, in our experimental concentration range of $\langle \bar{C}_T \rangle$ = (0.499 92 to 4.978 34) mol·dm^{-3}, the $(D_{11})_V$ values only vary by 3%.

The much larger decreases for $(D_{22})_V$ than for $(D_{11})_V$ parallel the concentration dependences of the diffusion coefficients of the limiting binary solutions Na_2SO_4(aq) and NaCl(aq). Larger numerical differences between D_V of Na_2SO_4(aq) and $(D_{22})_V$ might have been expected, since Na_2SO_4 is present as the minority electrolyte constituent. It is also typical for values of trace diffusion coefficients to monotonically decrease as the overall concentration increases.[30]

The $(D_{21})_V$ values are small. For D_{21}, the Nernst−Hartley value is much closer to the experimental $(D_{21})_V$, mainly because both are small. Values of $(D_{12})_V$ change even more dramatically than the other three $(D_{ij})_V$ with changes of $\langle \bar{C}_T \rangle$ for solutions with z_1 = 0.9500. The experimental $(D_{12})_V$ values differ from the Nernst−Hartley cross-term D_{12} (a constant) by -0.120×10^{-9} m^2·s^{-1} at $\langle \bar{C}_T \rangle$ = 0.499 92 mol·dm^{-3} to $+0.702 \times 10^{-9}$ m^2·s^{-1} at $\langle \bar{C}_T \rangle$ = 4.978 34 mol·dm^{-3}. This is a large overall increase of 239% between infinite dilution and $\langle \bar{C}_T \rangle$ = 4.978 34 mol·dm^{-3}.

A large cross-term diffusion coefficient with a significant concentration dependence was also observed for {(z_1)NaCl + (1 − z_1)$MgCl_2$}(aq) at 298.15 K as z_1 → 1,[10,12] and at high $\langle \bar{C}_T \rangle$ the $(D_{12})_V$ values exceed both $(D_{11})_V$ and $(D_{22})_V$. Although the ternary solution Nernst−Hartley equations predict that $(D_{12})_V$ should have fairly large values as z_1 → 1, they do not predict that $(D_{12})_V$ will exceed both main-term coefficients.

Even more extreme values of cross-term diffusion coefficients may be found in the diffusion of aqueous mixtures of proteins with electrolytes. For example, for {(z_1)lysozyme chloride + (1 − z_1)NaCl}(aq) at 298.15 K, the $(D_{21})_V$ values range from 6×$(D_{22})_V$ to 18×$(D_{22})_V$ and from 75×$(D_{11})_V$ to 260×$(D_{11})_V$.[1,2] Considerable amounts of NaCl are thus cotransported during diffusion of lysozyme chloride.

For the {(z_1)sucrose + (1 − z_1)NaCl}(aq) and {(z_1)sucrose + (1 − z_1)KCl}(aq) systems at 298.15 K and at a constant sucrose concentration, the $(D_{21})_V$ values become large at higher electrolyte concentrations,[47] and extrapolation of the results to even higher electrolyte concentrations suggests that the $(D_{21})_V$ values probably will eventually exceed those of $(D_{11})_V$. However, the ternary solution Nernst−Hartley equations are only applicable to strong electrolyte mixtures and cannot be used to predict the diffusion coefficients of solutions containing a nonelectrolyte such as sucrose.

These examples suggest that a very large cross-term diffusion coefficient may be a common feature of diffusion in ternary aqueous systems where the two solutes exhibit significant chemical differences. In the above examples these “significant chemical differences” are differences in the valence of the anion or cation, large differences in ionic mobilities, or large size differences between the two solutes.

Cross-term diffusion coefficients in common-ion mixtures of electrolytes of the same charge type are expected from the ternary Nernst−Hartley equations to be small in general, and this is usually observed experimentally.[8,15,21,33,35] However, a large cross-term $(D_{ij})_V$ is predicted even for such symmetrical mixtures when the mobilities of two different ions of the same charge type differ by very large amounts, and is observed, for example, for {(z_1)LiCl + (1 − z_1)KCl}(aq) as z_1 → 0.[28]

The measured $(D_{ij})_V$ values are based on Fick’s second law, in which diffusion is described as arising from concentration gradients of the solutes. A more fundamental analysis indicates that the true driving forces for diffusion are the gradients of the chemical potentials of the solutes, which for brevity we will refer to as “thermodynamic factors”.[23−25] Combining the ternary Nernst−Hartley equations with these thermodynamic factors yields fairly accurate predictions of $(D_{ij})_V$ values for {(z_1)NaCl + (1 − z_1)$MgCl_2$}(aq) and {(z_1)NaCl + (1 − z_1)$SrCl_2$}(aq) at 298.15 K to total concentrations as high as $\langle \bar{C}_T \rangle$ ≈ (0.3 to 1.0) mol·dm^{-3}, depending of the mole ratio of the solutes.[48,49]

However, at high concentrations these thermodynamic factor corrections generally overpredict the $(D_{ij})_V$ values by large amounts.

Thermodynamic factors probably largely account for the large cross-term $(D_{12})_V$ for $\{(z_1)NaCl + (1 - z_1)Na_2SO_4\}$(aq) observed in the present study. Available thermodynamic data are being compiled and critically analyzed for this system,[50] which should yield the accurate chemical potential derivatives required for this analysis. We intend to provide such a thermodynamic analysis for all our diffusion coefficients for $\{(z_1)NaCl + (1 - z_1)Na_2SO_4\}$(aq) in a future report.

For $\{(z_1)$lysozyme chloride $+ (1 - z_1)NaCl\}$(aq) at 298.15 K,[1,2] the large $(D_{21})_V$ value can be largely attributed to excluded volume effects, because the gradient of the considerably larger lysozyme ion creates an interstitial gradient of the NaCl. Similar but smaller excluded volume effects may be present for $\{(z_1)$sucrose $+ (1 - z_1)NaCl\}$(aq), although the authors of that study did not discuss this factor.[47] Additional differences also arise because the lysozyme ion is positively charged whereas the sucrose molecule is uncharged, and the charge on the lysozyme ion should vary with pH.

It should be clear from the brief discussion in the five preceding paragraphs that large cross-term diffusion coefficients can arise from several different factors. The assignment of the relative importance of these factors for any particular system requires knowledge of the chemistry, thermodynamics, and size and structure of the diffusing species.

Simple empirical corrections, such as dividing the Nernst−Hartley D_{ij} values by the ratio of the viscosity of the solution to the solvent, will not bring their values into conformity with the experimental $(D_{ij})_V$ values or with the $(D_{ij})_0$ values. Both cross-term diffusion coefficients increase with increasing concentration, whereas $(D_{11})_V$ has both a minimum and maximum and $(D_{22})_V$ continuously decreases. Similarly, although 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, the resulting predicted D_{ij} values may be considerably different than the experimental values at high concentrations as noted above. Factors that directly affect the variation of the ionic mobilities with changing concentration, such as the electrophoretic effect and relaxation of the ionic atmosphere,[45] are neglected in these quite oversimplified models.

Figure 2 is a plot of $(D_{ij})_V$ at $z_1 = 0.9500$ along with D_V of the limiting binary solutions as a function of the stoichiometric ionic strength I_S. The curves for the NaCl diffusion coefficients D_V and $(D_{11})_V$ are fairly similar to the corresponding curves of Figure 1, which is not surprising, since the I_S values of the mixtures are only 10% greater than the $\langle \bar{C}_T \rangle$ and since ionic strength and molarity are identical for NaCl(aq). The $(D_{11})_V$ curve for solutions with $z_1 = 0.9500$ is intermediate between the corresponding curve for solutions with $z_1 = 0.9000$ and the NaCl(aq) binary solution D_V curve,[19] which also was expected. However, Figure 2 indicates that D_V of Na_2SO_4 is higher than $(D_{22})_V$ at all ionic strengths, which is the opposite of the order observed in Figure 1. Even more surprising, the D_V and $(D_{22})_V$ values of Na_2SO_4 for solutions with $z_1 = 0.9500$ are very nearly the same at higher ionic strengths, even though the ionic strength fractions of Na_2SO_4 in the mixtures are only 0.136. The $(D_{22})_V$ values for solutions with $z_1 = 0.9500$ are even closer to the D_V values ($z_1 = 0$) on this plot than they are for the corresponding solutions with $z_1 = 0.9000$,[19] for ionic strengths $I_S < 4.0$ mol·dm^{-3}, and $(D_{22})_V$ values at both of these z_1 values are very close to D_V ($z_1 = 0$) for $I_S \approx (1.0$ to $3.5)$ mol·dm^{-3}. Further, the $(D_{22})_V$ values for solutions with $z_1 = 0.9000$ and $z_1 = 0.9500$ nearly coincide when $I_S > 4.0$ mol·dm^{-3}, although their curves fall slightly below the D_V curve for Na_2SO_4.

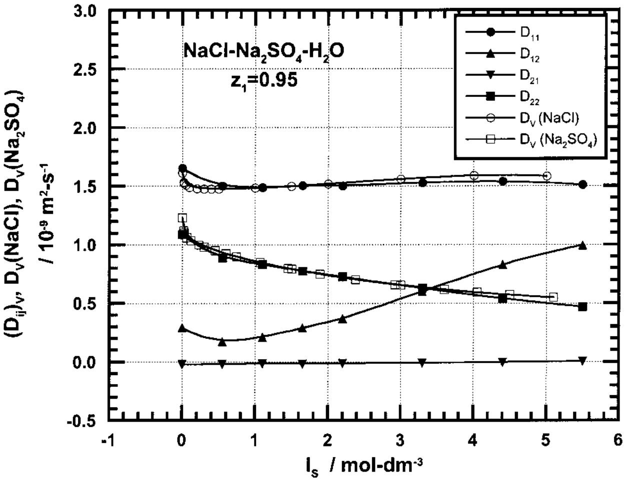

Figure 2. Plot of the volume-fixed mutual diffusion coefficients $(D_{ij})_V$ at 298.15 K for $NaCl + Na_2SO_4 + H_2O$ solutions as a function of the stoichiometric volumetric ionic strengths I_S, where $I_S = 1.1000\langle \bar{C}_T \rangle$, along with the corresponding values at infinite dilution ($I_S = 0$) from the Nernst−Hartley equation, at constant NaCl molarity fractions of $z_1 = 0.9500$. Also plotted are values of D_V for the limiting binary solutions NaCl(aq),[16−19] including some of the points of Rard and Miller[6] at lower concentrations ($z_1 = 1$), and for Na_2SO_4(aq)[7,16−19,46] ($z_1 = 0$).

Extrapolations of the Values of $(D_{ij})_V$ as $z_1 \rightarrow 1$ To Obtain $D^{tr}(SO_4^{2-})$ and the Limiting Values of $(D_{12})_V$

As pointed out in the Introduction, extrapolation of the NaCl main-term diffusion coefficient $(D_{11})_V$, measured at some type of constant concentration, to zero concentration fraction of NaCl ($z_1 \rightarrow 0$) yields the trace diffusion coefficient of the Cl$^-$ ion $D^{tr}(Cl^-)$ in the binary solution of Na_2SO_4(aq) at that same concentration. Correspondingly, the extrapolation of the Na_2SO_4 main-term diffusion coefficient $(D_{22})_V$, also at some type of constant concentration to zero concentration fraction of Na_2SO_4 ($z_1 \rightarrow 1$), yields the trace diffusion coefficient of the SO_4^{2-} ion in the binary solution of NaCl(aq) at that same concentration, $D^{tr}(SO_4^{2-})$. The other main-term diffusion coefficients become equal to their corresponding binary solution values as their solute composition fraction approaches unity; that is, $(D_{11})_V \rightarrow D_V$(NaCl) as $z_1 \rightarrow 1$ and $(D_{22})_V \rightarrow D_V(Na_2SO_4)$ as $z_1 \rightarrow 0$. Furthermore, the cross-term coefficient $(D_{12})_V \rightarrow 0$ as $z_1 \rightarrow 0$ and $(D_{21})_V \rightarrow 0$ as $z_1 \rightarrow 1$.

We previously reported $D^{tr}(SO_4^{2-})$ values at $C = I_S = (0.5, 1.0,$ and $1.5)$ mol·dm^{-3}.[16−18] Using our new results at $z_1 = 0.9500$, we now refine these earlier estimates and extend them to $C = I_S = (2.0$ to $5.0)$ mol·dm^{-3}. Similarly, we extrapolate $(D_{12})_V$ values to $z_1 \rightarrow 1$ at these concentrations. The earlier diffusion measurements also allowed us to estimate the $D^{tr}(Cl^-)$ values at $C = (0.5, 1.0,$ and $1.5)$ mol·dm^{-3} and $(D_{21})_V$ as $z_1 \rightarrow 0$.[16−18] We do not revise our earlier estimates of $D^{tr}(Cl^-)$ and of $(D_{21})_V$ as $z_1 \rightarrow 0$, because all of our subsequent measurements are restricted to high values of $z_1 = 0.9000$ and 0.9500; we still consider those reported extrapolated values as $z_1 \rightarrow 0$ to be accurate estimates.

Plots were made of the variation of $(D_{22})_V$ and $(D_{12})_V$ with various composition fraction scales at constant $\langle \bar{C}_T \rangle$, and these plots were then used to estimate the limiting values of these diffusion coefficients as $z_1 \rightarrow 1$. The four composition fraction scales used are the molarity fraction z_1 of NaCl,

$$z_1 = C_1/(C_1 + C_2) \tag{6}$$

the ionic strength fraction y_1 of NaCl,

$$y_1 = C_1/(C_1 + 3C_2) = z_1/(3 - 2z_1) \tag{7}$$

the ionic molarity ("osmolarity") fraction h_1 of NaCl,

$$h_1 = 2C_1/(2C_1 + 3C_2) = 2z_1/(3 - z_1) \tag{8}$$

and the equivalent concentration fraction e_1 of NaCl,

$$e_1 = C_1/(C_1 + 2C_2) = z_1/(2 - z_1) \tag{9}$$

Nonlinear graphical extrapolations of these two diffusion coefficients using each of these composition fractions yielded four separate $D^{tr}(SO_4^{2-})$ values and four values of the extrapolated $(D_{12})_V$ at each overall concentration. These extrapolated values for each quantity were then averaged. The same four types of extrapolations were also made using the commercial software package KaleidaGraph. All values of $(D_{22})_V$ or $(D_{12})_V$ measured at the same constant $\langle \bar{C}_T \rangle$ were used in making these extrapolations. Estimated extrapolated values from KaleidaGraph at higher ionic strengths of $I_S = (2.0 \text{ to } 5.0)$ mol·dm^{-3} are generally identical to the graphical estimates, since there is insufficient information for more than a linear extrapolation.

Our recommended $D^{tr}(SO_4^{2-})$ and the extrapolated $(D_{12})_V$ are given in Table 4, and each is the average of its two corresponding sets of four values. Examination of the precision of the $(D_{ij})_V$ values for individual compositions, of the agreement between extrapolated values using the different approaches, and of the smoothness of the individual $(D_{ij})_V$ values as a function of z_1 at each constant $\langle \bar{C}_T \rangle$ leads us to estimate that the uncertainties of the averaged extrapolated values given in Table 4 at $I_S = (0.5, 1.0, \text{ and } 1.5)$ mol·dm^{-3} are $\pm 0.01_5 \times 10^{-9}$ m^2·s^{-1}. At the higher ionic strengths of $I_S = (2.0 \text{ to } 5.0)$ mol·dm^{-3}, experimental $(D_{ij})_V$ values are available only at $z_1 = 0.9000$ and 0.9500 for any particular $\langle \bar{C}_T \rangle$. However, the differences between $(D_{22})_V$ values at $z_1 = 0.9000$ and 0.9500 at each constant $\langle \bar{C}_T \rangle$ vary smoothly with this concentration. This numerical value of this difference is $\Delta(D_{22})_V = 0.016 \times 10^{-9}$ m^2·s^{-1} at $\langle \bar{C}_T \rangle = 0.5$ mol·dm^{-3}, it increases regularly and gradually to $\Delta(D_{22})_V = 0.039 \times 10^{-9}$ m^2·s^{-1} at $\langle \bar{C}_T \rangle = 3.0$ mol·dm^{-3}, and it then decreases slightly at higher concentrations. The regular and slow variation of $\Delta(D_{22})_V$ with $\langle \bar{C}_T \rangle$ gives us confidence in the extrapolated values of $D^{tr}(SO_4^{2-})$ at $I_S = (2.0 \text{ to } 5.0)$ mol·dm^{-3}, and we estimate their uncertainties as $\pm 0.01_5 \times 10^{-9}$ m^2·s^{-1}.

Similar comparisons for $(D_{12})_V$ at $z_1 = 0.9000$ and 0.9500 indicate that $\Delta(D_{12})_V$ changes sign between $\langle \bar{C}_T \rangle = 3.0$ mol·dm^{-3} and $\langle \bar{C}_T \rangle = 4.0$ mol·dm^{-3}. This change in sign implies that the maximum in $(D_{12})_V$ as a function of z_1 at constant $\langle \bar{C}_T \rangle$, which is observed at $\langle \bar{C}_T \rangle = (0.5 \text{ to } 1.5)$ mol·dm^{-3} (see Figure 2 of ref 18), either must disappear when $\langle \bar{C}_T \rangle > 3.0$ mol·dm^{-3} or is shifted to $z_1 > 0.95$. Consequently, the extrapolated $(D_{12})_V$ values at high I_S are more uncertain than their corresponding extrapolated $D^{tr}(SO_4^{2-})$ values, possibly by $\pm 0.03 \times 10^{-9}$ m^2·s^{-1} or more.

Table 4. Values of $(D_{ij})_V$ for $\{(z_1)NaCl + (1 - z_1)Na_2SO_4\}(aq)$ Solutions as $z_1 \rightarrow 1$ at 298.15 K

quantity as $z_1 \rightarrow 1$	$10^9 D$/m^2·s^{-1}	interpretation (I_S is in mol·dm^{-3})
$(D_{11})_V$	$1.474_7 \pm 0.001$[a]	$D_V(NaCl)$ at $C_1 = I_S = 0.50$
$(D_{12})_V$	$0.16_6 \pm 0.01_5$	extrapolated value at $I_S = 0.50$
$(D_{21})_V$	0	by definition
$(D_{22})_V$	$0.90_6 \pm 0.01_5$	$D^{tr}(SO_4^{2-})$ at $I_S = 0.50$ [b]
$(D_{11})_V$	$1.482_2 \pm 0.001$[a]	$D_V(NaCl)$ at $C_1 = I_S = 1.00$
$(D_{12})_V$	$0.19_7 \pm 0.01_5$	extrapolated value at $I_S = 1.00$
$(D_{21})_V$	0	by definition
$(D_{22})_V$	$0.85_8 \pm 0.01_5$	$D^{tr}(SO_4^{2-})$ at $I_S = 1.00$ [b]
$(D_{11})_V$	$1.497_8 \pm 0.001$[a]	$D_V(NaCl)$ at $C_1 = I_S = 1.50$
$(D_{12})_V$	$0.27_7 \pm 0.01_5$	extrapolated value at $I_S = 1.50$
$(D_{21})_V$	0	by definition
$(D_{22})_V$	$0.80_8 \pm 0.01_5$	$D^{tr}(SO_4^{2-})$ at $I_S = 1.50$ [b]
$(D_{11})_V$	$1.518_2 \pm 0.001$[a]	$D_V(NaCl)$ at $C_1 = I_S = 2.00$
$(D_{12})_V$	$\approx 0.33_8$	extrapolated value at $I_S = 2.00$
$(D_{21})_V$	0	by definition
$(D_{22})_V$	$0.76_3 \pm 0.01_5$	$D^{tr}(SO_4^{2-})$ at $I_S = 2.00$ [b]
$(D_{11})_V$	$1.558_6 \pm 0.001$[a]	$D_V(NaCl)$ at $C_1 = I_S = 3.00$
$(D_{12})_V$	$\approx 0.59_1$	extrapolated value at $I_S = 3.00$
$(D_{21})_V$	0	by definition
$(D_{22})_V$	$0.66_6 \pm 0.01_5$	$D^{tr}(SO_4^{2-})$ at $I_S = 3.00$ [b]
$(D_{11})_V$	$1.586_8 \pm 0.001$[a]	$D_V(NaCl)$ at $C_1 = I_S = 4.00$
$(D_{12})_V$	$\approx 0.86_6$	extrapolated value at $I_S = 4.00$
$(D_{21})_V$	0	by definition
$(D_{22})_V$	$0.57_2 \pm 0.01_5$	$D^{tr}(SO_4^{2-})$ at $I_S = 4.00$ [b]
$(D_{11})_V$	$1.583_4 \pm 0.001$[a]	$D_V(NaCl)$ at $C_1 = I_S = 5.00$
$(D_{12})_V$	$\approx 1.01_9$	extrapolated value at $I_S = 5.00$
$(D_{21})_V$	0	by definition
$(D_{22})_V$	$0.50_0 \pm 0.01_5$	$D^{tr}(SO_4^{2-})$ at $I_S = 5.00$ [b]

[a] Values of $D_V(NaCl)$ are those determined previously at this laboratory with the Gosting diffusiometer.[16–19] As $z_1 \rightarrow 1$, C_1 and I_S become identical numerically. However, we distinguish these two quantities in column 3 because this does not happen at the other concentration fraction limit of $z_1 \rightarrow 0$, where $I_S = 3C_2$. Plots of $(D_{22})_V$ and $(D_{12})_V$ at constant $<\bar{C}_T>$, using the four composition fraction scales, were separately extrapolated to $z_1 \rightarrow 1$. Analogous extrapolations were made using the commercial software package KaleidaGraph. These two sets of $D^{tr}(SO_4^{2-})$ values and extrapolated $(D_{12})_V$ values were averaged to yield the recommended values given in this table. [b] Extrapolated.

Easteal and Woolf[31] measured $D^{tr}(SO_4^{2-})$ values in NaCl(aq) solutions at 298.15 K with a magnetically stirred diaphragm cell with ^{35}S-labeled sulfate ions using scintillation counting. Although this report was published at nearly the same time as our first paper on $(D_{ij})_V$ values of $\{(z_1)NaCl + (1 - z_1)Na_2SO_4\}(aq)$,[16] we previously overlooked the fact that it contained $D^{tr}(SO_4^{2-})$ values in NaCl(aq) that could be compared with our derived results. Four of their studied concentrations correspond exactly or closely to our $\langle \bar{C}_T \rangle$ values. At these four concentrations, their values are $D^{tr}(SO_4^{2-}) = 0.958 \times 10^{-9}$ m^2·s^{-1} at $I_S = 0.5001$ mol·dm^{-3}, $D^{tr}(SO_4^{2-}) = 0.924 \times 10^{-9}$ m^2·s^{-1} at $I_S = 1.000$ mol·dm^{-3}, $D^{tr}(SO_4^{2-}) = 0.768 \times 10^{-9}$ m^2·s^{-1} at $I_S = 2.000$ mol·dm^{-3}, and $D^{tr}(SO_4^{2-}) = 0.674 \times 10^{-9}$ m^2·s^{-1} at $I_S = 3.000$ mol·dm^{-3}. Our results at the two higher concentrations (Table 4), $D^{tr}(SO_4^{2-}) = (0.76_3 \pm 0.01_5) \times 10^{-9}$ m^2·s^{-1} at $I_S = 2.000$ mol·dm^{-3} and $D^{tr}(SO_4^{2-}) = (0.66_6 \pm 0.01_5) \times 10^{-9}$ m^2·s^{-1} at $I_S = 3.000$ mol·dm^{-3}, agree with theirs completely within the assigned uncertainties. However, the Easteal and Woolf $D^{tr}(SO_4^{2-})$ values are higher than our values by 5.7% and 7.7% at $I_S = (0.5 \text{ and } 1.0)$ mol·dm^{-3}, respectively.

Figure 3 gives a comparison of our values of $D^{tr}(SO_4^{2-})$, determined using optical interferometry, to those of Easteal and Woolf,[31] which were determined radiochemically. Also shown on this plot are our experimental values of $(D_{22})_V$ used for these extrapolations.

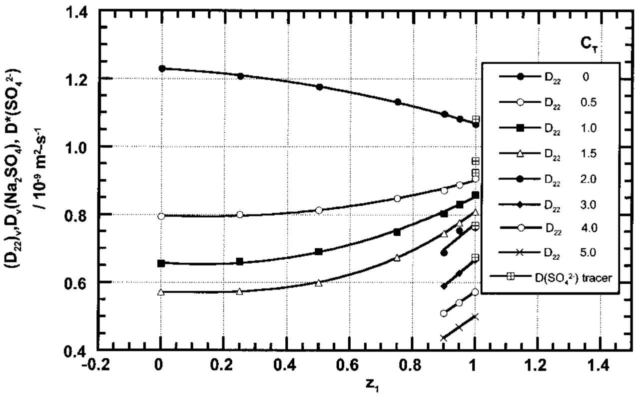

Figure 3. Plot of the Na_2SO_4 main-term volume-fixed mutual diffusion coefficients $(D_{22})_V$ at 298.15 K for NaCl + Na_2SO_4 + H_2O solutions at total molarity concentrations of $\langle \bar{C}_T \rangle = (0.5 \text{ to } 5.0)$ mol·dm^{-3}, along with the corresponding values at infinite dilution ($\langle \bar{C}_T \rangle = 0$) from the Nernst–Hartley equation, as a function of the NaCl molarity fraction z_1. Also plotted are the sulfate ion trace diffusion coefficients, $D^{tr}(SO_4^{2-})$, extrapolated from these experiments along with the tracer diffusion coefficients from Easteal and Woolf.[31]

We are reluctant to criticize experimental results from two such experienced and competent scientists, but we believe that our extrapolated $D^{tr}(SO_4^{2-})$ values in NaCl(aq) are more accurate than theirs[31] at $I_S = (0.5 \text{ and } 1.0)$ mol·dm^{-3}. We note that errors in $D^{tr}(SO_4^{2-})$ values from magnetically stirred diaphragm cell measurements, when present, generally become larger at lower concentrations and generally give high results,[30,45,51] whereas our uncertainties should be nearly independent of concentration. This systematic error results from the interaction of the diffusing electrolyte(s) with the electrical double layer at the walls of the diaphragm cell pores. However, this effect from the electrical double layer is usually only appreciable at lower concentrations, and is probably not significant by $I_S = (0.5 \text{ and } 1.0)$ mol·dm^{-3}. The concentrations of the nonradioactive carrier used in their experiments,[31] Na_2SO_4 or H_2SO_4, were probably too low to significantly affect their results.

Both Easteal and Woolf[31] and we[16−18] have pointed out that experimental $D^{tr}(SO_4^{2-})$ values at 298.15 K in solutions of NaCl(aq) and Na_2SO_4(aq) are nearly identical when the comparisons are made at the same volumetric ionic strength, and we[16−18] have also found this to be true for $D^{tr}(Cl^-)$. We repeat this comparison for $D^{tr}(SO_4^{2-})$ using our refined extrapolated values presented in Table 4, and also extend the comparisons to the higher ionic strengths. We also slightly refine our interpolated $D^{tr}(SO_4^{2-})$ values from the experimental results of Weingärtner *et al.*[52] in Na_2SO_4(aq) solutions by using graphical smoothing. *The first value given at each ionic strength is derived from our Rayleigh interferometric results, and the second is from the radiotracer measurements of Weingärtner et al.*[52] The new interpolated results, with $D^{tr}(SO_4^{2-})$ in units of m^2·s^{-1} and I_S in units of mol·dm^{-3}, are $D^{tr}(SO_4^{2-}) = (0.90_6 \pm 0.01_5) \times 10^{-9}$ and $0.93_9 \times 10^{-9}$ at $I_S = 0.5$, $D^{tr}(SO_4^{2-}) = (0.85_8 \pm 0.01_5) \times 10^{-9}$ and $0.86_9 \times 10^{-9}$ at $I_S = 1.0$, $D^{tr}(SO_4^{2-}) = (0.80_8 \pm 0.01_5) \times 10^{-9}$ and $0.81_3 \times 10^{-9}$ at $I_S = 1.5$, $D^{tr}(SO_4^{2-}) = 0.76_3 \times 10^{-9}$ and $0.74_7 \times 10^{-9}$ at $I_S = 2.0$, $D^{tr}(SO_4^{2-}) = 0.66_6 \times 10^{-9}$ and $0.63_9 \times 10^{-9}$ at $I_S = 3.0$, $D^{tr}(SO_4^{2-}) = 0.57_2 \times 10^{-9}$ and $0.54_4 \times 10^{-9}$ at $I_S = 4.0$, and $D^{tr}(SO_4^{2-}) = 0.50_0 \times 10^{-9}$ and $0.45_8 \times 10^{-9}$ at $I_S = 5.0$.

The uncertainties of radiotracer results are probably slightly larger than our average uncertainties. The $D^{tr}(SO_4^{2-})$ values from the two types of measurements in the two different ionic media agree well within their assigned uncertainties except probably at $I_S = 5.0$ mol·dm^{-3}, although the $D^{tr}(SO_4^{2-})$ values in Na_2SO_4(aq) are slightly higher than those in NaCl(aq) when $I_S < 1.5$ mol·dm^{-3}, but $D^{tr}(SO_4^{2-})$ in Na_2SO_4(aq) becomes lower when $I_S > 1.5$ mol·dm^{-3}. We previously pointed out that $D^{tr}(Cl^-)$ values in NaCl(aq) and Na_2SO_4(aq) are likewise nearly identical at $I_S = (1.5, 3.0, \text{ and } 4.5)$ mol·dm^{-3}.[16−18]

There is no obvious fundamental reason $D^{tr}(SO_4^{2-})$ should have nearly identical values in solutions of NaCl(aq) and Na_2SO_4(aq) at the same volumetric ionic strength, as have the $D^{tr}(Cl^-)$ values. Easteal and Woolf[31] suggested that the near equality of values of $D^{tr}(SO_4^{2-})$ in the two media may indicate that transport of SO_4^{2-} occurs largely in the form of $(NaSO_4)^-$ ion pairs. Although this may explain some of the observed behavior, it obviously cannot explain the near equality of $D^{tr}(Cl^-)$ in the two media. The reasons for the similarities of the trace diffusion coefficients in these two media are thus presently not completely understood.

Extrapolations of the Refractive Index Increments R_i^* as $z_1 \rightarrow 1$ and as $z_1 \rightarrow 0$ To Obtain Their Limiting (Trace) Values

For each set of experiments with a constant $\langle \bar{C}_T \rangle$, the refractive indices of all eight solutions from the four solution pairs were represented by the linear Taylor series expansion

$$\Delta n = R_1^*(C_1 - \langle \bar{C}_1 \rangle) + R_2^*(C_2 - \langle \bar{C}_2 \rangle) \qquad (10)$$

where Δn is the refractive index difference between an individual solution and a corresponding ternary solution with molarities of each solute equal to their overall averages $\langle \bar{C}_1 \rangle$ and $\langle \bar{C}_2 \rangle$. This equation was also applied to both limiting binary solutions by setting $(\bar{C}_i - \langle \bar{C}_i \rangle) = 0$ for the solute that is not present.

Our experiments yield accurate R_1 and R_2 values from their corresponding J values, as described in the Experimental Section. Values of R_1 and R_2 are reported in Table 2 and were also reported in the previous investigations[16−19] of the $\{(z_1)\text{NaCl} + (1 - z_1)\text{Na}_2\text{SO}_4\}$(aq) system at each overall composition, and the earlier studies include the limiting binary systems NaCl(aq) and Na_2SO_4(aq). We converted these R_1 and R_2 values to the corresponding R_1^* and R_2^* values using the relations $R_1^* = (\lambda/a)R_1$ and $R_2^* = (\lambda/a)R_2$, and they are summarized in Table 5. Figures 4 and 5 illustrate the variations of R_1^* and R_2^*, respectively, with $\langle \bar{C}_T \rangle$ at constant values of z_1. The concentration dependences of these two quantities are very similar, with R_2^* being about twice as large as R_1^*. Both R_1^* and R_2^* vary regularly and smoothly with $\langle \bar{C}_T \rangle$ and increase with z_1 at constant $\langle \bar{C}_T \rangle$.

The uncertainties in the R_1^* and R_2^* values depend mainly on the experimental uncertainties in the determinations of a, J, and the concentration differences ΔC_1 and ΔC_2. In the course of our extensive investigations of the $\{(z_1)\text{NaCl} + (1 - z_1)\text{Na}_2\text{SO}_4\}$(aq) system, we measured the a distance of cell C-1235-H on three separate occasions and observed a maximum difference between these three values of 7 μm (0.028%).[16−18] Examination of the agreement between the seven sets of four values of J(exptl) and J(calc) reported in Table 1 indicates that the uncertainty of a measured J value is almost always less than 0.1 fringe ($\leq 0.14\%$), and frequently is several times smaller, with at least part of the uncertainty arising from minor errors in the concentration differences ΔC_1 and ΔC_2 from the solu-

Table 5. Refractive Index Increments of NaCl(aq), Na_2SO_4(aq), and $\{(z_1)NaCl + (1 - z_1)Na_2SO_4\}$(aq) Solutions at 298.15 K

$\langle \bar{C}_T \rangle$/mol·dm^{-3}	z_1	R_1*/ mol^{-1}·dm^3	R_2*/ mol^{-1}·dm^3
0.499 98	1	0.009 787	0.020 11 ± 0.000 03[a]
0.499 92	0.950 00	0.009 742	0.020 02
0.500 02	0.900 00	0.009 686	0.019 86
0.499 99$_5$	0.749 99	0.009 558	0.019 57
0.500 00	0.500 04$_5$	0.009 324	0.019 11
0.500 00	0.249 98	0.009 134	0.018 70
0.500 00	0	0.008 96 ± 0.000 01[b]	0.018 33
0.500 00	0	0.008 96 ± 0.000 01[b]	0.018 27
1.001 38	1	0.009 462	0.018 95 ± 0.000 03[a]
0.999 57	0.950 01	0.009 394	0.018 81
1.000 25	0.900 03	0.009 315	0.018 60
0.999 30	0.750 43	0.009 125	0.018 18
0.999 95$_5$	0.500 02	0.008 789	0.017 53
0.999 98	0.250 00	0.008 528	0.016 98
1.000 02	0	0.008 28 ± 0.000 01[b]	0.016 45
0.999 99	0	0.008 28 ± 0.000 01[b]	0.016 36
1.500 02	1	0.009 144	0.017 96 ± 0.000 10[a]
1.499 91	0.950 01	0.009 115	0.017 82
1.499 01	0.900 00	0.008 971	0.017 52
1.499 44	0.749 93	0.008 714	0.017 02
1.499 91$_5$	0.500 00	0.008 333	0.016 23
1.500 21	0.250 00	0.008 003	0.015 55
1.500 07	0	0.007 70 ± 0.000 02[b]	0.014 94
1.500 01	0	0.007 70 ± 0.000 02[b]	0.014 85
1.999 94	1	0.008 931	≈0.0172[a]
1.999 04	0.950 00$_5$	0.008 860	0.016 96
2.000 04	0.900 01	0.008 747	0.016 75
3.000 19	1	0.008 556	≈0.0158[a]
2.995 36	0.950 00	0.008 427	0.015 56
3.000 28	0.900 00	0.008 314	0.015 33
4.000 17$_5$	1	0.008 228	≈0.0148[a]
3.988 87$_5$	0.950 00	0.008 084	0.014 39
4.001 01	0.900 00	0.007 938	0.014 01
4.999 38	1	0.007 958	≈0.0136[a]
4.978 34	0.950 00	0.007 800	0.013 33
5.007 09	0.900 00	0.007 625	0.013 01

[a] Values extrapolated to $z_1 = 1$ to yield $(R_2^*)^{tr}$. All values of R_1* and R_2* reported in this table pertain to the 543.366 nm laser green line used for the interferometric measurements. [b] Values extrapolated to $z_1 = 0$ to yield $(R_1^*)^{tr}$.

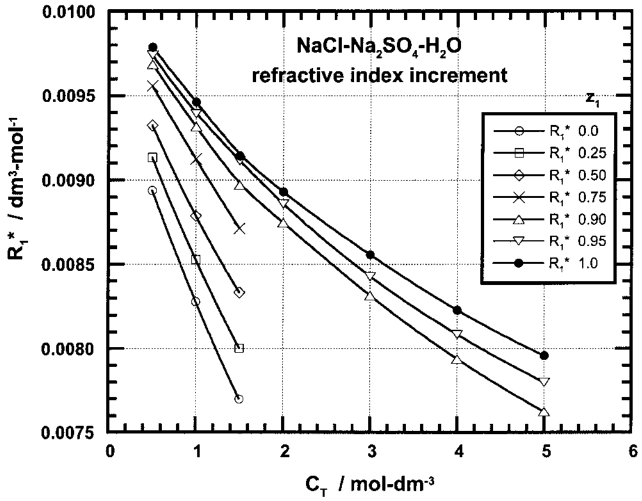

Figure 4. Plot of the refractive index increment with regard to the concentration increment of NaCl, R_1*, at 298.15 K of NaCl + Na_2SO_4 + H_2O as a function of the total molarity $\langle C_T \rangle$ at fixed values of the NaCl molarity fraction z_1.

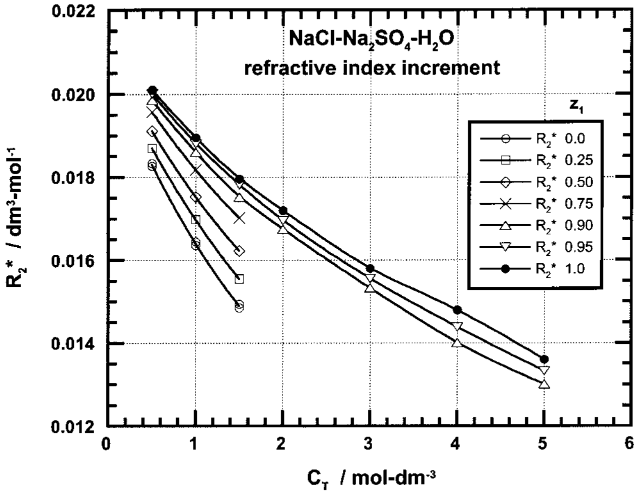

Figure 5. Plot of the refractive index increment with regard to the concentration increment of Na_2SO_4, R_2*, at 298.15 K of NaCl + Na_2SO_4 + H_2O as a function of the total molarity $\langle \bar{C}_T \rangle$ at fixed values of the NaCl molarity fraction z_1. Extrapolated values of R_2* at $z_1 = 1$ for $\langle \bar{C}_T \rangle \geq 2.0$ mol·dm^{-3} are somewhat uncertain because they are based on results at only two values of z_1.

tion preparations and density measurements. At three of the average concentrations of Na_2SO_4(aq) summarized in Table 5, there are duplicate determinations of R_2*, which involve several different Na_2SO_4(aq) stock solutions and several different cells. Comparison of these duplicate measurements should give a reasonable measure of the uncertainties in R_2* from all sources of error. The pairs of values of R_2* at the three total concentrations agree to $\Delta R_2^* = (6 \times 10^{-5}$ to $9 \times 10^{-5})$ mol^{-1}·dm^3 (≤0.6%). We expect the uncertainties for R_1* to be slightly less than this, because the mass of anhydrous NaCl added to each solution should be determined more accurately than the added mass of Na_2SO_4(aq) stock solution, and consequently ΔC_1 is generally known slightly more accurately than ΔC_2.

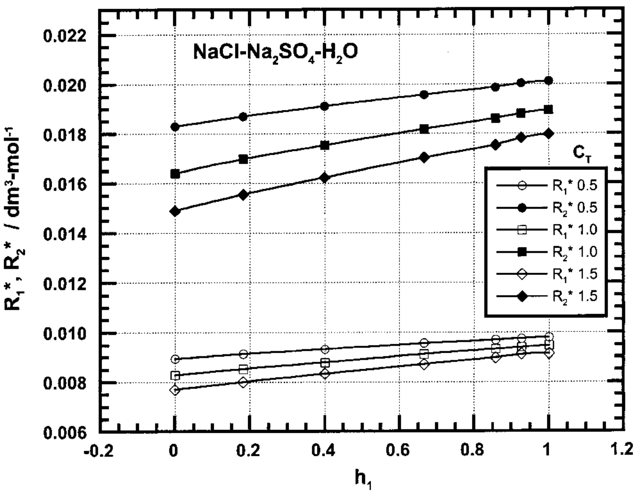

Figure 6. Plot of the refractive index increments with regard to the concentration increments of NaCl, R_1*, and of Na$_2$SO$_4$, R_2*, at 298.15 K of NaCl + Na$_2$SO$_4$ + H$_2$O at constant total molarity $\langle\bar{C}_T\rangle$ as a function of the NaCl ionic molarity (osmolarity) fraction h_1.

Plots of R_1* and R_2*, at constant total concentration $\langle\bar{C}_T\rangle$, were made as functions of the various concentration fractions z_1, y_1, h_1, and e_1. The plots against y_1 showed significant curvature, especially at low y_1, and were not conducive to accurate extrapolations to obtain limiting values of R_1*. The other three types of plots showed much smaller deviations from linearity, and their extrapolated R_1* and R_2* values were averaged to yield the recommended results given in Table 5. The deviations from linearity of the plots of R_1* and R_2* against z_1 were slightly concave, whereas the deviations for the analogous plots against e_1 were slightly convex. However, the plots against h_1, see Figure 6, generally show the least curvature, and those for R_2* are almost linear at $\langle\bar{C}_T\rangle$ = (0.5, 1.0, and 1.5) mol·dm^{-3}. At higher concentrations, the limiting R_2* values could only be obtained by linear extrapolations because of the limited range of composition fractions investigated.

The R_1* and R_2* values in Table 5 are refractive index increments with regard to the concentration increments; that is, $R_1^* = \Delta n/\Delta C_1$ and $R_2^* = \Delta n/\Delta C_2$, which differ slightly from the differential quantities dn/dC_1 and dn/dC_2 that have more theoretical interest. However, on the basis of our experience with the NaCl + KCl + H$_2$O system,[15] we expect the difference between the refractive index increments and refractive index derivatives to be small and of the order of the uncertainties in their determination. Thus, we assume that $R_1^* \approx \mathrm{d}n/\mathrm{d}C_1$ and $R_2^* \approx \mathrm{d}n/\mathrm{d}C_2$.

Refractive indices may be combined with densities to calculate molar refractivities, which at infinite dilution are additive ionic properties.[53] Our experimental measurements were made for solution pairs, with the sizes of the concentration differences being appropriate for the determination of accurate diffusion coefficients. Thus, they yield Δn values rather than values of n and cannot be converted to molar refractivities without a large number of additional measurements. Our observation that the R_i* values for the {(z_1)NaCl + (1 − z_1)Na$_2$SO$_4$}(aq) system are nearly linear functions of the ionic molarity fraction h_i at constant total molarity should be useful for estimating values of R_i* for mixtures from the corresponding values for the limiting binary solutions. However, at present it is not known if this mixing approximation is valid in general or whether it is merely a peculiarity of the {(z_1)NaCl + (1 − z_1)Na$_2$SO$_4$}(aq) system.

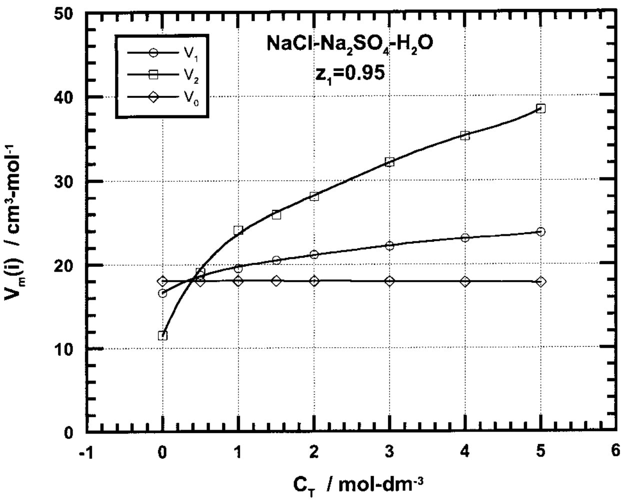

Figure 7. Plot of the partial molar volumes at 298.15 K of NaCl, V_m(NaCl), of Na$_2$SO$_4$, V_m(Na$_2$SO$_4$), and of H$_2$O, V_m(H$_2$O), for NaCl + Na$_2$SO$_4$ + H$_2$O solutions as a function of $\langle\bar{C}_T\rangle$ and at constant NaCl molarity fractions of z_1 = 0.9500. Partial molar volumes at infinite dilution ($\langle\bar{C}_T\rangle$ = 0) were calculated from the ionic values given in footnote d of Table 9. In the internal legend for this figure, 1 denotes NaCl, 2 denotes Na$_2$SO$_4$, and 0 denotes H$_2$O.

Table 6. Supplemental Densities of NaCl(aq) and Na$_2$SO$_4$(aq) at 298.15 K[a]

system	C/mol·dm^{-3}	ρ/g·cm^{-3}	C/mol·dm^{-3}	ρ/g·cm^{-3}
NaCl(aq)	0.406 53	1.013 584$_5$	0.593 45	1.021 050
NaCl(aq)	0.906 53	1.033 389	1.093 39$_5$	1.040 632
NaCl(aq)	1.441 18	1.054 082	1.558 84	1.058 567
NaCl(aq)	1.900 05$_5$	1.071 505	2.099 72$_5$	1.078 990
NaCl(aq)	1.906 57	1.071 762	2.093 51	1.078 776
NaCl(aq)	2.906 70	1.108 831	3.093 70$_5$	1.115 672
NaCl(aq)	3.906 68	1.144 926	4.093 56	1.151 586
NaCl(aq)	4.905 85	1.180 184	5.092 76	1.186 770
Na$_2$SO$_4$(aq)	0.452 58	1.052 444	0.547 40	1.063 656
Na$_2$SO$_4$(aq)	1.443 27	1.164 248	1.556 09	1.176 430

[a] These densities were measured using the Mettler-Parr DMA/40 vibrating tube densimeter and are needed for the evaluation of some of the parameters of Table 7.

Extrapolations of the Partial Molar Volumes of NaCl as $z_1 \rightarrow 0$ and of Na$_2$SO$_4$ to $z_1 \rightarrow 1$ To Obtain their Limiting (Trace) Values

Figure 7 is a plot of the partial molar volumes V_m(NaCl), V_m(Na$_2$SO$_4$), and V_m(H$_2$O) for solutions with z_1 = 0.9500. The curve for V_m(Na$_2$SO$_4$) decreases more rapidly with decreasing concentration below about 1.0 mol·dm^{-3} than at higher concentrations, which parallels the behavior of its binary aqueous solution. Values of V_m(NaCl) and V_m(Na$_2$SO$_4$) at infinite dilution were calculated for the binary solutions using the standard partial molar volumes tabulated by Millero.[54] Although the V_m(NaCl), V_m(Na$_2$SO$_4$), and V_m(H$_2$O) values are comparable in size at $\langle\bar{C}_T\rangle \approx$ 0.5 mol·dm^{-3}, the V_m(NaCl) and V_m(Na$_2$SO$_4$) values both increase with increasing concentration whereas those of V_m(H$_2$O) decrease. Also, V_m(Na$_2$SO$_4$) increases much more rapidly than V_m(NaCl), and at $\langle\bar{C}_T\rangle$ = 5.0 mol·dm^{-3} their ratio is {V_m(Na$_2$SO$_4$)/V_m(NaCl)} = 1.617, which is nearly identical to the ratio {V_m(Na$_2$SO$_4$)/V_m(NaCl)} = 1.622 when z_1 = 0.9000.[19]

The parameters of eq 2 were also evaluated for the binary solutions NaCl(aq) and Na$_2$SO$_4$(aq) using our published densities,[16−19] along with some additional densities for these solutions which are reported in Table 6. Table 7 lists the resulting values of H_1, H_2, and $\bar{\rho}$, and their

Table 7. Parameters for Taylor Series Representation of the Densities of NaCl(aq) and Na_2SO_4(aq) at 298.15 K[a]

system	$<\bar{C}>$/mol·dm^{-3}	$\bar{\rho}$/g·cm^{-3}	H_1/g·mol^{-1}	H_2/g·mol^{-1}	$s(\rho$ fit)/g·cm^{-3}
NaCl(aq)	0.499 98$_5$	1.017 307 ± 0.000 014	39.757 ± 0.015		4.0×10^{-5}
NaCl(aq)	1.000 67	1.037 050$_5$ ± 0.000 011	38.867 ± 0.118		3.1×10^{-5}
NaCl(aq)	1.500 01$_5$	1.056 319$_5$ ± 0.000 005	38.208 ± 0.059		1.3×10^{-5}
NaCl(aq)	1.999 96	1.075 237$_5$ ± 0.000 015	37.455 ± 0.159		4.3×10^{-5}
NaCl(aq)	3.000 20	1.112 252 ± 0.000 004	36.522 ± 0.043		1.1×10^{-5}
NaCl(aq)	4.000 15	1.148 264 ± 0.000 006	35.597 ± 0.061		1.6×10^{-5}
NaCl(aq)	4.999 34	1.183 488 ± 0.000 013	35.077 ± 0.136		3.5×10^{-5}
Na_2SO_4(aq)	0.500 00	1.058 054 ± 0.000 006		117.918$_5$ ± 0.120	1.6×10^{-5}
Na_2SO_4(aq)	1.000 00$_5$	1.115 416 ± 0.000 004		112.008 ± 0.082	1.1×10^{-5}
Na_2SO_4(aq)	1.499 92	1.170 364$_5$ ± 0.000 009		108.063 ± 0.178	2.7×10^{-5}

[a] Four to six densities were used for the evaluation of each H_1 and H_2 value.

Table 8. Limiting and Trace Density Increments H_i for $\{(z_1)NaCl + (1 - z_1)Na_2SO_4\}$(aq) Solutions as $z_1 \rightarrow 1$ and $z_1 \rightarrow 0$ at 298.15 K[a]

$<\bar{C}_T>$ mol·dm^{-3}	z_1	H_1 g·mol^{-1}	H_2 g·mol^{-1}	ρ g·cm^{-3}
0.5000	1	39.8$_4$ ± 0.1 (se)	123.3 ± 0.5 (tr)	1.017 308 ± 0.000 014
0.5000	0	37.6$_3$ ± 0.1 (tr)	117.7 ± 0.5 (se)	1.058 054 ± 0.000 006
1.0000	1	38.8$_8$ ± 0.2 (se)	119.4 ± 0.4 (tr)	1.037 024 ± 0.000 011
1.0000	0	35.4$_8$ ± 0.1 (tr)	112.0 ± 0.4 (se)	1.115 415 ± 0.000 004
1.5000	1	38.1$_9$ ± 0.1 (se)	116.7 ± 0.3 (tr)	1.056 316 ± 0.000 005
1.5000	0	33.9$_4$ ± 0.1 (tr)	107.8 ± 0.3 (se)	1.170 373 ± 0.000 009
2.0000	1	37.5 ± 0.2 (se)	≈114.7 (tr)	1.075 239 ± 0.000 015
3.0000	1	36.5 ± 0.1 (se)	≈110.5 (tr)	1.112 245 ± 0.000 004
4.0000	1	35.5 ± 0.1 (se)	≈107.8 (tr)	1.148 259 ± 0.000 006
5.0000	1	35.1 ± 0.1 (se)	≈104.3 (tr)	1.183 511 ± 0.000 013

[a] Values of H_1 and H_2 and their uncertainties were evaluated graphically, whereas ρ values and their uncertainties were calculated from the parameters listed in Table 7. Trace H_1 or H_2 values are denoted with (tr); those labeled (se) are for the binary solution of that single electrolyte.

statistical uncertainties. Four or more densities were used for the evaluation of each set of parameters.

Plots of the density increments of eq 2, H_1 and H_2, at constant total concentration $\langle\bar{C}_T\rangle$ were made as functions of the various concentration fractions z_1, y_1, h_1, and e_1. These plots were then used to obtain values of the trace density increments H_1^{tr} and H_2^{tr}, along with H_1 and H_2 values for the limiting binary solutions. The densities of the solutions at each of the fixed $\langle\bar{C}_T\rangle$ values in the limits as $z_1 \rightarrow 0$ and as $z_1 \rightarrow 1$ are also needed to calculate the trace partial volumes of the two solutes, V_m^{tr}(NaCl) and $V_m^{tr}(Na_2SO_4)$. However, for solutions with the same $\langle\bar{C}_T\rangle$, the density of the mixed electrolyte solution becomes equal to the density of the corresponding NaCl(aq) solution as $z_1 \rightarrow 1$, and becomes equal to that of the corresponding Na_2SO_4(aq) solution as $z_1 \rightarrow 0$, all at the same $\langle\bar{C}_T\rangle$. These binary solution densities and their uncertainties were calculated from the parameters of Table 7.

Table 8 gives a summary of the evaluated limiting and trace parameters of eq 2 for $\{(z_1)NaCl + (1 - z_1)Na_2SO_4\}$(aq), which were determined as described in the previous paragraph. At $\langle\bar{C}_T\rangle$ = (0.5000, 1.0000, and 1.5000) mol·dm^{-3}, the H_1 and H_2 parameters for the limiting binary solutions NaCl(aq) and Na_2SO_4(aq) were taken from the graphical evaluations in preference to their measured values as reported in Table 7, since the graphical evaluations smooth out any minor errors in their determination. There is a difference of $\leq$0.26 g·mol^{-1} between the Table 7 and Table 8 H_1 and H_2 values, which is comparable to the assigned uncertainties. Uncertainty limits for H_1, H_2, H_1^{tr}, and H_2^{tr} in Table 8 are based upon the consistency of their values as a function of the composition fractions, for all results at that particular constant $\langle\bar{C}_T\rangle$. At the higher concentrations of $\langle\bar{C}_T\rangle$ = (2.0000 to 5.0000) mol·dm^{-3}, the H_1 and H_2^{tr} parameters were obtained by linear extrapolation, since experimental results are available only at z_1 = 0.9000, 0.9500, and 1.

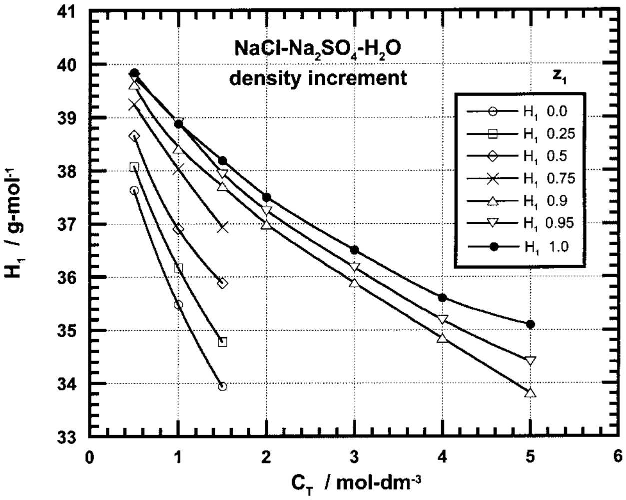

Figure 8. Plot of the density increment with regard to the concentration increment of NaCl, H_1, at 298.15 K of NaCl + Na_2SO_4 + H_2O solutions as a function of the total molarity $\langle\bar{C}_T\rangle$ at fixed values of the NaCl molarity fraction z_1. At $\langle\bar{C}_T\rangle$ = (0.5 and 1.0) mol·dm^{-3}, the few observed crossovers are probably not realistic, since they are within the assigned uncertainties.

Figures 8 and 9 are plots of H_1 and H_2, respectively, at constant z_1 as a function of $\langle\bar{C}_T\rangle$. Values of H_2 are approximately three times larger than H_1. These two properties vary regularly with $\langle\bar{C}_T\rangle$ and with z_1, except for some minor overlap of curves when $\langle\bar{C}_T\rangle$ = (0.5000 and 1.0000) mol·dm^{-3}. These apparent crossovers at lower concentrations are within the uncertainties of the H_1 and H_2 values, and probably are not real.

The H_1 and H_2 values for $\{(z_1)NaCl + (1 - z_1)Na_2SO_4\}$(aq) at constant values of $\langle\bar{C}_T\rangle$ have significant curvature as functions of the equivalence fraction e_i and, especially, as a function of the ionic strength fraction y_i. However, the

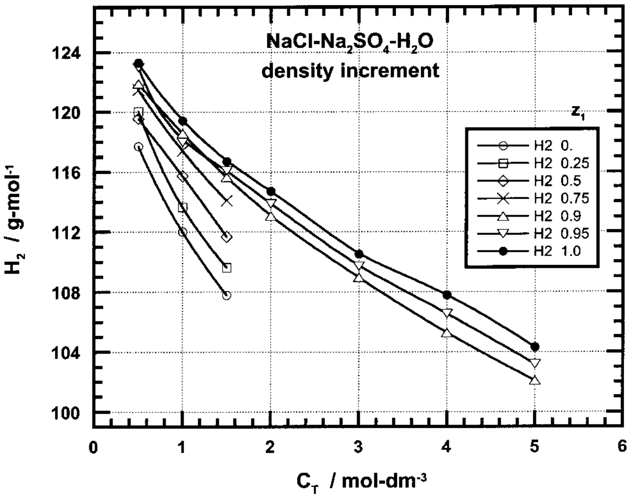

Figure 9. Plot of the density increment with respect to the concentration increment of Na_2SO_4, H_2, at 298.15 K of NaCl + Na_2SO_4 + H_2O solutions as a function of the total molarity $\langle \bar{C}_T \rangle$ at fixed values of the NaCl molarity fraction z_1. At $\langle \bar{C}_T \rangle$ = (0.5 and 1.0) mol·dm^{-3} the few observed crossovers are probably not realistic, since they are within the assigned uncertainties.

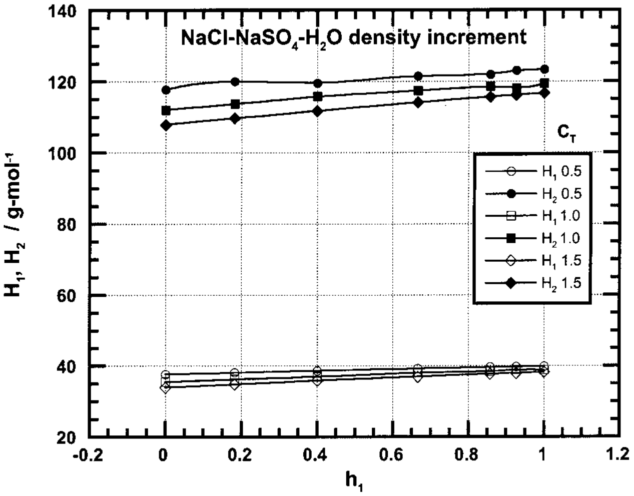

Figure 10. Plot of the density increments with regard to the concentration increments of NaCl, H_1, and of Na_2SO_4, H_2, at 298.15 K of NaCl + Na_2SO_4 + H_2O solutions at constant values of $\langle \bar{C}_T \rangle$ as a function of the NaCl ionic molarity (osmolarity) fraction h_1.

corresponding plots of H_1 and H_2 against the ionic molarity fraction h_i and against the molarity fraction z_i have only slight curvature. Figure 10 is a plot of H_1 and H_2 as a function of h_1 at constant $\langle \bar{C}_T \rangle$. We note that the values of R_i* for this system at constant total molarity were also found to be nearly linear functions of h_i.

Our measurements of H_1 and H_2 were made at constant $\langle \bar{C}_T \rangle$, and these two parameters were found to be nearly linear functions of z_1 and h_1. Analogously, V_m(NaCl) and $V_m(Na_2SO_4)$ at constant $\langle \bar{C}_T \rangle$ are also nearly linear functions of these two composition fractions, although the slopes are opposite in sign to those of the H_1 and H_2 plots. This can be understood by examining eq 3, which was used for calculation of the V_m(NaCl) and $V_m(Na_2SO_4)$ values. The denominator of eq 3 changes with concentration fraction by ≤0.26% at $\langle \bar{C}_T \rangle$ = 0.5 mol·dm^{-3} to ≤0.83% at $\langle \bar{C}_T \rangle$ = 1.5 mol·dm^{-3}, which implies that V_m(NaCl) varies with composition fraction nearly as $(M_1 - H_1)$ and $V_m(Na_2SO_4)$ varies with composition fraction nearly as $(M_2 - H_2)$.

Table 9. Limiting and Trace Partial Molar Volumes of NaCl and Na_2SO_4 for the $\{(z_1)NaCl + (1 - z_1)Na_2SO_4\}(aq)$ System at 298.15 K

quantity (C is in mol·dm^{-3})	$V_m(i)^a$ cm^3·mol^{-1}	$V_m(i)^b$ cm^3·mol^{-1}	$V_m(i)^c$ cm^3·mol^{-1}
$V_m(NaCl)^{se}$ at $C = 0$			16.61[d]
$V_m(NaCl)^{se}$ at $C = 0.5000$	$18.6_5 \pm 0.1_0$	18.5_8	18.6
$V_m(NaCl)^{se}$ at $C = 1.0000$	$19.6_0 \pm 0.2_0$	19.5_2	19.6
$V_m(NaCl)^{se}$ at $C = 1.5000$	$20.2_7 \pm 0.1$	20.2_6	20.3
$V_m(NaCl)^{se}$ at $C = 2.0000$	20.9 ± 0.2	20.8_9	20.9
$V_m(NaCl)^{se}$ at $C = 3.0000$	21.9 ± 0.1	21.9_1	21.9
$V_m(NaCl)^{se}$ at $C = 4.0000$	22.8 ± 0.1	22.7_0	22.7_5
$V_m(NaCl)^{se}$ at $C = 5.0000$	23.2 ± 0.1	23.3_1	23.2
$V_m(Na_2SO_4)^{se}$ at $C = 0$			11.56[d]
$V_m(Na_2SO_4)^{se}$ at $C = 0.5000$	$24.3_6 \pm 0.5_0$	24.4_5	24.4
$V_m(Na_2SO_4)^{se}$ at $C = 1.0000$	$29.9_3 \pm 0.4_0$	29.8_6	29.9
$V_m(Na_2SO_4)^{se}$ at $C = 1.5000$	$33.9_4 \pm 0.3_0$	33.9_4	33.9
$V_m(NaCl)^{tr}$ at $C = 0.5000$	$20.8_3 \pm 0.1_0$		20.8
$V_m(NaCl)^{tr}$ at $C = 1.0000$	$22.8_8 \pm 0.1_0$		22.9
$V_m(NaCl)^{tr}$ at $C = 1.5000$	$24.2_9 \pm 0.1_0$		24.3
$V_m(Na_2SO_4)^{tr}$ at $C = 0.5000$	$18.7_9 \pm 0.5_0$		18.8
$V_m(Na_2SO_4)^{tr}$ at $C = 1.0000$	$22.6_8 \pm 0.4_0$		22.7
$V_m(Na_2SO_4)^{tr}$ at $C = 1.5000$	$25.3_6 \pm 0.3_0$		25.4
$V_m(Na_2SO_4)^{tr}$ at $C = 2.0000$	≈27.3		≈27.3
$V_m(Na_2SO_4)^{tr}$ at $C = 3.0000$	≈31.5		≈31.5
$V_m(Na_2SO_4)^{tr}$ at $C = 4.0000$	≈34.0		≈34.0
$V_m(Na_2SO_4)^{tr}$ at $C = 5.0000$	≈37.4		≈37.4

[a] Calculated using eqs 11−14 and the parameters of Table 8. [b] Values of $V_m(NaCl)^{se}$ and $V_m(Na_2SO_4)^{se}$ were calculated from the binary solution equations for the densities as functions of the solute molar concentration using eqs 15 and 16. [c] Recommended value. [d] At 298.15 K, Millero[54] recommends the following standard ionic volumes for infinite dilution: $V_m(Na^+) = -1.21$ cm^3·mol^{-1}, $V_m(Cl^-) = 17.82$ cm^3·mol^{-1}, and $V_m(SO_4^{2-}) = 13.98$ cm^3·mol^{-1}. These values were used to calculate the standard partial molar volumes of the total electrolytes at infinite dilution using the additivity relations.

Dedick *et al.*[55] reported densities and apparent molar volumes for $\{(z_1)NaCl + (1 - z_1)Na_2SO_4\}(aq)$ at a constant ionic strength of I = 1.95 mol·kg^{-1}, and found that deviations from linearity were reasonably small for the apparent molar volume as a function of y_1. As discussed by Miller,[56] this variation at constant molality ionic strength corresponds to a distorted Young's rule (which was originally formulated for constant volumetric ionic strengths). Comparing their results[55] with the observations in the previous paragraph illustrates that the "best" mixing rule for a volumetric property depends strongly on which concentration scale was held constant during the measurements.

Values of the trace partial molar volumes and the binary solution partial molar volumes, of NaCl and of Na_2SO_4, were calculated at each experimental total concentration using the following limiting forms of eq 3:

$$V_m(NaCl)^{tr} = (M_1 - H_1^{tr})/(\rho - H_2^{se}C_2) \qquad (11)$$

$$V_m(Na_2SO_4)^{tr} = (M_2 - H_2^{tr})/(\rho - H_1^{se}C_1) \qquad (12)$$

$$V_m(NaCl)^{se} = (M_1 - H_1^{se})/(\rho - H_1^{se}C_1) \qquad (13)$$

$$V_m(Na_2SO_4)^{se} = (M_2 - H_2^{se})/(\rho - H_2^{se}C_2) \qquad (14)$$

Here the superscript tr refers to the limiting trace value of the quantity of interest and the superscript se to the corresponding value for the binary solution of a single electrolyte. The root-mean-square uncertainties of these four types of partial molar volumes were estimated by applying the standard propagation of error method, using the assigned standard uncertainties for ρ, H_1^{se}, H_1^{tr}, H_2^{se}, and H_2^{tr}. The calculated partial molar volumes and their uncertainties are summarized in Table 9. No uncertainties were assigned to $V_m(\mathrm{Na_2SO_4})^{tr}$ when $\langle \bar{C}_T \rangle$ exceeds 1.5000 mol·dm^{-3} because the uncertainties of the $H_2{}^{tr}$ are unknown. A plot of the variation of these four partial molar volumes as a function of the total concentration (not shown) indicates that $V_m(\mathrm{NaCl})^{se}$, $V_m(\mathrm{Na_2SO_4})^{se}$, and $V_m(\mathrm{NaCl})^{tr}$ are as internally consistent as implied by the derived uncertainties listed in Table 9, as are the values of $V_m(\mathrm{Na_2SO_4})^{tr}$ from (0.5000 to 1.5000) mol·dm^{-3}. The same plot indicates that the precision of the $V_m(\mathrm{Na_2SO_4})^{tr}$ values at higher concentrations is approximately ±0.4 cm^3·mol^{-1}.

The partial molar volumes of the two solutes in their binary solutions may also be calculated using the following equations:

$$V_m(\mathrm{NaCl})^{se} = \{M_1 - (10^3\ \mathrm{cm^3 \cdot dm^{-3}})(\partial\rho/\partial C_1)_{T,p}\}/\{\rho - C_1(\partial\rho/\partial C_1)_{T,p}\} \quad (15)$$

$$V_m(\mathrm{Na_2SO_4})^{se} = \{M_2 - (10^3\ \mathrm{cm^3 \cdot dm^{-3}})(\partial\rho/\partial C_2)_{T,p}\}/\{\rho - C_2(\partial\rho/\partial C_2)_{T,p}\} \quad (16)$$

where the factor of (10^3 cm^3·dm^{-3}) arises because of the different volumetric units used for ρ and C_i. These calculations require expressions for the binary solution densities as functions of the corresponding C_i. For $\mathrm{Na_2SO_4}$(aq) we chose the density expression presented by Rard *et al.*,[16] which is just the density equation of Rard and Miller[7] converted to modern volumetric units. These calculated $V_m(\mathrm{Na_2SO_4})^{se}$ values are tabulated in Table 9.

Values of $V_m(\mathrm{Na_2SO_4})^{se}$ calculated with eqs 14 and 16 have a maximum difference of 0.09 cm^3·mol^{-1} at any fixed concentration. Although these $V_m(\mathrm{Na_2SO_4})^{se}$ values were obtained by rather different approaches, their agreement is excellent, and the averages are recommended.

The densities of NaCl(aq) reported in Table 6 and in our earlier investigations[16−19] agree well with those calculated from the equation of Rard and Miller[6] up to about 1.5 mol·dm^{-3}, after conversion of their equation to modern volumetric units, although several of our experimental densities are discrepant from that equation by (4 × 10^{-5} to 8 × 10^{-5}) g·cm^{-3}. In contrast, our experimental densities at higher concentrations are systematically higher than those calculated from the Rard and Miller density equation by ≈5 × 10^{-5} g·cm^{-3} at 2.0 mol·dm^{-3}, by ≈9 × 10^{-5} g·cm^{-3} at 3.0 mol·dm^{-3}, by ≈12 × 10^{-5} g·cm^{-3} at 4.0 mol·dm^{-3}, and by ≈8 × 10^{-5} g·cm^{-3} at 5.0 mol·dm^{-3}. Their equation[6] was based on an analysis of published literature data, and did not include any new measurements. However, if our experimental densities are compared directly with those from the three published studies[57−59] judged by Rard and Miller[6] to be the most accurate, then no significant systematic discrepancies are observed.

Rard[34] studied the retention of water by NaCl(s) as a function of drying temperature in air and found that it was necessary to heat this material to ≈773 K to eliminate all traces of water present in the original sample; this temperature is considerably higher than the typical drying temperatures of (373 to 473) K used in most research. Rard found, for example, that samples of NaCl(s) dried at 473 K retained ≈0.13 mass % H_2O. These dehydration experiments were subsequently confirmed and extended to slightly lower temperatures, as reported by Albright *et al.*[60] If the systematic density discrepancies noted in the previous paragraph are due to concentration errors resulting from incomplete drying of the NaCl(s) used for preparing solutions by mass in some of the published NaCl(aq) density experiments included by Rard and Miller[6] in their evaluation, then on the average the NaCl(s) used in the earlier density studies at certain other laboratories must have contained ≈0.09 mass % H_2O. As expected, this ≈0.09 mass % H_2O is slightly lower than the amounts of residual water measured in the dehydration experiments.[34,60] Since the authors of some of the earlier studies determined their solution concentrations by chemical analysis, and thus avoided systematic concentration errors of the type just described, not all of the earlier density studies examined by Rard and Miller have such systematic errors.

The parameters of the following equation for the densities of NaCl(aq) at 298.15 K were then reevaluated by the method of least squares,

$$\rho = \rho° + A_1C_1 + A_2C_1{}^{3/2} + A_3C_1{}^2 + A_4C_1{}^{5/2} \quad (17)$$

with equal weight being given to the densities of Table 6, to those from our earlier studies,[16−19] and to those from three previous accurate studies.[57−59] Six of our density values,[16,19] including the C = (1.093 39$_5$ and 4.905 85) mol·dm^{-3} points of Table 6, and one of Vaslow's[59] deviate by ≥4 × 10^{-5} g·cm^{-3} from the composite data set and were given zero weight in these calculations, and the density of pure water was fixed at $\rho°$ = 0.997 045 g·cm^{-3}. The evaluated parameters are A_1 = (0.041 698 6 ± 0.000 013 3) g·cm^{-3}·mol^{-1}·dm^3, A_2 = −(0.001 220 6 ± 0.000 028 4) g·cm^{-3}·mol$^{-3/2}$·dm$^{9/2}$, A_3 = −(0.000 601 8 ± 0.000 019 2) g·cm^{-3}·mol^{-2}·dm,^{6} A_4 = (0.000 119 5 ± 0.000 004 1) g·cm^{-3}·mol$^{-5/2}$·dm$^{15/2}$, and $\sigma(\rho)$ = 7 × 10^{-6} g·cm^{-3}. The reported coefficient uncertainties are their standard deviations. We believe that eq 17 with these evaluated parameters gives a more accurate representation of the densities of NaCl(aq) than the equation of Rard and Miller,[6] and should be used in preference to the earlier equation.

Values of $V_m(\mathrm{NaCl})^{se}$ thus calculated with eqs 13 and 15 have a maximum difference of 0.15 cm^3·mol^{-1} at C_1 = 5.0 mol·dm^{-3} and ≤0.08 cm^3·mol^{-1} at C_1 ≤ 4.0 mol·dm^{-3}. These values are in excellent agreement, and their averages are recommended in Table 9.

We are not aware of any published $V_m(\mathrm{NaCl})^{tr}$ or $V_m(\mathrm{Na_2SO_4})^{tr}$ values that would allow a similar comparison to be made to our experimental results.

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