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Interdiffusion Coefficients, Densities, and Refractive Indices of NH_4Cl + H_2O and $(NH_4)_2SO_4$ + H_2O at 25 °C

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Interdiffusion coefficients of the systems $NH_4Cl + H_2O$ and $(NH_4)_2SO_4 + H_2O$ at 25 °C were measured by free-diffusion optical-interferometric methods over wide ranges of concentration. Density data were also obtained for these systems. The concentration dependence of the refractive index, n, for each system was determined from refractive index increments, Δn, the mean molar concentrations, $\bar{c}$, and the concentration differences, Δc, of the set of experiments performed on each system. This dependence was compared to the concentration dependence of n predicted from equations for the molar refraction of mixtures. The latter equations use the measured concentration dependence of the solution density and either apparent molar refractions or refractive indices and densities of the pure components.

Introduction

Interdiffusion coefficients, D_v, were measured for the systems $NH_4Cl + H_2O$ and $(NH_4)_2SO_4 + H_2O$ on the volume-fixed reference frame at 25 °C over a wide concentration range. This work represents an initial part of a study that will include the measurement of diffusion coefficients and osmotic coefficients for the three-component system $NH_4Cl + (NH_4)_2SO_4 + H_2O$ at 25 °C.

Interdiffusion coefficients were previously measured for the system $NH_4Cl + H_2O$ at 25 °C by Hall, Wishaw, and Stokes (*1*), and for the system $(NH_4)_2SO_4 + H_2O$ at 25 °C by Wishaw and Stokes (*2*) and more recently by Leaist and Hao (*3*). The $NH_4Cl + H_2O$ results of Hall et al. were obtained by the Gouy optical-interferometric method and should be comparable in accuracy to the Rayleigh optical-interferometric results presented here. The $(NH_4)_2SO_4 + H_2O$ data of Wishaw and Stokes were also obtained by the Gouy optical-interferometric method, but the tabulated diffusion coefficients are in error. Their tabulated diffusion coefficients are actually the reciprocals of their correct experimental diffusion coefficients (*2*). After our experimental work was completed, data for $(NH_4)_2SO_4 + H_2O$ were reported by Leaist and Hao. Their data were obtained by the Taylor dispersion method and should be considered less precise than the optical-interferometic free-diffusion data.

Densities of the mixtures were also measured as part of this study and are reported here.

The concentration dependence of the refractive index is needed for dilute solution corrections in the calculation of diffusion coefficients (*4*). An estimation method based on ionic refractivities and densities has been developed to aid in the correction procedure.

Experimental Section

Materials. All solutions were prepared from Mallinckrodt analytical reagent grade NH_4Cl or Mallinckrodt analytical reagent grade $(NH_4)_2SO_4$ without further purification. The molar masses were 53.50 g mol^{-1} for NH_4Cl, 132.15 g mol^{-1} for $(NH_4)_2SO_4$, and 18.02 g mol^{-1} for H_2O. Water distilled from deionized water was used to prepare all solutions. For most experiments, solutions were prepared directly by mass from salts that had been dried at 110 °C for several hours. All solutions used for density measurements were prepared in this way. Some NH_4Cl aqueous solutions for the diffusion experiments were prepared from one of two stock solutions. These stock solutions were analyzed gravimetrically from AgCl precipitations. Experiments performed with these stock solutions are identified in Table 4. Densities and concentrations of the stock solutions are also given in the table.

Measurements. All but two of the diffusion measurements reported here were made on a Beckman-Spinco Model-H electrophoresis-diffusion instrument operating in the Rayleigh optical-interferometric mode. The magnification factor of the instrument was 1.0017 for this set of measurements. Procedures used with this instrument are described in detail by Albright, Mathew, and Miller (*5*).

Kodak Tmax-100 or Technical Pan photographic glass plates were used to record Rayleigh fringe patterns photographed during the experiment. An x–y scanner that was interfaced to a computer was used to measure fringe positions of the Rayleigh fringe patterns on those photographs (*5*).

Two diffusion experiments on the system $NH_4Cl + H_2O$ were performed on the "Gosting" diffusiometer which is now located at Texas Christian University (*6*). These two measurements were made with that instrument operating in the Gouy optical-interferometric mode. The theory and methodology for measuring diffusion coefficients by the free-diffusion method with a Gouy interferometer are well established (*7, 8*).

Kodak Tmax-100 photographic plates were used for Gouy experiments. Gouy fringe positions on the photographs of Gouy patterns were measured with a Gaertner Tool-Makers microscope. This instrument is fitted with a scanning device which makes it possible to measure positions of fringe minima with an accuracy approaching ±1 μm (*9, 10*).

All diffusion coefficients, D_v, were initially calculated from fringe-position data by assuming that the diffusion coefficients are constant and that the refractive index depends only on the first power of the molar concentration, c (mol dm^{-3}). This assumption is valid for all experiments except those performed at low concentrations. At low concentrations, the $c^{1/2}$ and c dependences of D_v and the $c^{3/2}$ and c^2 dependences of n were sufficiently large that it was necessary to correct for concentration dependence. To make these corrections, polynomial fits of the concentration dependence of the diffusion coefficients were obtained from diffusion data at lower

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Table 1. Densities of $NH_4Cl + H_2O$ at 25 °C

c/(mol dm^{-3})	d/(g cm^{-3})	c/(mol dm^{-3})	d/(g cm^{-3})	c/(mol dm^{-3})	d/(g cm^{-3})
0.0497	0.997 92	0.9051	1.011 76	2.5981	1.036 60
0.0601	0.998 12	0.9912	1.013 05	2.9127	1.040 96
0.1494	0.999 57	1.4494	1.020 11	3.0331	1.042 60
0.1504	0.999 57	1.4731	1.020 30	3.4047	1.047 69
0.2501	1.001 49	1.5476	1.021 43	3.5281	1.049 30
0.2999	1.002 05	1.5515	1.021 57	3.9154	1.054 43
0.3997	1.003 73	1.8293	1.025 74	4.0405	1.056 06
0.4523	1.004 53	1.8939	1.026 60	4.4250	1.061 04
0.5399	1.005 98	1.9973	1.028 06	4.5481	1.062 62
0.6915	1.008 39	2.1411	1.030 18	4.9245	1.067 43
0.7952	1.010 00	2.3840	1.033 60	5.0611	1.069 17

Table 2. Densities of $(NH_4)_2SO_4 + H_2O$ at 25 °C

c/(mol dm^{-3})	d/(g cm^{-3})	c/(mol dm^{-3})	d/(g cm^{-3})	c/(mol dm^{-3})	d/(g cm^{-3})
0.0296	0.999 41	0.7195	1.049 75	2.4604	1.158 88
0.0502	1.000 98	0.7798	1.053 86	2.5392	1.163 34
0.1503	1.008 66	0.9637	1.066 32	2.5401	1.163 34
0.1750	1.010 57	1.0226	1.070 20	2.9247	1.184 83
0.2250	1.014 35	1.4693	1.099 15	2.9810	1.187 88
0.3249	1.021 76	1.5289	1.102 84	3.5401	1.217 63
0.3748	1.025 34	1.9597	1.129 42	3.6379	1.222 77
0.4737	1.032 48	2.0291	1.133 52	3.9571	1.238 87
0.5233	1.035 95	2.4594	1.158 75	4.0365	1.242 77

Table 3. Polynomial Coefficients of Equation 1 for Density Fits[a]

$NH_4Cl + H_2O$	$(NH_4)_2SO_4 + H_2O$
$d_0 = 0.997\,045$	$d_0 = 0.997\,045$
$a_2 = 0.017\,709\,4$	$a_2 = 0.081\,154\,6$
$a_3 = -0.001\,540\,7$	$a_3 = -0.008\,886\,0$
	$a_4 = -0.000\,598\,41$
$\sigma = \pm 0.000\,04$	$\sigma = \pm 0.000\,04$

[a] Units: d_0, g cm^{-3}; a_2, g cm^{-3} (dm^3 mol^{-1}); a_3, g cm^{-3} (dm^3 mol^{-1})$^{3/2}$; a_4, g cm^{-3} (dm^3 mol^{-1})^2; σ, g cm^{-3}.

Table 4. Diffusion Coefficients of $NH_4Cl + H_2O$ at 25 °C

$\bar{c}$/(mol dm^{-3})	Δc/(mol dm^{-3})	J	$D \times 10^9$/(m^2 s^{-1})	$\boldsymbol{M} \times 10^9$/(m^2 s^{-1})
0.0[a]			1.995	1.995
0.030 04[b]	0.060 08	58.44	1.8826	2.0195
0.039 50[d]	0.079 01	76.99	1.8725	2.0215
0.100 02[b]	0.100 74	97.08	1.8517	2.0422
0.100 13[d]	0.100 58	97.06	1.8500	2.0404
0.199 77[b]	0.100 73	110.70	1.8448	2.0612
0.234 46[c]	0.088 44	84.26	1.8453	2.0664
0.245 98[d]	0.093 51	88.89	1.8453	2.0677
0.349 80[b]	0.099 83	93.53	1.8514	2.0810
0.496 10[b]	0.087 57	82.01	1.8639	2.0956
0.500 19[d]	0.121 10	117.06	1.8646	2.0963
0.743 30[b]	0.103 71	96.51	1.8917	2.1166
0.948 12[b]	0.086 10	78.94	1.9201	2.1337
1.003 7[d]	0.123 08	112.56	1.9233	2.1326
1.500 4[b]	0.102 14	91.68	1.9872	2.1531
1.510 3[b]	0.074 47	66.54	1.9866	2.1514
1.945 6[b]	0.103 41	91.52	2.0436	2.1620
1.960 8[d]	0.100 68	88.92	2.0465	2.1633
1.985 2[b,e]	0.311 83	137.78	2.0515	2.1656
2.491 0[b,e]	0.214 10	93.21	2.1116	2.1695
2.511 0[d]	0.109 13	94.93	2.1133	2.1691
2.973 9[b]	0.120 38	103.43	2.1615	2.1707
3.466 4[b]	0.123 41	105.22	2.2076	2.1784
3.496 4[d]	0.106 76	90.75	2.2158	2.1846
3.978 0[b]	0.125 08	105.26	2.2453	2.1935
3.983 5[d]	0.104 00	87.64	2.2469	2.1949
4.486 6[b]	0.123 05	102.64	2.2643	2.2120
4.992 8[b]	0.136 62	112.82	2.2654	2.2356
5.398 2[c]	0.197 71	163.24	2.2691	2.2714

[a] Calculated from limiting equivalent ionic conductances. [b] Solutions prepared from dried salt. [c] Solutions prepared from a 5.497 mol dm^{-3} stock solution. [d] Solutions prepared from a 5.137 mol dm^{-3} stock solution. [e] Experiments performed on the Gosting diffusiometer.

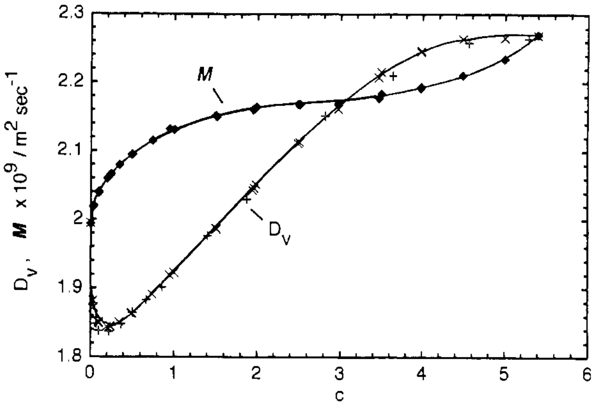

Figure 1. Variation of mutual diffusion coefficients, D_V, and thermodynamic diffusion coefficients, $\boldsymbol{M}$, with molarity c for $NH_4Cl + H_2O$ at 25 °C: D_V, ×, this work; +, Hall, Wishaw, and Stokes (*1*); $\boldsymbol{M}$, ♦, this work.

concentrations (0–1 M range). The polynomial fits of the refractive indices were obtained from data over the whole concentration range. (A method for estimating these coefficients is given below.) Substitution of these polynomial coefficients into equations developed by Miller and Albright (*4*) for the correction of diffusion coefficients gave the correction factors used here. For the system $NH_4Cl + H_2O$, D_V was changed from 1.8853×10^{-9} to 1.8826 m^2 s^{-1} at 0.030 04 M and from 1.8756×10^{-9} to 1.8725×10^{-9} m^2 s^{-1} at 0.039 50 M. For $(NH_4)_2SO_4 + H_2O$, D_V was changed from 1.3248×10^{-9} to 1.3217×10^{-9} m^2 s^{-1} at 0.014 81 M. Here M refers to the molarity (mol dm^{-3}).

Density measurements were made with a Mettler/Parr DMA 40 density meter interfaced to a computer. By time averaging the output, a precision of $\pm 1.0 \times 10^{-5}$ g cm^{-3} could be obtained. The temperature of the water surrounding the vibrating tube of the meter was regulated at 25.00 ± 0.01 °C; this water was circulated from a large well-regulated water bath. The instrument was calibrated with air and air-saturated water. The density of the air-saturated water was assumed to be 0.997 045 g cm^{-3}.

Results and Discussion

Densities. The values of measured densities of $NH_4Cl + H_2O$ and $(NH_4)_2SO_4 + H_2O$ are listed in Tables 1 and 2, respectively. Each set was fit by the method of least squares to equations of the form

$$d = d_0 + a_2c + a_3c^{3/2} + a_4c^2 \qquad (1)$$

The coefficients for these fits are listed in Table 3. The constant d_0 was fixed at 0.997 045 g cm^{-3} in each case. Good fits were obtained with just the constant d_0 and coefficients a_2 and a_3 for $NH_4Cl + H_2O$ and d_0, a_2, a_3, and a_4 for $(NH_4)_2SO_4 + H_2O$. Additional terms in either case could not be justified by the very small improvements of fit obtained by their inclusion. In both cases, the standard deviation appeared to be ±0.000 04 g cm^{-3}. Because of some uncertainty about the purity of the reagents and about prepared concentrations, the overall accuracy of the density measurements should be considered to be no better than ±0.0001 g cm^{-3}.

Diffusion Coefficients. The results of diffusion coefficient measurements are given in Table 4 and shown in Figure 1 for $NH_4Cl + H_2O$. Corresponding results are given in Table 5 and shown in Figure 2 for $(NH_4)_2SO_4 + H_2O$. Listed in the tables are the mean molar concentration, $\bar{c}$, and the difference, Δc, in molar concentration between the bottom and top

Table 5. Diffusion Coefficients of $(NH_4)_2SO_4 + H_2O$ at 25 °C

$\bar{c}$/(mol dm^{-3})	Δc/(mol dm^{-3})	J	$D_v \times 10^9/(m^2\ s^{-1})$	$M \times 10^9/(m^2\ s^{-1})$
0.0			1.5310	1.5310
0.014 81	0.029 61	61.446	1.3217	1.5997
0.100 2	0.100 06	197.278	1.2063	1.7037
0.200 0	0.049 98	95.243	1.1547	1.7220
0.306 7	0.049 38	91.901	1.1151	1.7166
0.349 9	0.049 92	92.088	1.1024	1.7134
0.498 5	0.049 60	88.956	1.0647	1.6985
0.749 7	0.060 27	103.530	1.0188	1.6751
0.993 2	0.058 93	97.386	0.9865	1.6515
1.499	0.059 60	92.299	0.9475	1.5904
1.994	0.069 42	100.788	0.9315	1.4857
2.500	0.079 63	108.629	0.9196	1.3075
2.953	0.056 29	72.613	0.9110	1.1085
3.589	0.097 80	116.309	0.8869	0.8076
3.997	0.079 40	89.812	0.8564	0.6266

solutions for each experiment. The value of the diffusion coefficient measured on the volume-fixed reference frame, D_v, is given for each experiment. (Since Δc and the volume change on mixing are small for our diffusion measurements, the diffusion coefficients measured relative to the apparatus are considered to be on the volume-fixed reference frame (*11*).)

Diffusion coefficients at infinite dilution were calculated with the Nernst–Hartley equation (*12*) by using values of limiting molar conductances of 73.56, 76.35, and 160.04 cm^2 Ω^{-1} mol^{-1} for NH_4^+, Cl^-, and SO_4^{2-} (*12*). (The value of 160.04 cm^2 Ω^{-1} mol^{-1} is twice the equivalent conductance listed in ref 12.)

It was found that the diffusion coefficients for both $NH_4Cl + H_2O$ and $(NH_4)_2SO_4 + H_2O$ could be fit significantly better with rational fractions than with polynomials having the same number of coefficients. Thus, a least-squares procedure was used to fit the diffusion coefficients to equations of the form

$$D_v = D_0 + \frac{A_{0.5}c^{1/2} + A_1c + A_2c^2 + A_3c^3 + ...}{1 + B_{0.5}c^{1/2} + B_1c + B_2c^2 + B_3c^3 + ...} \qquad (2)$$

Coefficients for the fits of $NH_4Cl + H_2O$ and $(NH_4)_2SO_4 + H_2O$ to our experimental data in Tables 4 and 5 are given in Table 6, as well as σ, the standard deviations of the fits. Generally good fits were obtained for both systems.

The two Gouy experiments performed on the Gosting instrument for the system $NH_4Cl + H_2O$ are in good agreement with the Rayleigh experiments performed on the Model-H instrument. In both cases the measured D_v and the value recalculated from eq 2 (with coefficients in Table 6 inserted) agreed within ±0.1%. Diffusion coefficients tabulated by Hall, Wishaw, and Stokes (*1*) (denoted below by D_{HWS}) were on average 0.0054×10^{-9} m^2 s^{-1} lower than values calculated from eq 2 (denoted below as $D_{eq\ 2}$). This is fairly good agreement (less than 0.3% different). The scatter of the quantity ($D_{HWS} - D_{eq\ 2}$) was 0.005×10^{-9} m^2 s^{-1}. The one point of Rard and Miller (*13*), also by Rayleigh interferometry, is in even better agreement, 0.15%. We believe that the measured values of diffusion coefficients presented here are accurate to at least ±0.3%.

In contrast, comparison with the data of Wishaw and Stokes (*2*) for $(NH_4)_2SO_4 + H_2O$ requires recognition that the reciprocals of their tabulated diffusion coefficients are actually the correctly measured diffusion coefficients. This problem with their tabulated data was recognized during our measurements, before it was noted independently by Leaist and Hao (*3*). Very close agreement is found between the corrected D_v of Wishaw and Stokes and D_v calculated from eq 2 with the coefficients from Table 6 inserted. On average, the corrected values of Wishaw and Stokes are only 0.001×10^{-9} m^2 s^{-1} higher than values calculated from eq 2. The scatter of their results is $\pm 0.003 \times 10^{-9}$ m^2 s^{-1}. The scatter of ours is $\pm 0.001 \times 10^{-9}$ m^2 s^{-1}. When the data of Wishaw and Stokes are included in the data base, the scatter of the fit becomes $\pm 0.002 \times 10^{-9}$ m^2 s^{-1}.

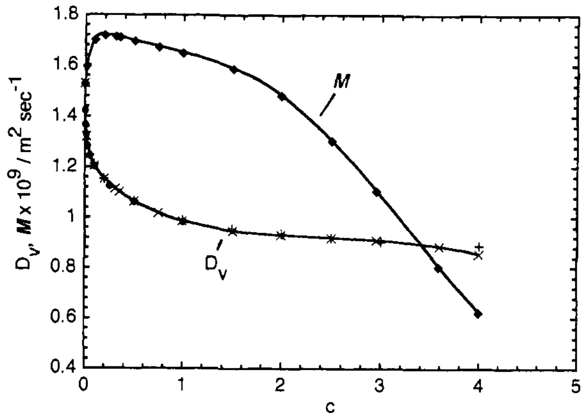

Figure 2. Variation of mutual diffusion coefficients, D_v, and thermodynamic diffusion coefficients, ***M***, with molarity *c* for $(NH_4)_2SO_4 + H_2O$ at 25 °C: D_v, ×, this work; +, Wishaw and Stokes (*2*) (corrected); ●, Leaist and Hao (*3*); ***M***, ♦, this work.

Table 6. Rational Fraction Coefficients of Equation 2 for Fits of Diffusion Data[a]

$NH_4Cl + H_2O$	$(NH_4)_2SO_4 + H_2O$
$D_0 = 1.995$	$D_0 = 1.531$
$A_{0.5} = -1.044\ 528$	$A_{0.5} = -3.318\ 284$
$A_1 = 0.953\ 080$	
$A_2 = -0.073\ 996\ 5$	
$B_{0.5} = 2.415\ 969$	$B_{0.5} = 8.418\ 527$
$B_1 = -1.156\ 761$	$B_1 = -4.434\ 515$
$B_2 = 0.058\ 995\ 5$	$B_2 = 1.276\ 245$
	$B_3 = -0.166\ 943$
$\sigma = \pm 0.0026$	$\sigma = \pm 0.0014$

[a] Units: D_0, σ, 10^9 m^2 s^{-1}; $A_{0.5}$, 10^9 m^2 s^{-1} (dm^3 mol^{-1})$^{1/2}$; A_1, 10^9 m^2 s^{-1} (dm^3 mol^{-1}); A_2, 10^9 m^2 s^{-1} (dm^3 mol^{-1})^2; $B_{0.5}$, (dm^3 mol^{-1})$^{1/2}$; B_1, dm^3 mol^{-1}; B_2, (dm^3 mol^{-1})^2; B_3, (dm^3 mol^{-1})^3.

Comparison of our and other optical results (*2, 13*) with the Taylor dispersion results of Leaist and Hao (*3*) is interesting. Over the concentration range where their data and our data overlap, their values are 0.01×10^{-9} m^2 s^{-1} lower than ours with a scatter of $\pm 0.004 \times 10^{-9}$ m^2 s^{-1}. Considering that the Taylor dispersion method is less accurate, this is very good agreement.

Thermodynamic Diffusion Coefficients. Also listed in Tables 4 and 5 and shown in Figures 1 and 2 are the values of the thermodynamic diffusion coefficients ***M*** for each experiment. These are defined by the equation

$$\boldsymbol{M} = D_v/[1 + m(d \ln(\gamma_\pm/dm))] \qquad (3)$$

Here m is the molality (mol kg^{-1}) of the solute and $\gamma_\pm$ is the mean ionic activity coefficient. Because of possible uncertainty of the activity coefficients, the values of ***M*** should be considered accurate to no better than 1%.

Activity coefficients used in eq 3 were calculated from equations of the form

$$\log \gamma_\pm = \frac{-|z_+z_-|AI^{1/2}}{1 + B^*I^{1/2}} + \beta I + CI^2 + DI^3 + EI^4 + ... \qquad (4)$$

Here $\gamma_\pm$ is the mean ionic activity coefficient, z_+ and z_-, are integer charges of the positive and negative ions, and I is the molal ionic strength ($I = (1/2)\sum m_iz_i^2$).

Coefficients for the system $NH_4Cl + H_2O$ at 25 °C used in eq 4 are those tabulated by Hamer and Wu (*14*): $A = 0.5108$,

$B^* = 1.325$, $b = -4.5787 \times 10^{-3}$, $C = 5.2712 \times 10^{-3}$, $D = -7.0557 \times 10^{-4}$, $E = 2.8434 \times 10^{-5}$. They reported the standard deviation of the activity coefficient, $\sigma(\gamma)$, to be 6.27×10^{-4}. However, significant systematic error is likely and hard to estimate.

Activity coefficients for $(NH_4)_2SO_4 + H_2O$ at 25 °C tabulated by Stokes and Robinson (*12*) were fit to eq 4. The coefficients obtained are $A = 0.5108$, $B^* = 0.965\,75$, $b = -0.023\,524$, and $C = 1.1307 \times 10^{-3}$. This was fit from smoothed data, so a meaningful $\sigma(\gamma)$ is not given here. Again, systematic error is likely and difficult to estimate.

Refractive Index. The number of fringes, J, for each experiment listed in Tables 4 and 5 were converted to refractive index differences, Δn, between the bottom and top solutions. The conversions were made by using the equation $\Delta n = J\lambda/(2a)$. Here λ ($= 5.4607 \times 10^{-5}$ cm) is the wavelength of the light source and a ($= 2.490$ cm) is the inside dimension of the cell along the optic axis. The values of Δn used below were taken only from experiments performed on the Model-H diffusiometer. It has an optical system in which light passes through the diffusion cell and is then reflected back through the cell with a mirror so that the effective optical distance through the cell is $2a$.

An equation of the form

$$\Delta n = \rho_0(c_B - c_T) + \rho_1(c_B^{3/2} - c_T^{3/2}) + \rho_2(c_B^2 - c_T^2) \quad (5)$$

was fit by the method of least squares to the set of Δn for a given system. Here c_T and c_B are the initial concentrations above and below the initial free-diffusion boundary. These may be calculated from tabulated values in Tables 4 and 5 as $\bar{c} - 0.5\Delta c$ and as $\bar{c} + 0.5\Delta c$, respectively. When data points for which $\bar{c} = 0.199\,77$, 0.3498, 0.500 19, 0.7433, and 5.3982 M were treated as outliers and not included in the analysis, the coefficients for $NH_4Cl + H_2O$ were found to be $\rho_0 = 0.010\,83$ M^{-1}, $\rho_1 = -0.000\,570$ M$^{-3/2}$, and $\rho_2 = 0.000\,012$ M^{-2}. The standard deviation of the recalculated fit of J was 0.15 fringe. Recalculated values of J for all outliers deviated from measured J by more than 4 times this value. The uncertainties of the coefficients ρ_0, ρ_1, and ρ_2 were 0.12%, 2.9%, and 41%. For $(NH_4)_2SO_4 + H_2O$, when the point at $\bar{c} = 0.3067$ M was treated as an outlier and removed from the calculation, the coefficients were found to be $\rho_0 = 0.023\,05$ M^{-1}, $\rho_1 = -0.002\,99$ M$^{-3/2}$, and $\rho_2 = -0.000\,21$ M^{-2}. The standard deviation of the recalculated fit of J was 0.28 fringe. The outlier deviated by more than 4 times this value. The uncertainties of the coefficients ρ_0, ρ_1, and ρ_2 were 0.21%, 2.4%, and 11%.

The refractive index expression which leads to eq 5 is the first four terms (up to ρ_2) of the more general expansion

$$n = n_0 + \rho_0 c + \rho_1 c^{3/2} + \rho_2 c^2 + \rho_3 c^{5/2} + \rho_4 c^3 + \ldots \quad (6)$$

Here, n_0 is the refractive index of pure water, which is taken to be 1.3340 for the Hg green line at 25 °C.

The form of eq 6 can be obtained from the theoretical equation for the molar refraction of a mixture in terms of the molar refractions of its constituents. The usual equation for the molar refraction, R_i, for pure component i was initially obtained by Lorentz (*15*) and Lorenz (*16*) in 1880, and is

$$R_i = \left(\frac{n_i^2 - 1}{n_i^2 + 2}\right)\frac{M_i}{d_i} \quad (7)$$

Here n_i, M_i, and d_i are the refractive index, molar mass, and density of pure component i. An expression for the molar refraction, R, of a binary mixture of solvent (denoted by subscript 0) and solute (denoted by subscript s) may be written in terms of the sum of mole fractions, x_0, and x_s, times the corresponding molar refractions of the pure components, R_0 and R_s (see for example ref 17):

$$R = \left(\frac{n^2 - 1}{n^2 + 2}\right)\frac{M_m}{d} = x_0 R_0 + x_s R_s \quad (8)$$

where

$$M_m = x_0 M_0 + x_s M_s \quad (9)$$

Here M_m, n, and d are the molar mass, refractive index, and density of the solution.

Both theory and experiment have shown that R is relatively independent of temperature but depends somewhat on wavelength. For nonelectrolytes, molar refractions from atomic or group contributions have been used to distinguish molecular structures (*17, 18*). Experiments have also shown that R_i is nearly the same in the liquid or gas (a few percent difference). It is more closely the same in ionic crystals and dilute electrolyte solutions (*18*).

The concentration dependence of molar refraction in electrolyte solutions is linear with molality above 1 *m*, and can be extrapolated to infinite dilution (*19*). This concentration dependence is relatively small (*19, 20*). For example, for NaI, which has one of the largest effects, the difference is only about 2% between 0 and 5 *m*. It should be noted that the highly precise measurements of Geffcken, Kruis, and co-workers showed that, below 1 *m*, linearity was no longer valid. The R_i of most salts begins to decrease below 1 *m*, with the final intercept about 0.02 lower than the value obtained from extrapolation of data above 1 *m* (*21*). This effect is small enough to ignore in our considerations. At infinite dilution, R can be split up into additive ionic contributions with good agreement with the extrapolated values for various salts (*19, 22–24*). The very extensive experimental studies of Heydweiler (*22*) and of Fajans and co-workers on ionic refractions were summarized by Fajans (*19, 25*) and mentioned by Partington (*18*) and Falkenhagen (*20*). A table of extrapolated ionic refractions (actually apparent equivalent ionic refractions) at infinite dilution for the Na D line (*24*) is given in Landolt-Bornstein (*26*), along with some ionic dispersions (*27*). (Another table of dispersions with a different reference value is given by Bauer and Fajans (*28*).)

Since the concentration dependence of apparent ionic refractions is relatively small, the infinite dilution values can be used as a first approximation in the mixture rule. If the ionic refractions are not available, a more approximate value for the compound can be obtained from tabulated values of the crystal n_s and d_s.

With these ideas in mind, we will explore the relations between n and d, starting with the mixture rule (eq 8). When x_i are converted to expressions in molar concentration, c, of the solute, eq 8 can be written as

$$\left(\frac{n^2 - 1}{n^2 + 2}\right) = \left\{r_0 d + r_0 M_s\left(\frac{r_s}{r_0} - 1\right)\frac{c}{1000}\right\} \quad (10)$$

where

$$r_i = \left(\frac{n_i^2 - 1}{n_i^2 + 2}\right)\frac{1}{d_i} \quad (11)$$

is the specific refraction given by R_i/M_i.

Equation 10 can be solved for n, yielding the exact expression for the mixture rule

$$n = \left(\frac{1 + 2\{\}}{1 - \{\}}\right)^{1/2} \quad (12)$$

Table 7. Comparison of Coefficients of Equation 6 from Least-Squares, Ionic, and Crystal Refractivities[a]

	NH_4Cl			$(NH_4)_2SO_4$		
	exptl	ionic ref	cryst	exptl	ionic ref	cryst
ρ_0	0.010 83	0.010 61	0.009 371	0.023 05	0.022 83	0.021 748
ρ_1	−0.000 570	−0.000 569	−0.000 569	−0.002 99	−0.003 28	−0.003 28
ρ_2	0.000 012	0.000 037	0.000 029 1	−0.000 21	−0.000 048	−0.000 064
ρ_3	0.	−0.99E−6	−3.53E−6	0.0	−0.000 050	−0.000 047
ρ_4	0.	4.05E−7	3.13E−7	0.0	3.20E−6	2.95E−6

[a] Units: ρ_0, $dm^3\ mol^{-1}$; ρ_1, $(dm^3\ mol^{-1})^{3/2}$; ρ_2, $(dm^3\ mol^{-1})^2$; ρ_3 $(dm^3\ mol^{-1})^{5/2}$; ρ_4, $(dm^3\ mol^{-1})^3$.

Table 8. Comparison of *n* from Least-Squares and Mixture Rule Approximations

	NH_4Cl				$(NH_4)_2SO_4$			
c/(mol dm^{-3})	exptl	exact	six-term	four-term	exptl	exact	six-term	four-term
0.1	1.3351	1.335 04	1.335 04	1.335 04	1.3362	1.336 18	1.336 18	1.336 18
0.3	1.3372	1.337 09	1.337 09	1.337 09	1.3404	1.340 30	1.340 30	1.340 31
0.5	1.3392	1.339 11	1.339 11	1.339 11	1.3444	1.344 23	1.344 23	1.344 24
1.0	1.3443	1.344 07	1.344 07	1.344 07	1.3538	1.353 45	1.353 45	1.353 50
2.0	1.3541	1.353 73	1.353 73	1.353 75	1.3708	1.369 93	1.369 93	1.370 18
3.0	1.3636	1.363 14	1.363 15	1.363 20	1.3857	1.384 30	1.384 32	1.385 01
5.0	1.3821	1.381 42	1.381 43	1.381 60	1.4106	1.407 76	1.407 89	1.410 26

where {} is the right-hand side of eq 10. If d is written as

$$d = d_0 + a_2 c + \sum_{i=3}^{k} a_i c^{i/2} \tag{13}$$

then an equally exact expression is obtained from eq 10:

$$n = \left[\frac{1 + 2P_0 + 2\sum_{i=2}^{k} b_i c^{i/2}}{1 - P_0 - \sum_{i=2}^{k} b_i c^{i/2}}\right]^{1/2} \tag{14}$$

where

$$b_2 = r_0\,(a_2 + M_s(r_s/r_0 - 1)/1000) = r_0 a_2{}^* \tag{15}$$

$$b_i = r_0 a_i \qquad i = 3, ..., k \tag{16}$$

$$P_0 = r_0 d_0 = \left(\frac{n_0{}^2 - 1}{n_0{}^2 + 2}\right) \tag{17}$$

Expansion of eq 14 in a Taylor series in c to c^3 (using the computer algebra program ALJABR, the Macintosh version of MACSYMA) yields n in exactly the same form as eq 6, where

$$\rho_0 = g_1 a_2{}^* \tag{18}$$

$$\rho_1 = g_1 a_3 \tag{19}$$

$$\rho_2 = g_1[a_4 + g_2(a_2{}^*)^2] \tag{20}$$

$$\rho_3 = g_1[a_5 + 2g_2 a_2{}^* a_3] \tag{21}$$

$$\rho_4 = g_1[a_6 + g_2(2a_2{}^* a_4 + a_3{}^2) + g_3(a_2{}^*)^3] \tag{22}$$

and where

$$g_1 = \frac{(n_0{}^2 - 1)(n_0{}^2 + 2)}{6n_0 d_0} \tag{23}$$

$$g_2 = \frac{(n_0{}^2 - 1)(3n_0{}^2 - 2)}{12n_0{}^2 d_0} \tag{24}$$

$$g_3 = \frac{(n_0{}^2 - 1)^2(5n_0{}^4 - 4n_0{}^2 + 4)}{72n_0{}^4 d_0{}^2} \tag{25}$$

Values of r_0, g_1, g_2, and g_3 for the Hg green line at 25 °C (n_0 = 1.3340 at 546.07 nm) are 0.206 87, 0.369 20, 0.122 24, and 0.034 09, respectively.

If we add the appropriate ionic equivalent refractions at infinite dilution from Landolt-Bornstein (*26*), then we find R_s = 13.375 and r_s = 0.250 00 for NH_4Cl, and R_s = 2[11.675] = 23.35 and r_s = 0.176 69 for $(NH_4)_2SO_4$. These are for the Na D line, but are reasonably close to Hg green line values.

Once given the values of a_i, d_0, n_0, and r_s, values of ρ_i and n can be calculated from eqs 14 and 18. Comparisons with experimental values of ρ_i and n are found in Tables 7 and 8.

Table 7 contains the ρ_i obtained by least squares from the data (as described above) for NH_4Cl and for $(NH_4)_2SO_4$ compared with the ρ_i (under the heading ionic ref) calculated from eqs 18–25 using n_0 = 1.3340 (Hg green line), d_0 = 0.997 045 for pure water, and the specific refractions r_s obtained above.

Table 7 shows clearly that the series converges fairly rapidly, and that calculated ρ_0 and ρ_1 are in good agreement with the experimental values. However, ρ_2 agrees less well, which is no doubt due to truncation of the "experimental" series and because this term is not well determined by least squares. Also included are values of ρ_i (under the heading cryst) based on the r_s values of the ionic crystals. These were calculated from eq 11 using (*29*) n_s = 1.642 (Na D line) and d_s = 1.527 for crystalline NH_4Cl, and n_s = 1.521 (Na D line) and d_s = 1.769 for crystalline $(NH_4)_2SO_4$. The resulting ρ_0 is not as good, owing to the less appropriate value of r_s from crystal data compared to solution values.

Table 8 contains the comparison of n calculated from the experimental ρ_i of Table 7 to the "exact" value of the mixture rule for n obtained by substitution into eqs 14–17 of molar refractions at infinite dilution (from ionic refractions (*26*)), the refractive index of pure water, and calculated densities. Also included in the table are values of n calculated from the series expansion of eq 14 (in the form of eq 6) by using the ρ_i listed under ionic ref of Table 7 (calculated from eqs 18–25) for all six ρ_i and from the first four ρ_i. For both salts, the exact mixture expression agrees with the six-term series approximation to 2 in the fifth place up to 3 M, and agrees with the four-term series to 5 in the fifth place up to 1 M. The disagreement of the experimental n with the exact mixture rule and its six- and four-term approximations is only 2 in the fourth place for both salts up to 0.5 M, which is the concentration region of interest for diffusion coefficient corrections. These results are quite good, since the ionic refractions used to calculate r_s are for the Na D line.

The first important result of this refractive index investigation is that the Taylor series form for $n(c)$ of the molar refraction mixture rule has exactly the same form as $d(c)$. Consequently assertions that n for electrolyte solutions can be written as a polynomial in c are incorrect (*18*) because d is a polynomial in $c^{1/2}$ starting with c. The second important result is that, with ionic refractions from Landolt-Bornstein (*26*), for example, the exact mixture rule and its six- and four-term approximations all give good approximations to the experimental values of n to 0.5 M. Thus, the corresponding ρ_i can be used for low-concentration D_v corrections. It seems likely that this second result will also apply to other binary electrolyte systems.

It will be of interest to see how much closer the agreement would be with experimental values using crystal values of n or with dilute solution ionic refractions for the Hg green line used in our diffusion experiments.

These considerations can be extended to ternary systems, and will be discussed elsewhere.

Conclusions

Good agreement is found for the interdiffusion data reported here for the systems $NH_4Cl + H_2O$ and $(NH_4)_2SO_4 + H_2O$ at 25 °C and the coefficients previously measured by the Gouy method. The data presented have less scatter. There is fair agreement between the measured concentration dependence of the refractive index, n, and the expected concentration dependence of n based on the concentration dependence of the density and values of the apparent molar refractions and densities of the pure components.

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