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Isopiestic Determination of the Osmotic and Activity Coefficients of Aqueous Mixtures of NaCl and $MgCl_2$ at 25 °C

Joseph A. Rard* and Donald G. Miller

University of California, Lawrence Livermore National Laboratory, Livermore, California 94550

The osmotic and activity coefficients of aqueous mixtures of NaCl and $MgCl_2$ have been determined at 25 °C by using the isopiestic method. These measurements extend from low concentrations to the crystallization limits of the mixtures. They are critically compared to published isopiestic, direct vapor pressure, and emf data for this system. Our data agree well with previous isopiestic data and two sets of emf values, but direct vapor pressure data are significantly discrepant. Osmotic and activity coefficients for NaCl–$MgCl_2$ mixtures are fairly reliably represented by both Pitzer's equations and Scatchard's neutral electrolyte equations.

Introduction

A wide variety of chemical, geochemical, biochemical, and industrial systems and processes involve aqueous electrolyte mixtures. Osmotic and activity coefficient data are essential for these systems in order to quantitatively characterize and to model their reaction thermodynamics, their chemical speciation, and their solubilities. Activity data and their derivatives are also needed to calculate thermodynamic diffusion coefficients, which are based on chemical potential gradient rather than concentration gradient driving forces (*1–3*).

Several important ternary brine salt mixtures have been reinvestigated recently at 25 °C. Seidel et al. (*4*) and Kuschel and Seidel (*5*) have provided accurate data for aqueous KCl–$MgSO_4$, KCl–$MgCl_2$, and K_2SO_4–$MgSO_4$ mixtures by using the isopiestic method. Ananthaswamy and Atkinson (*6*) studied NaCl-$CaCl_2$ mixtures by using Na^+ and Ca^{2+} ion-sensitive electrodes, and Filippov and Cheremnykh (*7*) studied $MgCl_2$–$MgSO_4$ mixtures by using the isopiestic method.

Another important brine salt mixture is NaCl–$MgCl_2$. An extensive series of diffusion coefficient measurements is currently in progress in our laboratory. To analyze and interpret these data requires accurate activity coefficient derivatives. Since differentiation magnifies experimental errors, very precise experimental data are required.

Several workers have previously studied aqueous NaCl-$MgCl_2$ at 25 °C. Experimental water activity data were reported from isopiestic measurements in two studies (*8*, *9*) and from direct water vapor measurements by the static method (*10*), and NaCl activities were reported in three studies (*11–13*) using emf measurements. Freezing point depression data (*14*) seem to be consistent with the 25 °C isopiestic values, but published enthalpy and heat capacity data are not adequate to convert the freezing point data to 25 °C. Thus, freezing point data will not be considered further. Additional enthalpy and heat capacity data would be desirable.

The most extensive investigation of NaCl–$MgCl_2$ activities is Platford's isopiestic study (*9*) which covers the ionic strength range of I = 0.11–8.02 mol·kg^{-1}, where the kg refers to H_2O. An et al.'s vapor pressure measurements (*10*) cover the ionic strength range of 6.37–13.84 mol·kg^{-1}, but they are restricted to NaCl ionic strength fractions of 0.021–0.065. Osmotic coefficients from these two studies differ by 1–4% in the overlap region, and this exceeds the usual experimental errors for these methods by an order of magnitude. In addition, both studies are somewhat scattered. The main source of these discrepancies seems to be the solution preparation method. Both studies (*9*, *10*) used direct weighing of "$MgCl_2$·6H_2O" that had been dried with a water aspirator at 50 °C. It has been our experience that attempts to dry hydrated chlorides to stoichiometric hydrates frequently results in samples that are overdried or underdried, so direct weighing of "$MgCl_2$·6H_2O" generally gives unreliable concentrations. Wu et al.'s isopiestic investigation (*8*) is free of this objection, but only 15 points were reported.

Christenson (*13*) reported NaCl activities in NaCl–$MgCl_2$ at I = 1 mol·kg^{-1} and Lanier (*11*) at I = 1, 3, and 6 mol·kg^{-1}. Both used sodium-sensitive glass electrodes and Ag/AgCl electrodes. Butler and Huston (*12*) did a more detailed study, I = 0.52–5.99 mol·kg^{-1}, using Na(Hg)/Na^+ and Ag/AgCl electrodes, but it was necessary to add ≤0.004 mol·kg^{-1} NaOH to their solutions in order to use the amalgam electrode.

The data of Christenson (*13*) and Lanier (*11*) at I = 1 mol·kg^{-1} are in excellent agreement, with maximum differences of about 0.002 in the activity coefficients of NaCl. Butler and Huston (*12*) are in general agreement with the other two studies (*11*, *13*), but have about 5 times as much scatter. Unfortunately, at I = 6 mol·kg^{-1} the only two studies (*11*, *12*) give inconsistent results. Lanier's values are in general agreement with the isopiestic data. We, therefore, reject Butler and Huston's data as inaccurate, most probably due to problems with the amalgam electrodes which are notoriously difficult to work with.

As noted above, we need very accurate data for the calculation of activity derivatives. However, some of the available data for aqueous NaCl–$MgCl_2$ solutions are of doubtful quality, and the remaining data do not completely cover the accessible concentration regions. Consequently, we decided to reinvestigate this system by the isopiestic method. Our data extend from moderately low concentrations (I = 0.295 mol·kg^{-1}) to the

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crystallization limits of the mixtures (I = 6.516–9.873 mol·kg^{-1}) at six different ionic strength fractions.

Experimental Section

All of the isopiestic measurements were performed at 25.00 ± 0.005 °C using isopiestic chambers and techniques that have been described in detail elsewhere (*15*, *16*). Aqueous $CaCl_2$ and NaCl solutions were used as isopiestic standards. Assumed molecular masses are 95.211 g·mol^{-1} for $MgCl_2$, 120.363 g·mol^{-1} for $MgSO_4$, 110.986 g·mol^{-1} for $CaCl_2$, 136.138 g·mol^{-1} for $CaSO_4$, and 58.443 g·mol^{-1} for NaCl. All water used for solution preparations and dilutions was first deionized and then distilled. All solution preparations and analyses were done by weight, and these weights were converted to masses.

The $CaCl_2$ stock solution is the same stock no. 1 used previously (*17*); its preparation, concentration analyses, and impurity analyses are described in detail there. The $MgCl_2$ stock solution was prepared by using a filtered solution made from Mallinckrodt AR $MgCl_2 \cdot 6H_2O$. An impurity analysis for a separate lot of this material indicates it contains a few thousandths of a percent or less of impurities by weight (*17*).

The concentration of this $MgCl_2$ stock solution was determined to be 5.5650 ± 0.0019 mol·kg^{-1} by conversion of triplicate samples to the anhydrous sulfate at 500–600 °C. Mass titration of samples in quadruplicate with $AgNO_3$ and a dichlorofluorescein indicator gave 5.5684 ± 0.0045 mol·kg^{-1}. The average of 5.5667 mol·kg^{-1} was used for calculations.

Two NaCl stock solutions were prepared by mass from oven-dried Mallinckrodt AR NaCl. The concentration of NaCl stock solution no. 1 was determined to be 4.9979 mol·kg^{-1} by direct weighing, and 4.9962 ± 0.0006 mol·kg^{-1} by dehydration of triplicate samples, and their average was used for calculations. NaCl stock solution no. 2 concentration analyses were done by direct weighing, by dehydration analysis, and by mass titration with $AgNO_3$; these results are in good agreement and were reported elsewhere (*17*). Its average analysis result of 4.9607 mol·kg^{-1} was used in calculations.

NaCl stock solution no. 1 was used for preparation of the NaCl–$MgCl_2$ mixtures, and as an isopiestic standard at high to moderate concentrations. A dilution from NaCl stock solution no. 2 was used as isopiestic standard at lower concentrations.

Solutions were allowed 5–7 days to reach isopiestic equilibrium at higher concentrations, but this was gradually increased to 31–44 days for the lowest concentrations. Required equilibration periods were longer than anticipated for NaCl reference concentrations below about 2 mol·kg^{-1} for mixtures with higher NaCl ionic strength fractions.

Duplicate samples of each solution were used for the isopiestic equilibrations, and the molalities of each solution at equilibrium agreed to ±0.10% or better in the majority of cases (most agreed to better than ±0.05%). However, for five of the equilibrations with NaCl reference concentrations of 1.2590 mol·kg^{-1} or lower, one or more of the solutions at equilibrium had concentration uncertainties of ±0.12–0.13%. Examination of the resulting osmotic coefficients at a fixed ionic strength fraction of NaCl and for the same isopiestic reference electrolyte indicates that the majority of points fall within 0.1% of a smooth curve, but a few points deviate by up to 0.25%. This scatter is commensurate with the imprecision of the equilibrations.

We have noted elsewhere (*17*) that the uncertainty in the osmotic coefficients of $CaCl_2$ can be as large as 0.2–0.4% in certain concentration regions, so we expect slight discrepancies between osmotic coefficients for NaCl–$MgCl_2$ mixtures when the reference standard is changed from NaCl to $CaCl_2$. The actual observed discrepancies are 0.001–0.003 in the osmotic coefficient Φ (0.05–0.2%) of NaCl–$MgCl_2$ mixtures for NaCl ionic strength fractions of 0.14519–0.43120, and about 0.004 in Φ ($\simeq$0.3%) for NaCl ionic strength fractions of 0.57390–0.85686.

Table I. Isopiestic Molalities of NaCl–$MgCl_2$ Mixtures with NaCl or $CaCl_2$ Reference Solutions at 25 °C

m_T, mol·kg^{-1}				
y_A = 0.85686	y_A = 0.71276	y_A = 0.57390	[ref], mol·kg^{-1}	Φ*(ref)
		NaCl Reference		
0.26654	0.26005	0.25209	0.27178	0.9204
0.31846	0.30975	0.29985	0.32413	0.9196
0.36834	0.35839	0.34687	0.37583	0.9194
0.42076	0.40902	0.39549	0.42986	0.9196
0.43984	0.42764	0.41343	0.44988	0.9198
0.59189	0.57396	0.55331	0.60579	0.9224
0.66004	0.63967	0.61609	0.67675	0.9241
0.88209	0.85172	0.81723	0.90446	0.9312
1.0589	1.0200	0.97617	1.0869	0.9381
1.1375	1.0944	1.0461	1.1691	0.9415
1.2270[a]	1.1775	1.1235	1.2590	0.9454
1.3485	1.2940	1.2333	1.3895	0.9514
1.4826	1.4205	1.3515	1.5300	0.9581
1.6310	1.5600	1.4811	1.6856	0.9659
1.8558	1.7707	1.6767	1.9214	0.9785
2.0568	1.9582	1.8501	2.1372	0.9906
2.2781	2.1630	2.0388	2.3796	1.0049
2.4043	2.2805	2.1468	2.5138	1.0131
2.5328	2.4011	2.2568	2.6524	1.0218
2.6726	2.5290	2.3744	2.8006	1.0312
2.7864	2.6345	2.4708	2.9235	1.0393
2.8778	2.7182	2.5475	3.0205	1.0457
2.9202	2.7587	2.5851	3.0635	1.0486
3.0811	2.9069	2.7200	3.2358	1.0602
3.2639	3.0752	2.8731	3.4321	1.0738
3.3988	3.1990	2.9859	3.5773	1.0841
3.5482	3.3359	3.1102	3.7383	1.0956
3.7732	3.5429	3.2982	3.9818	1.1133
3.9085	3.6662	3.4092	4.1273	1.1241
4.0208	3.7685	3.5020	4.2475	1.1330
4.0632	3.8071	3.5370	4.2945	1.1366
4.2066	3.9384	3.6557	4.4502	1.1483
4.3615	4.0794	3.7825	4.6174	1.1610
4.4356	4.1473	3.8439	4.6991	1.1673
4.4889	4.1951	3.8878	4.7553	1.1716
4.5416	4.2440	3.9309	4.8125	1.1760
		$CaCl_2$ Reference		
4.6592	4.3512	4.0273	2.5018	1.5677
4.8119	4.4889	4.1523	2.5695	1.5944
4.9529	4.6170	4.2674	2.6313	1.6190
5.0902	4.7408	4.3779	2.6913	1.6429
5.2437	4.8815	4.5036	2.7584	1.6698
5.4186	5.0391	4.6452	2.8333	1.7000
5.6061	5.2076	4.7971	2.9135	1.7325
5.7513	5.3379	4.9131	2.9752	1.7576
	5.4460	5.0082	3.0250	1.7780
5.8940	5.4692	5.0291	3.0361	1.7825
	5.5763	5.1238	3.0858	1.8029
	5.5942	5.1397	3.0939	1.8062
		5.2488	3.1500	1.8292

[a] This point was given zero weight in the least-squares fits.

Tables I and II contain the experimental isopiestic data. Here A denotes NaCl and B denotes $MgCl_2$. The quantities tabulated are the reference solution molalities, the total molalities m_T for the mixed salt solutions, the ionic strength fractions of NaCl y_A, and the osmotic coefficients of the standard solutions Φ^*. The total molalities are given by

$$m_T = m_A + m_B \tag{1}$$

and the ionic strength fractions by

$$y_A = m_A/(m_A + 3m_B) \tag{2}$$

and

$$y_B = 3m_B/(m_A + 3m_B) \tag{3}$$

Values of Φ^* for the NaCl standards were taken from Hamer

Table II. Isopiestic Molalities of NaCl–MgCl$_2$ Mixtures with NaCl or CaCl$_2$ Reference Solutions at 25 °C

m_T, mol·kg^{-1}				
y_A = 0.43120	y_A = 0.28569	y_A = 0.14519	[ref], mol·kg^{-1}	Φ*(ref)
		NaCl Reference		
0.24496	0.23211	0.21579	0.27634	0.9203
0.29883	0.28264	0.26230	0.33837	0.9195
0.36649	0.34606	0.32040	0.41695	0.9195
0.40728	0.38406	0.35512	0.46482	0.9199
0.53140	0.49923	0.45826	0.61028	0.9225
0.63481	0.59399	0.54439	0.73464	0.9257
0.72560	0.67718	0.61898	0.84515	0.9292
0.81001	0.75390	0.68715	0.94881	0.9328
0.92461	0.85803	0.77940	1.0920	0.9383
1.0100	0.93556	0.84836	1.2015	0.9429
1.0122	0.93752	0.84948	1.2029	0.9430
1.1010	1.0177	0.92021	1.3181	0.9481
1.2232	1.1276	1.0159	1.4761	0.9555
1.2379	1.1404	1.0273	1.4951	0.9564
1.3044	1.1996	1.0787	1.5816	0.9606
1.3855	1.2728	1.1420	1.6882	0.9660
1.4706	1.3484	1.2074	1.8018	0.9720
1.5748	1.4404	1.2865	1.9410	0.9795
1.7396	1.5857	1.4112	2.1644	0.9922
1.9162	1.7414	1.5439	2.4071	1.0066
2.0534	1.8591	1.6447	2.5934	1.0181
2.1131	1.9161	1.6969	2.6827	1.0237
2.2327	2.0211	1.7861	2.8515	1.0346
2.3664	2.1364	1.8835	3.0385	1.0469
2.4730	2.2296	1.9626	3.1919	1.0572
2.5726	2.3168	2.0362	3.3364	1.0672
2.6826	2.4119	2.1160	3.4937	1.0782
2.8001	2.5138	2.2017	3.6644	1.0903
2.9211	2.6179	2.2890	3.8401	1.1030
3.0639	2.7423	2.3936	4.0519	1.1185
3.2061	2.8636	2.4947	4.2607	1.1340
3.3787	3.0139	2.6196	4.5172	1.1534
3.5810	3.1848	2.7622	4.8198	1.1766
3.6934	3.2833	2.8436	4.9916	1.1899
3.7582	3.3383	2.8881	5.0868	1.1973
		CaCl$_2$ Reference		
3.8471	3.4115	2.9500	2.6129	1.6116
3.8695	3.4311	2.9658	2.6261	1.6169
3.9549	3.5029	3.0259	2.6785	1.6378
4.0412	3.5767	3.0870	2.7311	1.6589
4.1263	3.6484	3.1459	2.7832	1.6798
4.2216	3.7290	3.2114	2.8394	1.7025
4.3070	3.8013	3.2720	2.8917	1.7237
4.4231	3.9009	3.3537	2.9620	1.7523
4.5519	4.0098	3.4444	3.0398	1.7840
4.6868	4.1241	3.5382	3.1206	1.8171
4.8568	4.2667	3.6537	3.2203	1.8581
	4.3299	3.7055	3.2644	1.8763
	4.5099	3.8544	3.3915	1.9289
		3.9227	3.4527	1.9542
		4.0940	3.5995	2.0151
		4.2465	3.7280	2.0683

and Wu (*18*) with a small correction applied (*19*), and CaCl$_2$ Φ^* are from Rard et al. (*20*).

A total of 287 experimental points were measured for NaCl–MgCl$_2$ mixtures of which 224 have ionic strengths below I = 6.16 mol·kg^{-1}, the pure NaCl solubility limit (*17*). The highest experimental concentrations were obtained by removal of water vapor from the chambers during evacuation of air before starting the equilibrations, sometimes assisted by adding an extra cup with one or two drops of concentrated H_2SO_4 to absorb water. Attempts to reach even higher concentrations by this method resulted in spontaneous crystallization. Since neither pure NaCl nor MgCl$_2$ supersaturate very much under these conditions, we estimated that the highest m_T values in Tables I and II are within 0.05–0.2 mol·kg^{-1} of true saturation.

Although MgCl$_2$·6H$_2$O is much more soluble than SrCl$_2$·6H$_2$O (5.811 vs. 3.520 mol·kg^{-1}) at 25 °C (*15*, *17*), the highest m_T values for NaCl–SrCl$_2$ (*21*) are higher than for NaCl–MgCl$_2$ at all of our experimental y_A values. Thus salting out is greater for the NaCl–MgCl$_2$ case, although m_T for NaCl–MgCl$_2$ must obviously exceed m_T for NaCl–SrCl$_2$ when y_B approaches one. Visual inspection of the precipitating phases for NaCl–MgCl$_2$ mixtures indicates that cubic NaCl is the saturating phase for $y_A \geq 0.285\,69$, whereas either MgCl$_2$·6H$_2$O or a mixture precipitates when $y_A = 0.145\,19$.

Table III. Isopiestic Molalities of MgCl$_2$ with CaCl$_2$ Reference Solutions at 25 °C

m^*(CaCl$_2$), mol·kg^{-1}	m(MgCl$_2$), mol·kg^{-1}	Φ(MgCl$_2$)	ΔΦ[a]
3.2521	3.0039	2.0259	+0.0006
3.3110	3.0579	2.0525	−0.0006
3.4590	3.1913	2.1210	−0.0010
3.5307	3.2549	2.1549	−0.0001

[a] Experimental Φ minus value calculated from our eq 18, eq 2 of Rard and Miller (ref *17*).

Since the MgCl$_2$ stock solution used in mixed salt determinations was different from the one used for the binary solutions (*17*), we decided to measure a few more MgCl$_2$ osmotic coefficients for a consistency check. The results are given in Table III. These results fall well within the uncertainty of the earlier determinations. Similarly, the recent isopiestic study of Kuschel and Seidel (*5*) for MgCl$_2$ using a KCl standard shows a similar excellent agreement with our earlier values (*17*).

Calculations and Discussion

The molal osmotic coefficients of our NaCl–MgCl$_2$ solutions were calculated with the equation for isopiestic equilibrium

$$\Phi = \nu^* m^* \Phi^* / (\sum_i \nu_i m_i) \tag{4}$$

where ν is the number of ions formed by the complete dissociation of one molecule of solute, and Φ is the molal osmotic coefficient. The corresponding quantities for the isopiestic standards are denoted with asterisks. Values of Φ^* were taken from published equations (*18*, *20*).

Our isopiestic concentrations of NaCl–MgCl$_2$ mixtures are reported in terms of the total molality m_T, but calculations of Φ by eq 4 require the osmolality $\sum_i \nu_i m_i$. Also, most least-squares representations of ternary solutions activity data are in terms of ionic strength, and our least-squares fitting programs use m_A and m_B values as input. It is thus useful to give equations relating these quantities.

For NaCl–MgCl$_2$ mixtures, and other mixtures of salts of the same valence types, the following equations apply. The osmolality is given by

$$\sum_i \nu_i m_i = 2m_A + 3m_B \tag{5}$$

The osmolality can be related to m_T and I by the equations

$$\sum_i \nu_i m_i = \frac{3(1 + y_A)}{1 + 2y_A} m_T = (1 + y_A)I \tag{6}$$

$$I = \frac{\sum_i \nu_i m_i}{1 + y_A} = \frac{3m_T}{1 + 2y_A} = m_A + 3m_B \tag{7}$$

Similarly

$$m_A = y_A I = \frac{y_A \sum_i \nu_i m_i}{1 + y_A} = \frac{3y_A m_T}{1 + 2y_A} \tag{8}$$

$$m_B = \left(\frac{y_B}{3}\right) I = \frac{y_B \sum_i \nu_i m_i}{3(1 + y_A)} = \frac{y_B m_T}{1 + 2y_A} \tag{9}$$

Isopiestic data yield osmotic coefficients which are a direct measure of the solvent activity. It is then necessary to represent these ternary solution osmotic coefficients with some type of least-squares equation in order to calculate activity coefficients for the constituent electrolytes. We chose Pitzer's equations (*22*) and Scatchard's neutral electrolyte equations (*23*) since they generally work very well for NaCl–MCl_2 and KCl–MCl_2 solutions (*5*, *21*, *22*, *24*).

Pitzer's approach for ternary solutions first requires parameters for constituent binary solutions. These binary solution equations contain the Debye–Hückel term denoted by f^ϕ and two parameters B^ϕ and C^ϕ which are specific to the electrolyte of interest (B^ϕ depends on the specific parameters $\beta^{(0)}$ and $\beta^{(1)}$). These binary solution terms are then evaluated at the total ionic strength of the mixture, and the difference between the experimental Φ values and the binary solution parameter approximation is represented by a two-parameter mixing term weighted by a function of the molalities.

For NaCl–$MgCl_2$ mixtures, and other common anion mixtures of the same valence type, Pitzer's ternary solution equation for Φ takes the form

$$\frac{(\Phi - 1)}{2}\sum_i \nu_i m_i = If^\phi + m_A(m_A + 2m_B) \times$$
$$[B_A{}^\phi + (m_A + 2m_B)C_A{}^\phi] + m_B(m_A + 2m_B)\Bigg[B_B{}^\phi +$$
$$\left(\frac{m_A + 2m_B}{2^{1/2}}\right)C_B{}^\phi\Bigg] + m_A m_B[\Theta + (m_A + 2m_B)\psi] \quad (10)$$

where $f^\phi = -0.3920I^{1/2}/(1 + 1.2I^{1/2})$. Sometimes Θ is allowed to have an ionic strength dependence, i.e., $\Theta = \Theta^\circ + I\Theta'$. Binary solution parameters for NaCl were taken from Pitzer (*22*) and for $MgCl_2$ from Rard and Miller (*17*). Values used are $\beta_A{}^{(0)} = 0.0765$, $\beta_A{}^{(1)} = 0.2664$, $C_A{}^\phi = 0.001\,27$, $\beta_B{}^{(0)} = 0.350\,93$, $\beta_B{}^{(1)} = 1.650\,75$, and $C_B{}^\phi = 0.006\,507$.

Pitzer has extended his theory to include higher order electrostatic effects (*25*). These higher order electrostatic effects are most important for mixtures of HCl with higher valence chlorides, e.g., HCl–$SrCl_2$ and HCl–$AlCl_3$. A comparison of the standard deviation $\sigma(\Phi)$ for least-squares representations by using Pitzer's Φ equations for mixtures of alkali metal–alkaline earth metal chlorides with and without higher order electrostatic terms indicates that both approaches work almost equally well. Therefore, we chose not to include the higher order effects since the resulting equations are simpler in form and adequately represent the NaCl–$MgCl_2$ data.

Activity data were also represented by Scatchard's neutral electrolyte equations (*23*). His Φ equation for two electrolytes in one solvent can be written in the form (*21*)

$$\Phi\frac{(\sum_i \nu_i m_i)}{I} =$$
$$\frac{\nu_A m_A \phi_A{}^0}{I} + \frac{\nu_B m_B \phi_B{}^0}{I} + y_A y_B I(b_{01} + b_{02}I + b_{03}I^2) +$$
$$y_A y_B(y_A - y_B)I^2(b_{12} + b_{13}I) + y_A y_B(y_A - y_B)^2 I^3 b_{23} \quad (11)$$

Here $\phi_i{}^0$ is the osmotic coefficient of the pure aqueous constituent electrolyte i evaluated at the total ionic strength of the mixture. The first two terms on the right-hand side represent the binary mixing approximation, the next term containing b_{0j} parameters represents symmetrical mixing effects, whereas the term containing b_{1j} represents asymmetrical mixing effects. As many of these b_{ij} as are required to reliably represent the experimental data are included in the calculations; any other b_{ij} are fixed at zero. The b_{23} term has not been included by most workers. However, Leifer and Wigent (*26*) argue that it should be included since, like b_{03} and b_{13}, it is necessary to fully account for four-ion interactions.

Analysis of the experimental uncertainties indicates that Φ has a relatively constant error, about a factor of 2 variation, over the entire concentration range. To obtain an appproximately equal weighting of Φ without a complex weighting scheme, it is convenient to recast eq 11 in the form

$$g(I) = \Phi - \frac{\nu_A m_A \phi_A{}^0}{\sum_i \nu_i m_i} - \frac{\nu_B m_B \phi_B{}^0}{\sum_i \nu_i m_i} \quad (12)$$
$$= \Phi - h_A \phi_A{}^0 - h_B \phi_B{}^0$$

where $g(I)$ is the deviation from the binary mixing approximation and

$$h_j = \frac{\nu_j m_j}{\sum_i \nu_i m_i} \quad (13)$$

is the osmolality fraction of electrolyte j. Then

$$g(I) = \frac{y_A y_B I^2}{\sum_i \nu_i m_i}[b_{01} + b_{02}I + b_{03}I^2 + b_{12}(y_A - y_B)I +$$
$$b_{13}(y_A - y_B)I^2 + b_{23}(y_A - y_B)^2 I^2] \quad (14)$$

The parameters of this equation can then be obtained from the experimental activity data by standard linear least-squares methods. However, depending on the concentration dependence of Φ for a particular mixture, one or more of the b_{ij} may not be required and so can be set equal to zero. The least-squares variable associated with a particular b_{jk} for this equation has the general form

$$\frac{y_A y_B I}{\sum_i \nu_i m_i}(y_A - y_B)^j I^k \quad (15)$$

It is also possible to least-square the simpler looking expressions

$$g_1(I) = \frac{g(I)\sum \nu_i m_i}{y_A y_B I} = b_{01}I + b_{02}I^2 + \ldots \quad (16)$$

$$g_2(I) = \frac{g(I)\sum \nu_1 m_i}{y_A y_B I^2} = b_{01} + b_{02}I + \ldots \quad (17)$$

However, unless care is taken to use correct weights for the data, least-squares fits will be distorted in certain concentration regions. For example, unit weights for $g_1(I)$ heavily weight data with y_A near zero or one, and give little weight when $y_A \simeq 0.5$. Expression $g_2(I)$ distorts the weights in a similar manner but also weights lower I data too much relative to larger I. Thus, to get correct weighting for $g_1(I)$ and $g_2(I)$, much more complicated weighting schemes than for $g(I)$ are required.

Binary $\phi_i{}^0$ for Scatchard fits were taken from Hamer and Wu for NaCl (*18*) and from Rard and Miller for $MgCl_2$ (*17*). Since the NaCl $\phi_A{}^0$ equation is extrapolated beyond its range of validity, the values of b_{ij} obtained will depend more strongly on the chosen $\phi_A{}^0$ equation when $I \geq 6.16$ mol·kg^{-1} data are included.

Hamer and Wu's equation for NaCl (*18*) is in terms of the molality, which is equal to the ionic strength for a 1–1 salt. Thus, it can simply be evaluated at the total ionic strength of the mixture. The $MgCl_2$ $\phi_B{}^0$ equation with its numerical coefficients (*17*) is

$$\phi_B{}^0 =$$
$$1 - (4.0744/3)m^{1/2} + 5.315953m - 11.80327m^{3/2} +$$
$$17.48381m^2 - 16.412564m^{5/2} + 9.784278m^3 -$$
$$3.550148m^{7/2} + 0.7090234m^4 - 0.05938028m^{9/2} \quad (18)$$

For salts of this valence type $I = 3m$, so eq 18 should be evaluated at one-third of the ionic strength.

In order to compare the consistency of our isopiestic data with that of Wu et al. (*8*) and Platford (*9*), their data were recalculated to Hamer and Wu's Φ^* values (*18*). Each set was then separately least-squared to obtain the parameters of Scatchard's neutral electrolyte equations. Generally, the fits with b_{01}, b_{02}, and b_{12} (i.e., with b_{03}, b_{13}, and $b_{23} = 0$) were among the better ones, so they were used to compare data sets for consistency.

For this three-parameter fit our data gave a standard deviation $\sigma(\Phi) = 0.002\,48$ with a maximum deviation of 0.0061 with one point weighted zero. Although many of the points were fit within their experimental uncertainty, several points with $y_A = 0.145\,19$ or $0.856\,86$ had deviations of 3-4 times their precision. Restricting these fits to $I \leq 6.2$ mol·kg^{-1} reduced $\sigma(\Phi)$ by about 10% for several other b_{ij} combinations and the maximum deviation to about 0.0046. A similar fit to Platford's data (*9*) gave $\sigma(\Phi) = 0.005\,41$ with a maximum deviation of 0.0258 and for Wu et al. (*8*) $\sigma(\Phi) = 0.000\,93$ with a maximum deviation of 0.0015. However, it was reported that when the neural electrolyte equation was fitted to Platford's data for just I = 1.2 to 6.0 mol·kg^{-1} but with a different $\phi_B{}^0$ equation (*9*, *24*), then $\sigma(\Phi)$ is only about 40% as large as when we used his entire data set.

Much of the improvement in fits when Platford's data were restricted to $1.2 \leq I \leq 6.0$ came from eliminating some scattered low concentration points. However, some improvement also came because the equation was no longer required to represent the very high concentration behavior. Similar test calculations for our data gave slightly better fits when data for $I \geq 6.2$ mol·kg^{-1} were eliminated, but almost no improvement occurred when $I \leq 1.0$ mol·kg^{-1} data were removed. This implies that the high quality fits to Wu et al.'s data were partly fortuitous, i.e., they were due to a lack of experimental data above $I = 5.931$ mol·kg^{-1}.

We experienced no such fitting difficulties with NaCl–$SrCl_2$ (*21*). A comparison of the calculations indicates that much of the problem is related to the neutral electrolyte binary mixing approximation. The $\sigma(\Phi)$ for the difference between the experimental Φ values and the binary mixing term was 0.0041 for NaCl–$SrCl_2$, but it is 0.0184 for NaCl–$MgCl_2$ with $0.295 \leq I \leq 9.873$. Thus, the NaCl–$MgCl_2$ system has much larger deviations from the binary mixing approximation than for NaCl–$SrCl_2$, so the mixing terms make a much larger (and probably less accurate) contribution for NaCl–$MgCl_2$.

These separate Scatchard neutral electrolyte fits to the three sets of isopiestic data allow a detailed comparison to be made. Platford's Φ values (*9*) for $I \geq 2.05$ mol·kg^{-1} are of good precision, and they are in excellent agreement (0.0–0.3%) with our data; this is within experimental error. At lower concentrations most of his data still agree with ours, but some points show deviations several times larger than at higher concentrations.

Platford (*9*) denoted his individual equilibrations as "sets". His set 4 values of Φ(4 points) are 0.5–2.5% low, whereas his set 5 values (5 points) are 0.4–2.0% high. These values are systematically in error and were given weights of zero. Six of his other points were also given zero weights owing to large deviations of 0.5–1.0% (his set 1 with I = 0.1714 and 0.1835, his set 2 with I = 0.3076 and 0.3287, and his set 6 with I = 1.1631 and 1.1852). After these 15 unreliable points were eliminated, some combinations of b_{ij} with three or more coefficients gave $\sigma(\Phi)$ as low as 0.0016 for his data. Platford's (*9*) other 72 points were each given unit weights in subsequent calculations, as were all but one of our points.

The Φ data of Wu et al. (*8*) are within 0.4% of our data and were also assigned unit weights.

This agreement between the three independent sets of isopiestic data is remarkably good, and it indicates that the direct vapor pressure data (*10*) are significantly in error.

Table IV. Parameters for Pitzer's Equation Treatment of Aqueous NaCl–$MgCl_2$[a]

θ°	θ'	ψ	$\sigma(\Phi)$	max dev
		Our Data with $I \leq 6.2$ mol·kg^{-1}		
			0.0036[b]	0.0085
−0.002 187			0.0035	0.0090
0.010 668		−0.003 360	0.0033	0.0079
0.007 238	0.008 567	−0.012 810	0.0032	0.0073
		Our Data with $I \leq 9.8726$ mol·kg^{-1}		
			0.0052	0.0207
−0.006 596			0.0044	0.0100
0.016 130		−0.004 633	0.0036[b]	0.0089
0.017 405	0.007 786	−0.014 628	0.0033	0.0083
		All Isopiestic Data with $I \leq 6.2$ mol·kg^{-1}		
			0.0034[b]	0.0085
−0.001 738			0.0033	0.0089
0.011 765		−0.003 563	0.0031	0.0077
0.008 503	0.008 999	−0.013 663	0.0030	0.0072
		All Isopiestic Data with $I \leq 9.8726$ mol·kg^{-1}		
			0.0049	0.0207
−0.005 923			0.0043	0.0099
0.016 271		−0.004 585	0.0036[b]	0.0095
0.017 374	0.009 032	−0.016 158	0.0031	0.0094

[a] Fifteen of Platford's points (*9*) were given zero weight; see the text for details. [b] Our preferred fit for this concentration range.

Scatchard et al. (*27*) showed that their ion-component approach often gave a much better binary mixing approximation than the neutral electrolyte approach, but when mixing terms were included both approaches represented experimental data with very nearly equal accuracy. Thus, there is little advantage to using the much more complicated ion-component approach for common ion mixtures.

Table IV contains the parameters for Pitzer's equation for the one-, two-, and three-parameter fits and the four conditions: (1) our data only with $I \leq 6.2$ mol·kg^{-1}; (2) our data only for the entire concentration range; (3) all isopiestic data sets $I \leq 6.2$ mol·kg^{-1}; and (4) all isopiestic data sets for the entire concentration range. Tables V and VI give the corresponding parameters for Scatchard's neutral electrolyte equations. There were 44 different combinations of b_{ij} parameters tested for these Scatchard fits; only selected coefficients are given because of the large number calculated.

For $I \leq 6.2$ mol·kg^{-1}, Pitzer's equation for the binary mixing case (i.e., no mixing parameters) is quite good, and little improvement occurs when mixing parameters were optimized. When the entire concentration range was considered, two mixing parameters were required for comparable accuracy. These mixing parameters may be partially compensating for problems with the NaCl equation which is being used outside its range of validity.

Table V shows the Scatchard parameters for our data with $I \leq 6.2$ mol·kg^{-1}. Including just b_{01} reduced $\sigma(\Phi)$ and the maximum deviation by a factor of 4 from the binary mixing approximation. With more than one parameter it was possible to reduce $\sigma(\Phi)$ to 0.0021 and maximum deviations of 0.0045–0.0046. Three of these cases had large standard errors for one or more of the coefficients and so were rejected. The other two were of nearly identical quality (b_{01}, b_{02}, b_{12}, and b_{13}; b_{01}, b_{03}, b_{12}, and b_{13}), so there is little basis for choosing between them. The use of b_{23} was not justified, since it had large uncertainty and did not improve the fits.

In contrast, when the entire concentration range of our data was represented, the b_{23} coefficient had much smaller standard error (<20%) in many cases, and it was required for the best quality fits. These better fits to our data had $\sigma(\Phi)$ = 0.0023–0.0024 and maximum deviations of 0.0050–0.0061. Five or six parameters were required, but these fits were only

Table V. Parameters for Scatchard Neutral Electrolyte Treatment of Aqueous NaCl-MgCl$_2$ with Our Data Only[a]

b_{01}	b_{02}	b_{03}	b_{12}	b_{13}	b_{23}	$\sigma(\Phi)$	max dev
			$I \le 6.2$ mol·kg^{-1}				
						0.0145	0.0304
0.029 966 (0.02)						0.0033	0.0085
0.042 332 (0.04)	−0.002 677 (0.13)					0.0029	0.0074
0.045 957 (0.08)	−0.004 666 (0.42)	0.000 244 (0.96)				0.0029	0.0076
0.045 170 (0.08)	−0.004 404 (0.40)	0.000 216 (0.99)	−0.001 442 (0.15)			0.0026	0.0062
0.043 446 (0.06)	−0.004 334 (0.33)	0.000 267 (0.64)	−0.012 502 (0.08)	0.002 170 (0.09)		0.0021	0.0045
0.043 635 (0.06)	−0.004 458 (0.32)	0.000 269 (0.64)	−0.012 475 (0.08)	0.002 173 (0.09)	0.000 109 (0.69)	0.0021	0.0045
	0.005 882 (0.03)					0.0059	0.0123
0.029 747 (0.01)			−0.001 477 (0.17)			0.0031	0.0074
0.039 484 (0.03)	−0.002 156 (0.12)		−0.012 466 (0.08)	0.002 162 (0.09)		0.0021[b]	0.0046
0.035 185 (0.02)		−0.000 248 (0.12)	−0.012 527 (0.08)	0.002 173 (0.09)		0.0022	0.0045
			$I \le 9.8726$ mol·kg^{-1}				
						0.0184	0.0346
0.028 668 (0.01)						0.0035	0.0095
0.035 017 (0.03)	−0.001 035 (0.18)					0.0034	0.0080
0.049 000 (0.05)	−0.006 470 (0.14)	0.000 478 (0.16)				0.0032	0.0081
0.042 706 (0.05)	−0.003 205 (0.23)	0.000 091 (0.72)	−0.001 558 (0.08)			0.0025	0.0061
0.045 056 (0.05)	−0.004 472 (0.20)	0.000 234 (0.37)	−0.002 883 (0.19)	0.000 206 (0.40)		0.0025[b]	0.0056
0.045 697 (0.04)	−0.005 077 (0.16)	0.000 289 (0.28)	−0.004 767 (0.12)	0.000 580 (0.17)	0.000 266 (0.16)	0.0023	0.0050
	0.004 272 (0.02)					0.0067	0.0157
0.027 546 (0.01)			−0.000 910 (0.13)			0.0032	0.0093
0.040 266 (0.02)	−0.002 219 (0.07)		−0.001 629 (0.06)			0.0025	0.0061
0.039 828 (0.03)	−0.002 137 (0.08)		−0.002 060 (0.22)	0.000 062 (1.01)		0.0025	0.0059
0.041 042 (0.02)	−0.002 435 (0.07)		−0.001 341 (0.10)		0.000 115 (0.28)	0.0024	0.0061
0.039 266 (0.03)	−0.002 187 (0.08)		−0.003 650 (0.14)	0.000 381 (0.21)	0.000 250 (0.17)	0.0024	0.0055
0.033 719 (0.02)		−0.000199 (0.09)	−0.003 044 (0.18)	0.000 274 (0.32)	0.000 237 (0.19)	0.0024	0.0061

[a] In parentheses is the standard error of the coefficient divided by the coefficient. [b] Our preferred fit for this concentration range.

Table VI. Parameters for Scatchard Neutral Electrolyte Treatment of Aqueous NaCl-MgCl$_2$ with All Isopiestic Sets[a]

b_{01}	b_{02}	b_{03}	b_{12}	b_{13}	b_{23}	$\sigma(\Phi)$	max dev
			$I \le 6.2$ mol·kg^{-1}				
						0.0143	0.0318
0.030 342 (0.01)						0.0032	0.0084
0.042 919 (0.03)	−0.002 724 (0.10)					0.0028	0.0073
0.048 444 (0.07)	−0.005 807 (0.29)	0.000 380 (0.53)				0.0028	0.0075
0.046 788 (0.06)	−0.004 960 (0.29)	0.000 258 (0.69)	−0.001 622 (0.10)			0.0025	0.0060
0.046 648 (0.05)	−0.005 852 (0.21)	0.000 441 (0.35)	−0.010 553 (0.08)	0.001 740 (0.10)		0.0021	0.0060
0.046949 (0.05)	−0.006 067 (0.20)	0.000 439 (0.34)	−0.010 728 (0.08)	0.001 804 (0.09)	0.000 224 (0.28)	0.0021	0.0052
	0.005 933 (0.03)					0.0059	0.0122
0.029 822 (0.01)			−0.001 518 (0.13)			0.0030	0.0077
0.040 333 (0.03)	−0.002 299 (0.10)		−0.010 287 (0.09)	0.001 682 (0.10)		0.0022[b]	0.0060
0.035 730 (0.02)		−0.000 263 (0.11)	−0.010 309 (0.09)	0.001 684 (0.10)		0.0022	0.0061
			$I \le 9.8726$ mol·kg^{-1}				
						0.0179	0.0346
0.029 023 (0.01)						0.0036	0.0100
0.035 768 (0.03)	−0.001 110 (0.15)					0.0034	0.0079
0.050 209 (0.04)	−0.006 856 (0.12)	0.000 514 (0.13)				0.0032	0.0086
0.044 051 (0.04)	−0.003 607 (0.17)	0.000 115 (0.50)	−0.001 705 (0.06)			0.0024	0.0059
0.046 143 (0.04)	−0.004 793 (0.16)	0.000 252 (0.30)	−0.003 009 (0.16)	0.000 205 (0.35)		0.0024[b]	0.0056
0.046 973 (0.04)	−0.005 512 (0.13)	0.000 322 (0.22)	−0.004 774 (0.10)	0.000 565 (0.15)	0.000 256 (0.14)	0.0022	0.0061
	0.004 346 (0.02)					0.0067	0.0166
0.027 642 (0.01)			−0.001 018 (0.11)			0.0032	0.0085
0.041 067 (0.02)	−0.002 380 (0.06)		−0.001 790 (0.05)			0.0024	0.0061
0.040 736 (0.02)	−0.002 319 (0.07)		−0.002 108 (0.19)	0.000 046 (1.20)		0.0024	0.0061
0.041 833 (0.02)	−0.002 601 (0.05)		−0.001 472 (0.08)		0.000 123 (0.23)	0.0023	0.0059
0.040 130 (0.02)	−0.002 352 (0.06)		−0.003 497 (0.12)	0.000 337 (0.20)	0.000 234 (0.15)	0.0023	0.0057
0.034 265 (0.02)		−0.000 216 (0.07)	−0.002 838 (0.17)	0.000 220 (0.35)	0.000 218 (0.17)	0.0024	0.0060

[a] In parentheses is the standard error of the coefficient divided by the coefficient. Fifteen of Platford's points (*9*) were given zero weight: see the text for details. [b] Our preferred fit for this concentration range.

marginally less reliable than the $I \le 6.2$ mol·kg^{-1} case. Although there were several three-parameter fits of nearly comparable accuracy with $\sigma(\Phi) = 0.0025$, including the b_{23} term helped reduce the maximum deviation size. Representative Scatchard parameters for this concentration range are also given in Table V.

The corresponding Scatchard neutral electrolyte parameters for our data combined with Platford (*9*) and Wu et al. (*8*) are given in Table VI. For the same combinations of parameters and concentration range, this combined data set and also our data alone, Table V, gave fits of very nearly equal quality. For each concentration range in Tables V and VI, there were several of the better fits that had very nearly equal standard deviations. In each case, we have indicated our subjective "preferred" fits. They were selected by consideration of standard deviations, maximum deviations, coefficient errors, and the minimum number of coefficients necessary for a reliable representation of the data.

There are several things to note about the neutral electrolyte coefficients in Tables V and VI. (1) At least one symmetrical mixing term was required, and the b_{01} term was required for all of the higher quality fits. (2) The highest quality fits required

Table VII. Negative of the Natural Logarithm of the Activity Coefficient of NaCl in NaCl-MgCl$_2$ Mixtures

I, mol·kg^{-1}	y_A				
	0.00	0.25	0.50	0.75	1.00
	Pitzer Equation^a				
0.5	0.348	0.359	0.369	0.379	0.387
1.0	0.367	0.384	0.399	0.412	0.423
2.0	0.330	0.353	0.374	0.391	0.406
3.0	0.250	0.278	0.303	0.323	0.339
4.0	0.146	0.178	0.205	0.229	0.247
5.0	0.027	0.062	0.092	0.117	0.137
6.0	−0.104	−0.067	−0.035	−0.008	0.014
	Scatchard Neutral Electrolyte Equation^a				
0.5	0.360	0.366	0.372	0.378	0.384
1.0	0.383	0.393	0.403	0.412	0.420
2.0	0.345	0.362	0.377	0.391	0.403
3.0	0.262	0.286	0.306	0.323	0.337
4.0	0.155	0.186	0.211	0.230	0.244
5.0	0.032	0.070	0.099	0.120	0.134
6.0	−0.104	−0.058	−0.024	0.000	0.014

[a] Based on fits of isopiestic data with $I \leq 9.8726$ mol·kg^{-1}. Binary mixing approximation used for Pitzer's equation ($\Theta = \psi = 0$). Scatchard parameters used are $b_{01} = 0.046143$, $b_{02} = -0.004793$, $b_{03} = 0.000252$, $b_{12} = -0.003009$, and $b_{13} = 0.000205$.

Table VIII. Negative of the Natural Logarithm of the Activity Coefficient of MgCl$_2$ in NaCl-MgCl$_2$ Mixtures

I, mol·kg^{-1}	y_B				
	0.00	0.25	0.50	0.75	1.00
	Pitzer Equation^a				
0.5	0.679	0.688	0.696	0.702	0.706
1.0	0.701	0.721	0.736	0.748	0.755
2.0	0.603	0.638	0.667	0.689	0.705
3.0	0.426	0.475	0.515	0.547	0.572
4.0	0.207	0.267	0.318	0.360	0.393
5.0	−0.044	0.028	0.089	0.141	0.183
6.0	−0.318	−0.235	−0.163	−0.101	−0.050
	Scatchard Neutral Electrolyte Equation^a				
0.5	0.712	0.711	0.711	0.710	0.710
1.0	0.746	0.749	0.752	0.755	0.758
2.0	0.655	0.666	0.678	0.691	0.705
3.0	0.483	0.502	0.523	0.546	0.572
4.0	0.269	0.295	0.324	0.358	0.395
5.0	0.029	0.059	0.096	0.140	0.187
6.0	−0.227	−0.195	−0.153	−0.102	−0.045

[a] Based on fits of isopiestic data with $I \leq 9.8726$ mol·kg^{-1}. Binary mixing approximation used for Pitzer's equation ($\Theta = \psi = 0$). Scatchard parameters used are $b_{01} = 0.046143$, $b_{02} = -0.004793$, $b_{03} = 0.000252$, $b_{12} = -0.003009$, and $b_{13} = 0.000205$.

at least two symmetrical and one or two asymmetrical mixing terms. (3) The b_{23} term was significant only when the entire concentration range was used. Also, five-parameter fits without b_{23} were almost as reliable as the two five-parameter fits with it.

Comparison of the $\sigma(\Phi)$ and maximum deviations for Pitzer's (Table IV) and Scatchard's neutral electrolyte (Tables V and VI) equations indicates the following:

(1) Pitzer's equations are clearly superior to Scatchard's for the binary mixing approximation (no adjustable mixing parameters), since maximum deviations and standard deviations are about a factor of 2–4 and 4 lower, respectively, for Pitzer's approach.

(2) The two approaches are about equal in quality for one mixing parameter case (i.e., Θ or b_{01}) when $I \leq 6.2$ mol·kg^{-1}, but Scatchard's approach is definitely better when higher concentration data are included.

(3) The quality of fits are comparable for the two mixing parameter cases, although Scatchard's approach is marginally better for some parameter combinations.

(4) Scatchard's approach for some three-parameter cases is more accurate. The quality of the fits are even better with 4–6 Scatchard parameters, obviously because more parameters are used than are allowed by the Pitzer approach.

Tables VII and VIII report the natural logarithm of the mean molal activity coefficients of NaCl and MgCl$_2$, respectively, in the mixed salt solutions. These were calculated by using the "selected" parameters from Tables IV and VI for the combined isopiestic data set. Values of ln $\gamma_\pm$ at $y_i = 0$ are trace activity coefficients for component i, whereas they are pure component values at $y_i = 1$.

Table VII gives a comparison of ln $\gamma_\pm$ for NaCl using both Pitzer's and Scatchard's equations. Results are in reasonably good agreement with a maximum difference of 0.016 in ln $\gamma_\pm$ of NaCl. For MgCl$_2$ (Table VIII) agreement is less good with a maximum difference of 0.09 in trace ln $\gamma_\pm$ at $I = 6.0$ mol·kg^{-1}. Thus, even though the osmotic coefficients are fairly reliably represented by both approaches, the ln $\gamma_\pm$ values in some cases show large differences. Unfortunately, differences of this size are not uncommonly encountered when different equations are used to represent ternary solution isopiestic data.

There are three experimental sets of ln $\gamma_\pm$ values for NaCl using emf measurements (*11–13*), two of which seem to be reliable (*11*, *13*). The ln $\gamma_\pm$ values from our Scatchard fits to $I \leq 6.2$ mol·kg^{-1} of isopiestic data are in excellent agreement with the emf data at $I = 1.0$ mol·kg^{-1} whereas the Pitzer values of ln $\gamma_\pm$ are too high by up to 0.015. At $I = 3.0$ mol·kg^{-1} the Scatchard values are lower than the experimental values by up to 0.006, whereas the Pitzer values are higher by about an equal amount. Also, at $I = 6.0$ mol·kg^{-1} the Pitzer and Scatchard equations for $I \leq 6.2$ mol·kg^{-1} given ln $\gamma_\pm$ values in about as good agreement, ≤0.01, with emf results (*11*). However, the trace ln $\gamma_\pm$ values show larger variations.

Pitzer's equation with and without mixing parameters for $I \leq 6.2$ mol·kg^{-1} had very similar $\sigma(\Phi)$ values. Calculated ln $\gamma_\pm$ for each case showed maximum differences for the trace cases, with a maximum variation of 0.015 for NaCl and 0.017 for MgCl$_2$. The better quality Scatchard fits showed only about one half this variation for NaCl and about two-thirds for MgCl$_2$. Including the data up to $I = 9.8726$ mol·kg^{-1} in the fits had very little effect on the calculated ln $\gamma_\pm$ from Pitzer's equation. However, for $I \leq 6.2$ and $I \leq 9.8726$ mol·kg^{-1}, much larger differences were found for the corresponding Scatchard equations (maximum difference 0.04 in trace ln $\gamma_\pm$ of MgCl$_2$).

Including data to $I = 9.8726$ mol·kg^{-1} in the Scatchard fits gives ln $\gamma_\pm$ values for NaCl at $I = 6.0$ mol·kg^{-1} that agree better with Lanier's (*11*) emf results than when only $I \leq 6.2$ mol·kg^{-1} data are used. This suggests that slight "end effects" are present in the Scatchard fits for some parameter combinations near the upper concentration cutoff values. This was confirmed by repeating these calculations using $I \leq 7.0$ mol·kg^{-1} for determining the Scatchard parameters. Consequently, we used the Scatchard fits for the entire concentration range for calculating the recommended ln $\gamma_\pm$ values, since they gave equally good representations of the experimental Φ data and avoid the "end effects" present when lower concentration cutoff values were used. We do not recommend calculating ln $\gamma_\pm$ above $I = 6.2$ mol·kg^{-1} because of the uncertain extrapolation of the NaCl binary equation above its solubility limit.

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Glossary

A	symbols subscripted A refer to NaCl
B	symbols subscripted B refer to MgCl$_2$
*	symbols with asterisks refer to NaCl or CaCl$_2$ isopiestic standards

m_i	molal concentration of electrolyte i, mol·kg^{-1}
m_T	total molality of mixed electrolyte, mol·kg^{-1}
I	total ionic strength of mixed electrolyte, mol·kg^{-1}
y_i	ionic strength fraction of electrolyte i in mixture
Φ	molal osmotic coefficient of solution
ν_i	number of ions formed by the dissociation of one molecule of electrolyte i
f^ϕ	Debye–Hückel term in Pitzer's equations for single electrolytes [$= -0.3290I^{1/2}/(1 + 1.2I^{1/2})$]
B^ϕ	ionic-strength-dependent parameter in Pitzer's equations for single electrolytes
$\beta^{(0)}$, $\beta^{(1)}$	coefficients of B^ϕ term in Pitzer's equations for single electrolytes
C^ϕ	constant parameter in Pitzer's equations for single electrolytes
Θ°, Θ', ψ	mixing parameters for Pitzer's ternary solution equations
$\sigma(\Phi)$	standard deviation of fitting equations for Φ
ϕ_i^0	osmotic coefficient of pure electrolyte i at the total ionic strength of the mixture for Scatchard's neutral electrolyte equations
b_{ij}	mixing parameters for Scatchard's neutral electrolyte equations
h_i	osmolality fraction of electrolyte i in mixture
$\gamma_\pm$	mean molal activity coefficient

Registry No. NaCl, 7647-14-5; $MgCl_2$, 7786-30-3.

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Osmotic and Activity Coefficients of Aqueous $La(NO_3)_3$ and Densities and Apparent Molal Volumes of Aqueous $Eu(NO_3)_3$ at 25 °C

Joseph A. Rard

University of California, Lawrence Livermore National Laboratory, Livermore, California 94550

The osmotic coefficients of aqueous $La(NO_3)_3$ have been measured from 1.3435 to 8.4591 mol·kg^{-1} at 25 °C by using the isopiestic method. Some earlier osmotic coefficients for this salt are too high, apparently due to a stock solution concentration error, and have been normalized to the present results. These combined data and other activity data were then used to generate recommended values for the osmotic coefficients, water activities, and mean molal activity coefficients of $La(NO_3)_3$. The solubility of $La(NO_3)_3 \cdot 6H_2O(cr)$ was determined to be 4.6147 ± 0.0056 mol·kg^{-1} by the isopiestic method; this is in excellent agreement with the IUPAC recommended value of 4.610 ± 0.005 mol·kg^{-1}. Density data were measured for aqueous $Eu(NO_3)_3$ from 0.03996 to 1.1014 mol·kg^{-1} at 25 °C by using pycnometry. These results are in fairly good agreement with published low-concentration densities measured with a magnetic float.

Introduction

Activity and osmotic coefficient data for aqueous electrolyte solutions have numerous applications including solubility, chemical speciation, and reaction thermodynamics calculations. Density data are required for buoyancy calculations, for the interconversion of mass and volumetric concentration scales, and for the calculation of partial molal volumes which are related to the pressure derivatives of solute and solvent activities.

We have published isopiestic data for a total of 40 aqueous rare earth chloride, perchlorate, and nitrate solutions from low concentrations to saturation or supersaturation at 25 °C (*1–6*). Isopiestic measurements yield water activities, osmotic coefficients, and activity coefficients as a function of molality. For the first three parts of this series (*1–3*), the stock solution preparations, analyses, and the isopiestic measurements were done at Ames Laboratory (Iowa State University). For the last part (*6*) all of this was done at Lawrence Livermore National Laboratory (LLNL). However, for six of the rare earth nitrates,