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Osmotic Coefficients of the System $NH_4Cl + (NH_4)_2SO_4 + H_2O$ at 298.15 K and Calculation of Onsager Transport Coefficients[†]

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Osmotic coefficients are reported for the system $NH_4Cl + (NH_4)_2SO_4 + H_2O$ at 298.15 K over a wide range of concentrations. Scatchard's mixed electrolyte equation is used to fit these data with six fitting parameters, b_{ij}. For comparison, we insert extended Debye−Hückel equations and separately Pitzer's equations as the necessary binary salt equations within Scatchard's equation. Three sets of the six b_{ij} are obtained in each case from fits with two subsets and the full set of the osmotic coefficients. We examine the consequence of including different binary osmotic coefficient expression equations and applying different data ranges in these fits. The results are combined with available ternary diffusion coefficients to calculate and report solvent frame thermodynamic transport coefficients, $(L_{ij})_0$. These are intercompared relative to the Onsager Reciprocal Relations requirement. Finally, we use Pitzer's mixed electrolyte equation to calculate thermodynamic properties of the ternary system directly and to calculate $(L_{ij})_0$ coefficients for comparison with the $(L_{ij})_0$ obtained using Scatchard's equations.

Introduction

Although there is an extensive database of thermodynamic data for binary aqueous salt solutions, the database for aqueous systems with two or more salt components is less extensive. Such data are useful for testing models for more complex multicomponent aqueous salt systems. We report here osmotic coefficients for the ternary system $NH_4Cl + (NH_4)_2SO_4 + H_2O$ at 298.15 K. These salts are used in numerous industrial and scientific applications. For example, both salts may be included in solutions used to precipitate proteins for purification and also for determination of their tertiary structure by X-ray crystallography. We analyze our osmotic coefficient data by applying Scatchard's equation.[1,2] Scatchard's equation includes within it equations for the osmotic coefficients of the corresponding aqueous binary salt solutions. The choice of these binary solution equations is important since they are the dominant terms within Scatchard's equation. For comparison, we used two separate choices for these binary solution equations, the extended Debye−Hückel equations[3] and Pitzer equations.[4] For each of these choices, we fit our data using Scatchard's equation with three different concentration ranges of our osmotic coefficient data giving a total of six fits that we intercompare.

Chemical potential derivatives are the ultimate driving force for diffusion. These derivatives permit calculation solvent frame thermodynamic transport coefficients,[5] $(L_{ij})_0$, from measured ternary diffusion coefficients. We calculate and intercompare the $(L_{ij})_0$ obtained by using chemical potential derivatives calculated from the various fits of Scatchard's equation. We include, for an important comparison, the $(L_{ij})_0$ obtained using chemical potential derivatives calculated directly from Pitzer's mixed electrolyte equations based only on binary solution parameters.

Finally, we acknowledge that osmotic coefficients measured by a hygrometric method have previously been reported for this ternary system.[6] Those values are generally lower than values reported here at comparable ionic strength fractions. The differences average about −0.003 at lower total ionic strengths to roughly −0.03 at the highest comparable ionic strengths.

Experimental

Solutions. All solutions were prepared gravimetrically. Deionized water was distilled and used to prepare all solutions. Mallinckrodt analytical reagent grade $CaCl_2$ was used without further purification to prepare a stock solution for the isopiestic reference. The molarity of the aqueous $CaCl_2$ solution, 6.960 $mol \cdot kg^{-1}$, was determined gravimetrically by precipitating AgCl from weighed aliquots, separating, and drying at 110 °C. Mallinckrodt analytical reagent grade NH_4Cl and $(NH_4)_2SO_4$ were dried for 2 h at 120 °C and then used without further purification to prepare the ternary solutions. Molar masses used for all calculations were: 110.986 $g \cdot mol^{-1}$ for $CaCl_2$, 53.50 $g \cdot mol^{-1}$ for NH_4Cl, 132.15 $g \cdot mol^{-1}$ for $(NH_4)_2SO_4$, and 18.015 $g \cdot mol^{-1}$ for H_2O.

Isopiestic Apparatus. The isopiestic apparatus has been previously described.[7] There were three separate water baths controlled to (25.00 ± 0.01) °C in which an isopiestic apparatus was immersed. The outside container of each isopiestic apparatus was a plastic desiccator in which a partial vacuum could be pulled. A cylindrical copper block 15 cm in diameter and 6.2 cm high was placed in the desiccator and supported on a rim normally used to support the desiccator platform. This block held eight tantalum cups in a ring of eight evenly spaced holes with flat bottoms. The tantalum cups slid all the way into these holes with close tolerance. These cups were 25 mm in diameter and 25 mm high with a wall thickness of 0.5 mm (two sets of 8 cups) or 0.7 mm (one set of 8 cups). During the assembly process, each cup with its solution was placed in the block. A fan with flat vertical copper blades was mounted on an axle at the center of the cylindrical block. A 1.2 cm thick copper lid with a small vent hole in the center was then screwed onto a 1 cm high flange at the perimeter of the block to enclose the

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Table 1. Osmotic Coefficients ϕ for NH_4Cl (1) + $(NH_4)_2SO_4$ (2) + H_2O at 298.25 K[a]

m_R/mol·kg^{-1}	m_1/mol·kg^{-1}	m_2/mol·kg^{-1}	ϕ
0.21642	0.21627	0.07920	0.83484
0.21642	0.13382	0.14615	0.79234
0.21642	0.05994	0.20804	0.75197
0.25585	0.25847	0.09465	0.83158
0.25585	0.16074	0.17555	0.78526
0.25585	0.07204	0.25007	0.74472
0.27892	0.28081	0.10283	0.83812
0.27892	0.17601	0.19223	0.78524
0.27892	0.07970	0.27665	0.73711
0.40862	0.43090	0.15779	0.82266
0.40862	0.27133	0.29634	0.76720
0.40862	0.12333	0.42807	0.71749
0.54325	0.59591	0.21822	0.81643
0.54325	0.37813	0.41298	0.75557
0.54325	0.17301	0.60052	0.70196
1.07090	1.35539	0.49633	0.81332
1.07090	0.87237	0.95277	0.74207
1.07090	0.40523	1.40660	0.67905
0.80359	0.97046	0.32550	0.81702
0.80359	0.50294	0.76573	0.72163
0.80359	0.28732	0.97418	0.68157
1.31471	1.80874	0.60667	0.82549
1.31471	0.94748	1.44252	0.72135
1.31471	0.54339	1.84243	0.67864
1.68828	2.52606	0.84727	0.84255
1.68828	1.32058	2.01056	0.73774
1.68828	0.75587	2.56286	0.69544
1.57029	2.28683	0.76702	0.83771
1.57029	1.19681	1.82213	0.73270
1.57029	0.68578	2.32520	0.68994
1.43581	2.02846	0.68036	0.83165
1.43581	1.06210	1.61703	0.72705
1.43581	0.60868	2.06378	0.68452
1.77384	2.69798	0.90492	0.84867
1.77384	1.40722	2.14247	0.74480
1.77384	0.80483	2.72886	0.70265
1.58114	1.52240	1.52615	0.76298
1.58114	2.30657	0.77064	0.83990
1.58114	1.19929	1.84021	0.73447
2.00900	2.10886	2.11405	0.78704
2.00900	3.21201	1.07316	0.86183
2.00900	1.65789	2.54389	0.75918
2.25891	2.48782	2.49393	0.80144
2.25891	3.80270	1.27051	0.87448
2.25891	1.95009	2.99223	0.77533
1.47670	1.38974	1.39315	0.75815
1.47670	2.10533	0.70341	0.83468
1.47670	1.09527	1.68059	0.72949
1.57198	1.51157	1.51529	0.76204
1.57198	2.29059	0.76530	0.83871
1.57198	1.19107	1.82759	0.73337
2.04876	2.16925	2.17459	0.78864
2.04876	1.70409	2.61477	0.76129
2.31299	2.57420	2.58105	0.80413
2.31299	3.94044	1.31653	0.87632
2.31299	2.01781	3.09614	0.77809
3.05746	3.92770	3.93736	0.83539
3.05746	6.09544	2.03653	0.89780
2.46653	2.82393	2.83088	0.81310
2.46653	4.33554	1.44854	0.88330
2.46653	2.21130	3.39304	0.78742
2.81374	3.44301	3.45147	0.82850
2.81374	5.31880	1.77705	0.89448
2.81374	2.68786	4.12427	0.80478

[a] m_R are the average molalities of the $CaCl_2$ reference solutions; m_1 and m_2 are the average molalities of NH_4Cl and $(NH_4)_2SO_4$ in the ternary solutions; and ϕ are the calculated osmotic coefficients of the ternary solutions.

chamber for isopiestic equilibration. This block now holding the eight tantalum cups was placed in the plastic vacuum desiccator. A vacuum was pulled to (20 to 30) % above the vapor pressure of water at 25 °C. The desiccators were each mounted on a stirring assembly, lowered into a large water bath, and turned slowly at a 15 degree tilt from vertical to continually stir the solutions. The center of mass of the fan blades was to one side so that they remained relatively stationary as the chambers with cups rotated under them. In this design, the heat transfer rate between the thermostat and the copper block is very slow compared to the heat transfer rate within the copper block. Thus, all isopiestic solutions will be very close to the same temperature. We have found that the apparatus gives reproducible results.[7]

Measurements. The mass of each empty tantalum cup was carefully measured. Approximately 1 g of solution of known molality was placed in each cup, and a preweighed cap with an O-ring seal was immediately placed on the cup. (The slight roughness of the cups permitted pressure equilibration.) The assembled cap, cup, and solution was weighed to 0.1 mg and the mass of solution calculated. Two cups contained reference solutions of $CaCl_2 + H_2O$, and the remaining three pairs of cups contained three different ternary mixtures of NH_4Cl + $(NH_4)_2SO_4 + H_2O$. The caps were removed, and the cups were placed in the apparatus and equilibrated for one to three weeks, the longer times being for the more dilute solutions. When the chambers were opened to remove the cups, the set of 8 caps, which were again preweighed, was simultaneously pushed onto the cups using a special cap holder. The cups were then lifted out of the copper block and weighed to 0.1 mg. Final molal concentrations were calculated from weight changes and initial concentrations.

The osmotic coefficient of each reference solution was calculated from its molality using eq 14 with parameters of Table 6 in ref 8. We used the averages of the two reference osmotic coefficients, ϕ_R, and their average molality, m_R, in the formula below to calculate the osmotic coefficients, ϕ, for each of the ternary solutions.

$$\phi = \frac{3m_R\phi_R}{2m_1 + 3m_2} \tag{1}$$

Here, m_1 and m_2 are the average molalities of NH_4Cl and $(NH_4)_2SO_4$ for each of the three pairs of ternary solutions. The ϕ and the corresponding averages of m_R, m_1, and m_2 are listed in Table 1 for each osmotic coefficient, ϕ, measurement.

Results

Osmotic Coefficients. Molalities, m_R, of the $CaCl_2$ reference solutions and the corresponding molalities, m_1, m_2, and ϕ, of the aqueous NH_4Cl and $(NH_4)_2SO_4$ solutions are listed in Table 1. These data are listed in chronological order of measurement. The three results from a given run are grouped together. They were performed at four ratios of $m_1/(m_1 + m_2) \approx 0.23$, 0.39, 0.50, and 0.75. These ratios were chosen to provide thermodynamic data for calculation of thermodynamic transport coefficients from a series of aqueous ternary diffusion coefficient measurements.

Equations for Fitting the Osmotic Coefficients. To fit the measured osmotic coefficients to expressions that will yield chemical potentials and their derivatives, we use the expressions of Scatchard et al.[2]

$$(\phi - 1) = \frac{2m_1}{2m_1 + 3m_2}(\phi_1^0 - 1) + \frac{3m_2}{2m_1 + 3m_2}(\phi_2^0 - 1) + [y_1y_2/(1 + y_1)][\beta^0 + \beta^1(y_1 - y_2) + \beta^2(y_1 - y_2)^2] \tag{2}$$

where

$$y_1 = m_1/(m_1 + 3m_2) \text{ and } y_2 = 3m_2/(m_1 + 3m_3)$$

Here ϕ is the osmotic coefficient of the mixture and the ϕ_i^0 are the osmotic coefficients of the corresponding binary solutions at the same molal ionic strength: $I = (m_1 + 3m_2)$. The β^i denote expansions in ionic strength

$$\beta^0 = b_{01}I + b_{02}I^2 + b_{03}I^3$$
$$\beta^1 = b_{12}I^2 + b_{13}I^3$$
$$\beta^2 = b_{23}I^3$$

This choice of six independent fitting parameters follows that of Scatchard.[2]

Choice of Binary Osmotic Coefficient Equations. Again, it must be emphasized that the contribution of the ϕ_i^0 terms is dominant relative to the contribution of the b_{ij} terms. Thus, the choice of expressions to represent these ϕ_i^0 is important. A serious problem is associated with the choice ϕ_1^0 of aqueous NH_4Cl. The experimentally measured osmotic coefficients for binary solutions of aqueous NH_4Cl at 25 °C only extend to 7.4 molal due to saturation limitations, while the ionic strength of our measurements extends to about 15 molal. At the higher ionic strength, any algebraic expression used to represent the osmotic coefficient of aqueous NH_4Cl in terms of ionic strength will be well outside its range of experimental verification. We will use and compare two standard approaches for the calculation of the binary osmotic coefficients, ϕ_i^0.

(1) First Approach. We use the following extended Debye−Hückel equation to represent the osmotic coefficients ϕ_i^{o} of the binary solutions.

$$\phi_i^0 - 1 = -\frac{|z_+z_-|A}{B^3 I}[(1 + B\sqrt{I}) - 2\ln(1 + B\sqrt{I}) - (1 + B\sqrt{I})^{-1}] + (1/2)\beta m + (2/3)Cm^2 + (3/4)Dm^3 + (4/5)Em^4 \quad (3)$$

The series is truncated at the fourth power of molality, m, for both binary solutions for this system. The corresponding expressions for the logarithm of the mean ionic activity coefficients and derivatives with respect to I are

$$\ln \gamma_\pm = \frac{-|z_+z_-|A\sqrt{I}}{(1 + B\sqrt{I})} + \beta m + Cm^2 + Dm^3 + Em^4 \quad (4)$$

The derivatives of $\ln \gamma_\pm$ with respect to ionic strength are written

$$\frac{d\ln \gamma_\pm}{dI} = \frac{-|z_+z_-|A}{2(1 + B\sqrt{I})^2\sqrt{I}} + g[\beta + 2Cm + 3Dm^2 + 4Em^3] \quad (5)$$

The Debye−Hückel parameter $A = 1.1762\ (\text{kg}\cdot\text{mol}^{-1})^{1/2}$ (for 298.25 K). We let $g = 1$ and $m = I$ for NH_4Cl and $g = (1/3)$ and $m = I/3$ for $(NH_4)_2SO_4$ when applying the above equations for ternary solution calculations. For NH_4Cl, $B = 1.325$, and we convert values given in ref 9 into natural logarithm values: $\beta = -0.0105428$, $C = 0.0121374$, $D = -0.00162463$, and $E = 0.000065472$ where the standard deviation of fit, $\sigma(\phi)$, was 0.00087. For aqueous $(NH_4)_2SO_4$, $|z_+z_-| = 2$, we applied the method of least-squares to binary ϕ coefficients in ref 10 to obtain fitting parameters. We obtained: $B = 1.001511$, $\beta = -0.221136$, $C = 0.0562419$, $D = -0.00648820$, and $E = 0.000293231$ with $\sigma(\phi) = 0.0010$. Systematic errors in the fits are possible and hard to estimate, but we believe these coefficients give accuracy within their experimental range.

(2) Second Approach. We use Pitzer's equations[5] to calculate the binary solution ϕ_i^0.

The necessary equations for the binary calculations of $NH_4Cl + H_2O$ (and 1:1 electrolytes in general) are

$$\phi_i^0 - 1 = \frac{-A_\phi\sqrt{I}}{(1 + 1.2\sqrt{I})} + I\left(\beta_{\text{MX}}^{(0)} + \beta_{\text{MX}}^{(1)}e^{-2\sqrt{I}}\right) + I^2C_{\text{MX}}^\phi \quad (6)$$

$$\ln \gamma_\pm = -A_\phi\left(\frac{\sqrt{I}}{1 + 1.2\sqrt{I}} + \frac{2\ln(1 + 1.2\sqrt{I})}{1.2}\right) + 2\beta_{\text{MX}}^{(0)}I + \frac{\beta_{\text{MX}}^{(1)}}{2}(1 - (1 + 2\sqrt{I} - 2I)e^{-2\sqrt{I}}) + \frac{3}{2}I^2C_{\text{MX}}^\phi \quad (7)$$

$$\frac{\partial \ln \gamma_\pm}{\partial I} = -\frac{A_\phi(3 + 2.4\sqrt{I})}{2\sqrt{I}(1 + 1.2\sqrt{I})^2} + 2\beta_{\text{MX}}^{(0)} + \beta_{\text{MX}}^{(1)}(2 - \sqrt{I})e^{-2\sqrt{I}} + 3IC_{\text{MX}}^\phi \quad (8)$$

For $(NH_4)_2SO_4$ (and 1:2 or 2:1 electrolytes generally), the equations are

$$\phi_i^0 - 1 = \frac{-2A_\phi\sqrt{I}}{(1 + 1.2\sqrt{I})} + \frac{4I}{9}\left(\beta_{\text{MX}}^{(0)} + \beta_{\text{MX}}^{(1)}e^{-2\sqrt{I}}\right) + \frac{4\sqrt{2}}{27}I^2C_{\text{MX}}^\phi \quad (9)$$

$$\ln \gamma_\pm = -2A_\phi\left(\frac{\sqrt{I}}{1 + 1.2\sqrt{I}} + \frac{2\ln(1 + 1.2\sqrt{I})}{1.2}\right) + \frac{8}{9}\beta_{\text{MX}}^{(0)}I + \frac{2}{9}\beta_{\text{MX}}^{(1)}(1 - (1 + 2\sqrt{I} - 2I)e^{-2\sqrt{I}}) + \frac{2\sqrt{2}}{9}I^2C_{\text{MX}}^\phi \quad (10)$$

$$\frac{\partial \ln \gamma_\pm}{\partial I} = -\frac{A_\phi(3 + 2.4\sqrt{I})}{2\sqrt{I}(1 + 1.2\sqrt{I})^2} + \frac{8}{9}\beta_{\text{MX}}^{(0)} + \beta_{\text{MX}}^{(1)}\left(\frac{8 - 4\sqrt{I}}{9}\right)\exp(-2\sqrt{I}) + \frac{4\sqrt{2}}{9}IC_{\text{MX}}^\phi \quad (11)$$

In all cases, we use parameters that equal or are directly calculated from Pitzer's tabulated values[4] at 298.15 K. Pitzer's Debye−Hückel parameter is $A_\phi = 0.3915\ (\text{kg}\cdot\text{mol}^{-1})^{1/2}$. (This should equal one-third the Debye−Hückel 'A' coefficient of the first approach but differs slightly.) NH_4Cl parameters are $\beta_{\text{MX}}^{(0)} = 0.0522$, $\beta_{\text{MX}}^{(1)} = 0.1918$, and $C_{\text{MX}}^\phi = -0.00301$. The corresponding $(NH_4)_2SO_4$ parameters are $\beta_{\text{MX}}^{(0)} = 0.039075$, $\beta_{\text{MX}}^{(1)} = 0.663825$, and $C_{\text{MX}}^\phi = -0.000827315$. These were calculated from the values in Table 7 of ref 4. (Note that the heading for C^ϕ in Table 7 should be $(2^{(5/2)}/3)C^\phi$.) There are two listings for $(NH_4)_2SO_4$ in Pitzer's Table 7, and we used the set that starts with $(4/3)\beta^{(0)} = 0.0521$.

The Pitzer equations for binary aqueous electrolyte solutions have fewer coefficients and a format that may permit a more valid extrapolation of ϕ to higher concentrations than the extended Debye−Hückel equations previously given. Shown in Figure 1 are curves for the binary osmotic coefficient for aqueous NH_4Cl, ϕ_1^0, versus ionic strength, I, calculated with the extended Debye−Hückel equation and with the Pitzer equation. As expected,we see good overlap of the two curves within the solubility range of aqueous NH_4Cl at 298.15 K. However, at higher concentrations, the curves radically deviate where the extended Debye−Hückel values increase, and the Pitzer calculated values decrease with increasing ionic strength.

In both approaches, fitting the b_{ij} from our ϕ data will partly compensate for this problem of extrapolation of expressions for aqueous NH_4Cl. As an important comparison to the above approaches, we will also examine direct use of the Pitzer mixed

Table 2. b_{ij} Fitting Parameters for Three Data Regions Where the Binary ϕ's Were Based on Extended Debye−Hückel Equations (D) or Pitzer Equations (P)

	D1	P1	D2	P2	D3	P3
b_{01}	−0.035739	−0.031579	−0.041288	−0.025549	−0.092036	−0.036849
b_{02}	0.004195	0.003875	0.006739	0.001669	0.024194	0.007185
b_{03}	0.000322	0.000287	0.000048	0.000482	−0.001350	−0.000148
b_{12}	0.000455	−0.005084	−0.000030	−0.002680	0.002323	0.001029
b_{13}	−0.000025	0.001066	0.000223	0.000726	−0.000117	−0.000082
b_{23}	−0.000243	0.000148	0.000045	0.000219	0.000190	−0.000005
$\sigma(\phi)$	0.000878	0.001152	0.001000	0.001285	0.005523	0.002420
no pts	29	29	38	38	64	64

electrolyte equations[5] applied to the ternary case to obtain thermodynamic properties.

Analysis of Osmotic Coefficients. We used two subsets of our ϕ data and the full set of ϕ for our fits to obtain the b_{ij} coefficients of eq 2 which we present in Table 2.

(1) First Subset. We chose a subset of our measured osmotic coefficients whose ionic strengths, $(m_1 + 3m_2)$, are below 7.0 mol·kg^{-1} and whose total molality, $(m_1 + m_2)$, is above 0.6 mol·kg^{-1}. The ionic strength of 7.0 mol·kg^{-1} was chosen because it is near the upper experimental range on which the binary aqueous NH_4Cl osmotic coefficient equations are based. The lower limit of 0.6 mol·kg^{-1} was chosen because aqueous $(NH_4)_2SO_4$ solutions shift from acting like a 1:2 salt at the lower concentrations to acting more like a 1:1 salt as the concentration increases above (1 to 2) mol·kg^{-1} (see the Discussion on page 383 in ref 11). Also, this avoids the low concentration range where the osmotic coefficients are difficult to measure and where there is a sharp increase to unity as the concentration of each binary salt solution goes to zero. Finally, it is an appropriate lower limit of the data range for obtaining thermodynamic expressions needed to calculate the $(L_{ij})_0$ thermodynamic transport coefficients.

(2) Second Subset. We chose as a second subset ϕ values measured at total molalities above 0.6 mol·kg^{-1} and below 4.4 mol·kg^{-1}. This restriction places the upper ionic strength of osmotic coefficients from our data set to be just below 10 mol·kg^{-1}. This choice kept the molality range low enough that there was not an excessive increase in the standard deviations $\sigma(\phi)$ of the fits relative to subset (1).

(3) Full Set. We include fits to the complete set of data for comparison and analysis.

Types of Fits. For each of the three data sets, we made two types of fits to obtain the b_{ij} coefficients of equation 2. The b_{ij} in columns D1, D2, and D3 of Table 2 were obtained using the extended Debye−Hückel equations for the binary ϕ_i^0. The b_{ij} in columns P1, P2, and P3 of Table 2 were obtained using Pitzer's equations[5] for the binary ϕ_i^0. Included in Table 2 are the standard deviations, $\sigma(\phi)$, of each of the six fits and the number of data points used in the fits.

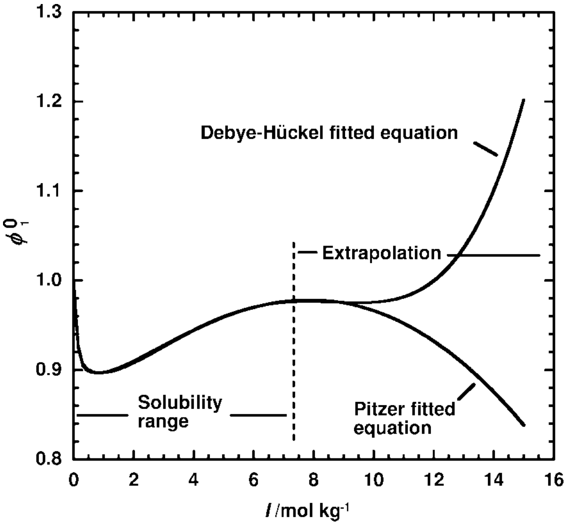

Figure 1. Calculated binary osmotic coefficients ϕ_1^0 for NH_4Cl.

Calculation of Chemical Potential Derivatives. As previously noted, a primary objective of our measurements of osmotic coefficients is to use them to calculate chemical potential derivatives which when combined with the available ternary diffusion coefficients[12,13] make possible the calculation of the solvent frame thermodynamic transport coefficient $(L_{ij})_0$. The ternary diffusion coefficients were measured at total molar concentrations $C_1 + C_2 = (1, 2, 3, \text{and } 4)$ mol·L^{-1} at mole fractions $m_1/(m_1 + m_2)$ of 0.75, 0.50, and 0.25 for a total of 12 compositions. We first calculate molal chemical potential derivatives at molalities corresponding to these molarities.

The standard expressions for molal chemical potentials for our experimental systems are

$$\frac{1}{RT}\frac{\partial\mu_1}{\partial m_1} = \frac{1}{m_1} + \frac{1}{m_1 + 2m_2} + 2\frac{\partial \ln\gamma_1}{\partial m_1} \tag{12}$$

$$\frac{1}{RT}\frac{\partial\mu_1}{\partial m_2} = \frac{1}{RT}\frac{\partial\mu_2}{\partial m_1} = \frac{2}{m_1 + 2m_2} + 2\frac{\partial \ln\gamma_1}{\partial m_2} = \frac{2}{m_1 + 2m_2} + 3\frac{\partial \ln\gamma_2}{\partial m_1} \tag{13}$$

$$\frac{1}{RT}\frac{\partial\mu_2}{\partial m_2} = \frac{1}{m_2} + \frac{4}{m_1 + 2m_2} + 3\frac{\partial \ln\gamma_2}{\partial m_2} \tag{14}$$

The appropriate expressions for the derivatives of the mean activity coefficients, γ_i, based on eq 2 have been derived by Miller.[3]

$$\left(\frac{\partial \ln\gamma_1}{\partial m_1}\right)_{m_2} = \frac{r_1 z_1^2}{2}\left[\sum_{i=1}^{2}\frac{y_i}{z_i}\frac{d\ln\gamma_i^0}{dI} - \frac{2y_2}{I}\Phi + \frac{1}{2}\left\{y_2[(b_{02} + b_{12})I + 2(b_{03} + b_{13} + b_{23})I^2] - y_2^2\left[\frac{2b_{03}}{3} + 2b_{13} + \frac{10b_{23}}{3}\right]I^2\right\}\right] \tag{15}$$

$$r_1\left(\frac{\partial \ln\gamma_1}{\partial m_2}\right)_{m_1} = r_2\left(\frac{\partial \ln\gamma_2}{\partial m_1}\right)_{m_2} = \frac{r_1 r_2 z_1 z_2}{2}\left[\sum_{i=1}^{2}\frac{y_i}{z_i}\frac{d\ln\gamma_i^0}{dI} + \frac{(y_1 - y_2)}{I}\Phi + \frac{1}{2}\left\{[b_{01} + b_{02}I + (b_{03} + b_{23})I^2] + (y_1 - y_2)\cdot[b_{12}I + b_{13}I^2] + y_1 y_2\left[\left(\frac{2b_{03}}{3} - \frac{14b_{23}}{3}\right)I^2\right]\right\}\right] \tag{16}$$

$$\left(\frac{\partial \ln \gamma_2}{\partial m_2}\right)_{m_1} = \frac{r_2 z_2^2}{2}\left[\sum_{i=1}^{2}\frac{y_i}{z_i}\frac{d \ln \gamma_i^0}{dI} + \frac{2y_1}{I}\Phi + \frac{1}{2}\left\{y_1[(b_{02} - b_{12})I + 2(b_{03} - b_{13} + b_{23})I^2] - y_1^2\left[\left(\frac{2b_{03}}{3} - 2b_{13} + \frac{10b_{23}}{3}\right)I^2\right]\right\}\right] \quad (17)$$

where

$$\Phi = \left[\frac{(\phi_2^0 - 1)}{z_2} - \frac{(\phi_1^0 - 1)}{z_1}\right] \text{ and } r_1 = 2,\ r_2 = 3,\ z_1 = 1,\ z_2 = 2$$

The derivatives of the activity coefficients can also be calculated directly from Pitzer's mixed electrolyte expressions.[4,14] Derivatives of the activity coefficients of Pitzer's mixed electrolyte expressions where only binary coefficients are kept may be written

$$\frac{\partial \ln \gamma_1}{\partial m_1} = f^{\gamma\prime} + 2B_1 + 4(m_1 + m_2)B_{1\prime} + 2m_2 B_{2\prime} + (2m_1 m_2 + m_1^2)B_{1\prime\prime} + (m_1 m_2 + 2m_2^2)B_{2\prime\prime} + 6m_1 C_1^{\dagger} + 2m_2(4C_1^{\dagger} + C_2^{\dagger}) \quad (18)$$

$$\frac{\partial \ln \gamma_2}{\partial m_1} = 2f^{\gamma\prime} + (4/3)B_1 + (2/3)B_2 + 4(4m_1/3 + m_2)B_{1\prime} + (2/3)(m_1 + 7m_2)B_{2\prime} + 2(2m_1 m_2 + m_1^2)B_{1\prime\prime} + 2(m_1 m_2 + 2m_2^2)B_{2\prime\prime} + (16/3)(m_1 + m_2)C_1^{\dagger} + (4/3)(m_1 + 4m_2)C_2^{\dagger} \quad (19)$$

$$\frac{\partial \ln \gamma_2}{\partial m_2} = 6f^{\gamma\prime} + (8/3)B_2 + 8m_1 B_{1\prime} + 4(m_1 + 4m_2)B_{2\prime} + 6(2m_1 m_2 + m_1^2)B_{1\prime\prime} + 6(m_1 m_2 + 2m_2^2)B_{2\prime\prime} + (16/3)m_1 C_1^{\dagger} + 16(m_1/3 + m_2)C_2^{\dagger} \quad (20)$$

where

$$f^{\gamma\prime} = -\frac{A_\phi(3 + 2.4\sqrt{I})}{2\sqrt{I}(1 + 1.2\sqrt{I})^2} \quad (21)$$

$$B_i = \beta_i^{(0)} + \beta_i^{(1)}[1 - (1 + 2\sqrt{I})e^{-2\sqrt{I}}]/2I \quad (22)$$

$$B_i' = \beta_i^{(1)}[-1 + (1 + 2\sqrt{I} + 2I)e^{-2\sqrt{I}}]/2I^2 \quad (23)$$

$$B_i'' = \beta_i^{(1)}[1 - (1 + 2\sqrt{I} + 2I + I\sqrt{I})e^{-2\sqrt{I}}]/I^3 \quad (24)$$

$$C_1^{\dagger} = C^{\phi}/2 \text{ and } C_2^{\dagger} = C^{\phi}/2^{3/2} \quad (25)$$

(The expression for $\partial \ln \gamma_1/\partial m_2$ is redundant and not included.)

Molar Chemical Potential Derivatives. Expressions for calculation of molar chemical potential derivatives from molal chemical potential derivatives are

$$\mu_{ij} \equiv \left(\frac{\partial \mu_i}{\partial C_j}\right)_{C_{i\neq j}} = \left(\frac{\partial \mu_i}{\partial m_1}\right)_{m_2}\left(\frac{\partial m_1}{\partial C_j}\right)_{C_{i\neq j}} + \left(\frac{\partial \mu_i}{\partial m_2}\right)_{m_1}\left(\frac{\partial m_2}{\partial C_j}\right)_{C_{i\neq j}} \quad [i, j = 1, 2] \quad (26)$$

where

$$\left(\frac{\partial m_i}{\partial C_i}\right) = \frac{\rho - H_i C_i - M_j C_j}{(\rho - C_1 M_1 - C_2 M_2)^2} \quad [i, j = 1, 2 \quad j \neq i] \quad (27a)$$

$$\left(\frac{\partial m_i}{\partial C_j}\right) = \frac{C_i(M_j - H_i)}{(\rho - C_1 M_1 - C_2 M_2)^2} \quad [i, j = 1, 2 \quad j \neq i] \quad (27b)$$

$$H_i = (\partial \rho/\partial C_i)$$

Here ρ is the solution density and the M_i are the solute molecular weights. Values of H_i and ρ may be found in ref 13. Molar chemical potential derivatives obtained with the sets of b_{ij} are given in the Tables S2(a−f) in the Supporting Information. Table S2(g) gives molar chemical potential derivatives directly obtained from Pitzer's mixed electrolyte equations using only coefficients listed above for the aqueous binary solutions.

Thermodynamic Transport Coefficients. Isothermal flow equations for a ternary system may be written.

$$-J_i = \sum_{i=1}^{2}(D_{ij})_0(\partial C_j/\partial x) = \sum_{i=1}^{2}(L_{ij})_0(\partial \mu_j/\partial x) \quad (28)$$

Thermodynamic transport coefficients are related to molar chemical potential derivatives, μ_{ij}, and solvent frame diffusion coefficients by the following equations

$$(L_{ii})_0 = [\mu_{jj}(D_{ii})_0 - \mu_{ji}(D_{ij})_0]/(\mu_{11}\mu_{22} - \mu_{12}\mu_{21}) \quad \{i, j = 1, 2 \text{ and } i \neq j\} \quad (29a)$$

$$(L_{ij})_0 = [\mu_{ii}(D_{ij})_0 - \mu_{ij}(D_{ii})_0]/(\mu_{11}\mu_{22} - \mu_{12}\mu_{21}) \quad \{i, j = 1, 2 \text{ and } i \neq j\} \quad (29b)$$

Given in Tables 3a−c are the calculated $(L_{ij})_0$ based on the ternary diffusion coefficients for this system[13] and molar chemical potentials in Supporting Information Tables S2(a−g). In the Supporting Information, we include in Tables S3(a−d) values $(L_{ij})_0$ calculated with chemical potential derivatives based on the D1, D3, P1, and P3 b_{ij} coefficients.

Discussion

Examination of the b_{ij} Fitting Parameters. The values of the fitting parameters, b_{ij}, given in Table 2 show comparisons among strategies for fitting the experimental ternary ϕ_i data.

It is of specific interest to compare the standard deviations $\sigma(\phi)$ of the fits. First, we examine and compare cases D1 and P1 where only the narrow range of ternary ϕ_i values, between total molalities of 0.6 mol·kg^{-1} for the lower limit and ionic strength of 7 mol·L^{-1} for the upper limit, was used in the fits. The fits were better in the D1 case which used eq 3 for binary osmotic coefficient expressions. This was expected because more parameters are used for the aqueous NH_4Cl fits than are used for the Pitzer fits of NH_4Cl. However, it must be emphasized that the $\sigma(\phi)$ were small for both D1 and P1 and satisfactory. We next examine the D2 and P2 cases. Again the $\sigma(\phi)$ is lower for D2 than for the P2 case. This indicates that the extrapolation to 10 mol·kg^{-1} for the binary osmotic coefficient of the NH_4Cl does not greatly increase the $\sigma(\phi)$. We show in Figures 2a and 2b deviation graphs for fits D2 and P2, respectively. The figures are similar, but the D2 deviation graph is a little tighter and the scatter less random than for the P2 graph particularly at the lower concentrations. This indicates that the extended Debye−Hückel binary expression factor for $(NH_4)_2SO_4$ is better than the Pitzer expression. However, the $\sigma(\phi)$ is much greater for the D3 case than for the P3 case where all data are included in the fits. This suggests that Pitzer expressions for the binary osmotic coefficients of NH_4Cl extrapolate better at the higher concentrations.

Calculated Molal Activity Coefficient Derivatives. Molal activity coefficient derivatives obtained using the b_{ij} parameters in Table 2 are reported in the Supporting Information Tables S1(a−f). Those calculated using Pitzer's mixed electrolyte equation are given in Table S1(g). The agreement is reasonable

Table 3. Thermodynamic Transport Coefficients

(a) Calculated Using D2 Set of b_{ij} Values Given in Table 2

$\frac{C_1 + C_2}{\text{mol}\cdot\text{L}^{-1}}$	$\frac{m_1 + 3m_2}{\text{mol}\cdot\text{kg}^{-1}}$	$\frac{10^9RT(L_{11})_0}{\text{m}^2\cdot\text{s}^{-1}\cdot\text{mol}\cdot\text{L}^{-1}}$	$\frac{10^9RT(L_{12})_0}{\text{m}^2\cdot\text{s}^{-1}\cdot\text{mol}\cdot\text{L}^{-1}}$	$\frac{10^9RT(L_{21})_0}{\text{m}^2\cdot\text{s}^{-1}\cdot\text{mol}\cdot\text{L}^{-1}}$	$\frac{10^9RT(L_{22})_0}{\text{m}^2\cdot\text{s}^{-1}\cdot\text{mol}\cdot\text{L}^{-1}}$
		$m_1/(m_1 + m_2) = 0.75$			
1.0	1.6	0.99459	−0.12132	−0.12030	0.22324
2.0	3.3	1.91263	−0.22503	−0.22707	0.43609
3.0	5.2	2.71254	−0.31406	−0.30644	0.63090
4.0	7.4	3.40688	−0.39886	−0.37221	0.79768
		$m_1/(m_1 + m_2) = 0.50$			
1.0	2.1	0.75320	−0.13661	−0.14194	0.37951
2.0	4.5	1.39074	−0.26232	−0.25785	0.71859
3.0	7.2	1.85490	−0.33493	−0.33835	0.99771
4.0	10.3	2.18076	−0.47534	−0.40261	1.11614
		$m_1/(m_1 + m_2) = 0.25$			
1.0	2.8	0.41925	−0.09035	−0.09393	0.49729
2.0	5.7	0.70904	−0.15829	−0.15997	0.87870
3.0	9.2	0.89840	−0.20873	−0.19836	1.14589
4.0	13.4	0.98859	−0.35766	−0.27554	1.15218

(b) Calculated Using P2 Set of b_{ij} Values Given in Table 2

$\frac{C_1 + C_2}{\text{mol}\cdot\text{L}^{-1}}$	$\frac{m_1 + 3m_2}{\text{mol}\cdot\text{kg}^{-1}}$	$\frac{10^9RT(L_{11})_0}{\text{m}^2\cdot\text{s}^{-1}\cdot\text{mol}\cdot\text{L}^{-1}}$	$\frac{10^9RT(L_{12})_0}{\text{m}^2\cdot\text{s}^{-1}\cdot\text{mol}\cdot\text{L}^{-1}}$	$\frac{10^9RT(L_{21})_0}{\text{m}^2\cdot\text{s}^{-1}\cdot\text{mol}\cdot\text{L}^{-1}}$	$\frac{10^9RT(L_{22})_0}{\text{m}^2\cdot\text{s}^{-1}\cdot\text{mol}\cdot\text{L}^{-1}}$
		$m_1/(m_1 + m_2) = 0.75$			
1.0	1.6	1.00102	−0.12898	−0.12516	0.22773
2.0	3.3	1.93315	−0.24295	−0.23942	0.45124
3.0	5.2	2.73887	−0.34226	−0.32411	0.64695
4.0	7.4	3.39542	−0.45442	−0.40540	0.81655
		$m_1/(m_1 + m_2) = 0.5$			
1.0	2.1	0.76058	−0.14820	−0.14986	0.39127
2.0	4.5	1.41876	−0.29119	−0.27570	0.73714
3.0	7.2	1.89627	−0.37641	−0.36252	1.01484
4.0	10.3	2.19347	−0.47002	−0.43671	1.24556
		$m_1/(m_1 + m_2) = 0.25$			
1.0	2.8	0.42268	−0.09893	−0.09958	0.50898
2.0	5.7	0.72165	−0.17506	−0.16952	0.88301
3.0	9.2	0.92032	−0.22574	−0.21154	1.17843
4.0	13.4	0.99064	−0.24674	−0.23122	1.38417

(c) Calculated Using Pitzer Mixed Electrolyte Equations to Calculate Chemical Potential Derviatives

$\frac{C_1 + C_2}{\text{mol}\cdot\text{L}^{-1}}$	$\frac{m_1 + 3m_2}{\text{mol}\cdot\text{kg}^{-1}}$	$\frac{10^9RT(L_{11})_0}{\text{m}^2\cdot\text{s}^{-1}\cdot\text{mol}\cdot\text{L}^{-1}}$	$\frac{10^9RT(L_{12})_0}{\text{m}^2\cdot\text{s}^{-1}\cdot\text{mol}\cdot\text{L}^{-1}}$	$\frac{10^9RT(L_{21})_0}{\text{m}^2\cdot\text{s}^{-1}\cdot\text{mol}\cdot\text{L}^{-1}}$	$\frac{10^9RT(L_{22})_0}{\text{m}^2\cdot\text{s}^{-1}\cdot\text{mol}\cdot\text{L}^{-1}}$
		$m_1/(m_1 + m_2) = 0.75$			
1.0	1.6	1.00356	−0.13260	−0.12745	0.22987
2.0	3.3	1.94272	−0.25224	−0.24629	0.46104
3.0	5.2	2.77195	−0.33630	−0.32824	0.67109
4.0	7.4	3.49176	−0.35459	−0.37076	0.85846
		$m_1/(m_1 + m_2) = 0.50$			
1.0	2.1	0.76094	−0.14976	−0.15100	0.39350
2.0	4.5	1.41564	−0.28572	−0.27443	0.74504
3.0	7.2	1.89717	−0.33114	−0.34202	1.02833
4.0	10.3	2.24268	−0.31531	−0.34597	1.25210
		$m_1/(m_1 + m_2) = 0.25$			
1.0	2.8	0.42195	−0.09780	−0.09901	0.50963
2.0	5.7	0.71591	−0.16204	−0.16229	0.88273
3.0	9.2	0.90948	−0.18041	−0.18250	1.17140
4.0	13.4	0.99524	−0.14477	−0.14878	1.35758

for the D1, D2, P1, and P2 cases within the specified ranges but much more discordant for the D3 case.

Molar Chemical Potential Derivatives. Calculated values of the molar chemical potential derivatives from the parameters of Table 2 are reported in the Supporting Information Tables S2(a−f). These are used to calculate the thermodynamic transport coefficients $(L_{ij})_0$. Those calculated using Pitzer's mixed electrolyte equation are given in Table S2(g) The general agreement, as expected, follows that of the molal activity coefficients.

Thermodynamic Transport Coefficients, $(L_{ij})_0$. Three sets of calculated $RT(L_{ij})_0$, where $(L_{ij})_0$ are the solvent frame thermodynamic transport coefficients, are reported in Table 3(a−c). Set 3a is based on the b_{ij} of the D2 case, set 3b on the b_{ij} of the P2 case, and set 3c on chemical potential derivatives obtained from Pitzer's mixed electrolyte equations. Values of $RT(L_{ij})_0$ for the four other cases are listed in the Supporting Information Tables S3(a−d). We note that at mole fractions, $m_1/(m_1 + m_2)$, 0.50 and 0.25 at $C_1 + C_2 = 4\ \text{mol}\cdot\text{L}^{-1}$, the molal ionic strengths of (10.3 and 13.4) $\text{mol}\cdot\text{kg}^{-1}$ exceed the database of up to 10 $\text{mol}\cdot\text{kg}^{-1}$ used to obtain the D2 and P2 b_{ij} coefficients, and the values of the $RT(L_{ij})_0$ in these cases appear significantly more discordant than the other coefficients. Excluding the (0.50, 0.25, and 4) $\text{mol}\cdot\text{L}^{-1}$ cases, the P2 values of $RT(L_{11})_0$ average 1.3

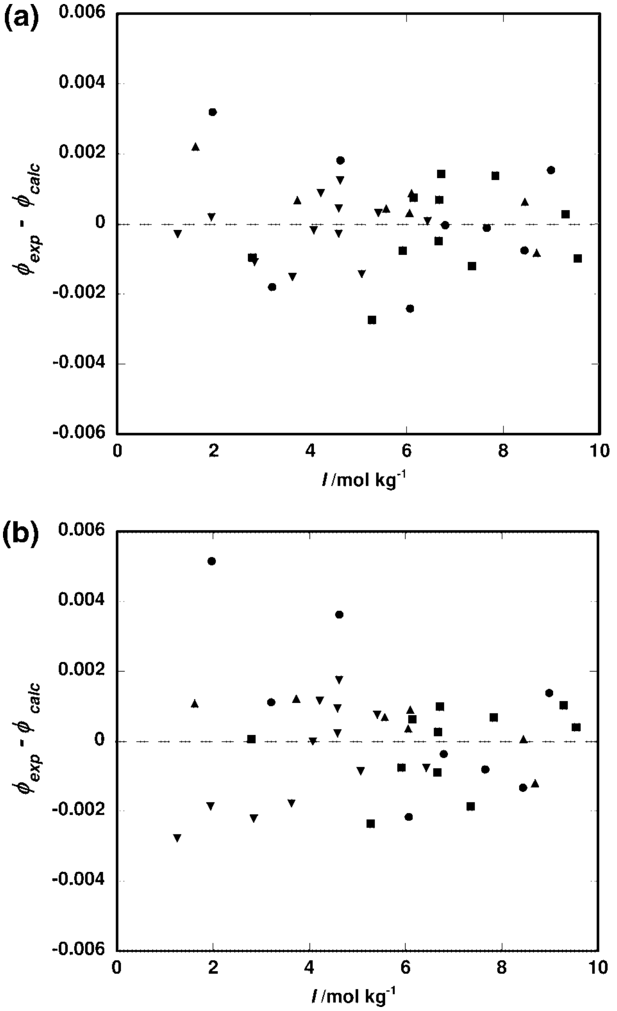

Figure 2. (a) Osmotic coefficient deviation graph for the D2 case. $m_1/(m_1 + m_2)$: ●, 0.23; ■, 0.4; ▲, 0.5; ▼, 0.75. (b) Osmotic coefficient deviation graph for the P2 case. $m_1/(m_1 + m_2)$: ●, 0.23; ■, 0.4; ▲, 0.5; ▼, 0.75.

% greater than those for D2. For $RT(L_{22})_0$, the P2 values are 2.3 % greater than for D2. Thus, values of $(L_{ij})_0$ show some dependence on the way the osmotic coefficients are analyzed. The values of the $(L_{11})_0$ and $(L_{22})_0$ obtained using the Pitzer mixed electrolyte equations average 1.5 % and 3.8 % greater than those with the D2 case.

Onsager Reciprical Relations (ORR). The ORR[15] can be expressed by the equation[5] $(L_{12})_0 = (L_{21})_0$. They give an important check of validity of the calculations. We use averages and standard deviations, σ's, of $\{(L_{12})_0 - (L_{21})_0\}/\{(L_{11})_0 + (L_{22})_0\}$ as measures of the ORR fits. For the D1 and P1 cases with molal ionic strength, $I < 7$ mol·kg^{-1}, the averages = 0.00002 and 0.00265 and $\sigma = 0.0036$ and 0.0035, respectively. For the D2 and P2 cases with $I < 10$ mol·kg^{-1}, the averages = 0.00049 and 0.00416, and the σ = 0.0036 and 0.0039, respectively. For the Pitzer mixed electrolyte case, the average is 0.00060, and the STD is 0.0039. This suggests that the use of extended Debye−Hückel equations for the binary salt mixtures gives better results than the use of the binary Pitzer equations at the lower ionic strengths. They also appear to be better than the Pitzer mixed electrolyte equations at the lower concentrations. However, the Pitzer mixed electrolyte equations gave reasonably good averages and σ's of the ORR relation over the whole concentration range in spite of the fact that the parameters used in the equation are from the binary mixtures where there is a problem with the NH_4Cl case at higher ionic strengths.

Of course, even though the approximations $(L_{12})_0 \approx (L_{21})_0$ suggest that the experimental values of $(L_{ij})_0$ themselves are reasonably accurate, one must be cautious with this assessment. The $(L_{ij})_0$ could be seriously in error even if $(L_{12})_0 \approx (L_{21})_0$. There does appear to be a (1 to 2) % dependence of the values of the $(L_{ij})_0$ on the method of analysis used to obtain the chemical potential derivatives.

Conclusion

A set of osmotic coefficients, ϕ are reported for the ternary system $NH_4Cl + (NH_4)_2SO_4 + H_2O$ at 298.15 K. These ϕ were used to obtain approximate expressions based on Scatchard's equation that relates osmotic coefficients to solute molalities. Six different strategies were used to obtain values of the b_{ij} parameters in Scatchard's equations. Coefficients b_{ij} in columns D1, D2, and D3 of Table 2 were obtained using the extended Debye−Hückel equation, to express the osmotic coefficients of the binary aqueous salt solutions. Coefficients b_{ij} in columns P1, P2, and P3 were obtained using Pitzer's binary equations to express the osmotic coefficients of the binary aqueous salt solutions. The b_{ij} in columns D1 and D2 and P1 and P2 were obtained by the method of least-squares using two subsets [$(m_1 + m_2) > 0.6$ mol·kg^{-1} and $(m_1 + 3m_2) < 7$ mol·kg^{-1}] and [$0.6 < (m_1 + m_2) < 4.4$ mol·kg^{-1}]. Those in columns D3 and P3 were obtained using the full set of the experimental ternary ϕ values.

For molalities under (7 and 10) mol·kg^{-1} ionic strength, the b_{ij} in columns D1 and D2, respectively, are recommended. At higher concentrations, Pitzer mixed electrolyte equations should be considered.

Finally, we recognize that there are many approaches that could be used to fit our ϕ data. For example, expressions based on normality rather than ionic strength could be used, but ionic strength and the Debye−Hückel constant should still be used for the square root of concentration terms. The mean-spherical-approximation equations might be used to give thermodynamic expressions for the binary salt solutions. Pitzer's mixed electrolyte equations for osmotic coefficients do include ternary fitting parameters, but there are complicating factors when using the corresponding equations for activity coefficients and their derivatives. However, the Pitzer mixed electrolyte equations might be combined with the Scatchard expressions that use the b_{ij} coefficients for the ternary mixtures. We have limited our approach to using Scatchard's equations with just two ways to express the osmotic coefficients for the binary aqueous salt solutions. We believe we have obtained useful expressions for the calculation of the ternary osmotic coefficients, chemical potential derivatives, and then the $(L_{ij})_0$ for the system $NH_4Cl + (NH_4)_2SO_4 + H_2O$ at 298.15 K.

Acknowledgment

It is a pleasure to dedicate this paper to Professor Robin Stokes on the occasion of his 90th birthday. His book (with R. A. Robinson) "Electrolyte Solutions" remains a frequently cited reference (including here). The senior author has had the privilege of knowing Robin Stokes and has benefitted from his many research advances. The Authors wish to thank Dr. Onofrio Annunziata for his very helpful suggestions during the preparation of this manuscript.

Supporting Information Available:

Tables S1−S3. This material is available free of charge via the Internet at http://pubs.acs.org.

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