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Reviews

Review of the Thermodynamic Properties of $Mg(NO_3)_2(aq)$ and Their Representation with the Standard and Extended Ion-Interaction (Pitzer) Models at 298.15 K

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Published thermodynamic data yielding the osmotic coefficients, relative apparent molar enthalpies, and apparent molar heat capacities of $Mg(NO_3)_2(aq)$ have been collected, recalculated consistently, and critically assessed. The more reliable of these data have been used to evaluate the parameters of the standard three-parameter form of Pitzer's ion-interaction model to higher molalities than previously available, along with the parameters of Archer's four-parameter, extended ion-interaction model at 298.15 K. Published experimental thermodynamic data were essentially represented equally well by these two models, provided that the exponential coefficient α_1 of the standard Pitzer model is fixed at the optimum value of $\alpha_1 = 1.55\ kg^{1/2}\cdot mol^{-1/2}$ rather than the traditional value of $\alpha_1 = 2.0\ kg^{1/2}\cdot mol^{-1/2}$. The use of the standard Pitzer model with this modified α_1 value is recommended for $Mg(NO_3)_2(aq)$. In addition, an empirical equation is given for the variation of the water activity of a saturated solution with temperature, from 273.54 to 328.20 K, with $Mg(NO_3)_2\cdot 6H_2O(s)$ as the solid phase.

Introduction

Many fluids resulting from the dissolution and processing of spent nuclear reactor fuel are aqueous electrolyte solutions with high concentrations of the nitrate ion. Significant concentrations of all of the rare earths from lanthanum through dysprosium, and also yttrium, occur as fission products in high-level, liquid, nuclear reactor wastes. These fluids include the Savannah River Plant and Hanford Reservation aqueous alkaline tank wastes.[1] Nitrate salts of several of the alkali metals and ammonium nitrate are present in agricultural runoff and in the effluent from the synthesis of conventional explosives. In addition, nitrate salts and hydrates of nitric acid are present at high concentrations in some atmospheric aerosol particles.[2] Furthermore, nitrate salts may occur at high concentrations in brines formed by the evaporative concentration of groundwaters and pore waters from rocks, whose initial nitrate concentrations were low. This includes waters found at the proposed Yucca Mountain Site nuclear waste repository.[3]

The need for thermodynamic data for these systems was one of the motivating factors behind the extensive isopiestic measurements for the rare earth nitrates, $R(NO_3)_3(aq)$, at 298.15 K.[4−9] Comprehensive critical evaluations of the thermodynamic properties of two of the alkali metal and alkaline earth metal nitrates of environmental interest, $NaNO_3(aq)$ and $Ca(NO_3)_2(aq)$, have been published recently.[10,11]

We are unaware of any recent critical review of the thermodynamic properties of $Mg(NO_3)_2(aq)$, which is another electrolyte of environmental interest. The available ion-interaction models for this system are restricted to the temperature 298.15 K.[13,14,17] Pitzer and Mayorga's[17] parameters for osmotic and activity coefficients were constrained only with data for solutions having molalities $m \leq 2.0\ mol\cdot kg^{-1}$, whereas the apparent molar enthalpy parameters of Silvester and Pitzer[13] were constrained only for $m \leq 0.1\ mol\cdot kg^{-1}$. The upper molality limits for these models are considerably below the saturation molality of $\sim 5\ mol\cdot kg^{-1}$ for the thermodynamically stable phase at 298.15 K, $Mg(NO_3)_2\cdot 6H_2O(cr)$, especially for the enthalpy parameters.

We searched the published literature and located 10 articles that reported isopiestic vapor pressure measurements for $Mg(NO_3)_2(aq)$,[18−27] several studies that reported the results from direct water vapor pressure measurements,[28−33] and four studies reporting freezing temperature measurements.[34−37] There are also three published studies that report enthalpies of dilution or relative apparent molar enthalpies of $Mg(NO_3)_2(aq)$,[28,38,39] two determinations of the enthalpy of solution of $Mg(NO_3)_2\cdot 6H_2O(cr)$ at 298.15 K,[28,40] and two determinations of the heat capacities of $Mg(NO_3)_2(aq)$.[41,42] Although not all of these published studies are reliable, enough reliable data are available to permit the parametrization of the standard Pitzer ion-interaction model[12−14] at 298.15 K to much higher molalities than done previously and to evaluate the parameters of the extended ion-interaction model of Archer.[15,16] Our critical analysis of the thermodynamic properties of $Mg(NO_3)_2(aq)$ and evaluation of the ion-interaction model parameters are described below. We found that when the exponential coefficient was fixed at $\alpha_1 = 1.55\ kg^{1/2}\cdot mol^{-1/2}$, both Pitzer's

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Table 1. Summary in Chronological Order (by Property) of Available Activity and Calorimetric Results for $Mg(NO_3)_2$(aq) at Various Temperatures

molality range (mol·kg^{-1})	T/K	no. of points	property (method)[a]	relative weight[b]	reference
0.1322–2.197	298.15	24	ϕ (isopiestic)	1	18
m(sat)[c]	298.15	1	ϕ (isopiestic)	(1)	54
1.502–5.123	298.15	11	ϕ (isopiestic)	1	19
0.5345–5.0710	298.15	8	ϕ (isopiestic)	1, n.a.	20
0.572–3.701	298.15	14	ϕ (isopiestic)	0	21
0.2567–4.8836	298.15	26	ϕ (isopiestic)	1	22
0.09284–4.9297	298.15	49	ϕ (isopiestic)	1, n.a.	23
0.5553–0.9982	298.15	10	ϕ (isopiestic)	n.a.	24
0.4055–1.0504	298.15	10	ϕ (isopiestic)	n.a.	25
0.2243–0.6807	298.15	9	ϕ (isopiestic)	n.a.	26
0.90–5.46	273.1$_5$, 323.1$_5$	23	ϕ (isopiestic)	0	27
0.1–5.0	298.15	14	ϕ (hygro.)	0	50
0.8718–5.893	293.15–343.15	53	ϕ (v.p.)	0	28
m(sat)[c]	293.15–362.91	36[d]	ϕ (v.p.)	(1)	28
m(sat)[c]	273.54–321.25	6	ϕ (v.p.)	(1)	29
1.22–9.93	313.1$_5$–378.7$_5$	48	ϕ (v.p.)	0	30
m(sat)[c]	283.95–311.29	12	ϕ (v.p.)	(0)	32
m(sat)[c]	277.56–322.25	19	ϕ (v.p.)	(0)	33
4.732–7.848	$\approx$ 294.9$_5$	38	ϕ (e.d.b.)	n.a.	55
0.020–1.042	266.64–273.04	7	ϕ (f.t.)	n.a.	34
0.1509–0.7743	268.76–272.40	7	ϕ (f.t.)	n.a.	35
0.0806–0.7650	269.00–272.77	8	ϕ (f.t.)	n.a.	36
0.034–3.038	247.49–272.92[d]	12	ϕ (f.t.)	0	37
0.00016–0.1[e]	298.15	34	$\Delta_{\mathrm{dil}}H_{\mathrm{m}}$	1	38
0.00032–0.1[e]	288.15	25	$\Delta_{\mathrm{dil}}H_{\mathrm{m}}$	n.a.	39
0.427–4.514	298.15	10	L_ϕ	0	28
0.0019–0.0196	298.15	11	$\Delta_{\mathrm{sol}}H_{\mathrm{m}}$	0	40
0.215–2.921	298.15	15[f]	$c_{p,\mathrm{s}}$	0	41
0.03774–0.24551	298.15	8	σ_{s}	1	42

[a] The following abbreviations are used: ϕ(isopiestic) denotes osmotic coefficients calculated from isopiestic equilibrium molalities, ϕ(hygro.) denotes osmotic coefficients determined by the hygrometric method, ϕ(v.p.) denotes osmotic coefficients calculated from direct vapor pressure measurements, ϕ(e.d.b.) denotes osmotic coefficients derived from electrodynamic balance measurements, ϕ(f.t.) denotes osmotic coefficients at the freezing temperature of the solution in equilibrium with H_2O(cr), $\Delta_{\mathrm{dil}}H_{\mathrm{m}}$ denotes enthalpies of dilution, L_ϕ denotes relative apparent molar enthalpies derived by the authors from enthalpy of solution measurements, $\Delta_{\mathrm{sol}}H_{\mathrm{m}}$ denotes enthalpies of solution, $c_{p,\mathrm{s}}$ denote mass heat capacities measured with "batch" calorimetry, and σ_{s} denotes volumetric heat capacities measured with a Picker-type flow calorimeter. The isopiestic reference standards used are described in the text. [b] These are the relative weights assigned to each thermodynamic property value from that study. One experimental value of ϕ from the study of Platford[20] for a slightly supersaturated solution was assigned zero weight in the model fits, $m = 5.071$ mol·kg^{-1} with $\phi = 2.4286$, because this ϕ value is about 0.03 higher than other experimental results at high molalities. Weights given in parentheses pertain to fits of the water activities of saturated solutions as a function of temperature with eq 25, whereas weights not in parentheses pertain to model fits used to evaluate the parameters of Pitzer's standard model or Archer's model. The notation n.a. (for "not analyzed") is used for several of the isopiestic studies involving KNO_3(aq),[24–26] $Mg(ClO_4)_2$(aq),[23] $MgCl_2$(aq),[20] and $Ca(NO_3)_2$(aq)[20] as the isopiestic reference standards, which we did not reanalyze because the osmotic coefficients of these nontraditional reference standards are not sufficiently well characterized. However, we did reanalyze the remaining measurements of Sadowska and Libuś[23] and of Platford,[20] which were made using the traditional standard KCl(aq) or $CaCl_2$(aq), respectively. The freezing temperature depressions of Rivett[36] and of Jones et al.[34,35] are not completely consistent, but it was not possible to assess which of these studies is more reliable. [c] m(sat) denotes the molality of the saturated solution at the experimental temperatures. Although the vapor pressures of the solutions were measured, the molalities of these saturated solutions were not measured or reported. [d] Seven experiments were carried out for saturated solutions involving $Mg(NO_3)_2\cdot 2H_2O$(s) as the solid phase.[28] Twenty nine additional vapor pressure measurements involved solutions with $Mg(NO_3)_2\cdot 6H_2O$(s) as the solid phase, but only the 8 experiments on the ascending solubility branch were reanalyzed. Freezing temperature measurements were also reported by Ewing et al.,[37] at various temperatures, for solutions with several different $Mg(NO_3)_2\cdot xH_2O$(s) species as the equilibrium solid phases, where $x = 9$, $9 + 6$, and 6. [e] The concentrations of these studies were reported in units of mol·L^{-1}. The 34 experiments of Lange and Streeck[38] involved 10 unique combinations of the initial and final concentrations and those of Hammerschmid and Lange[39] involved 8 unique combinations of the initial and final concentrations. [f] Duplicate or triplicate heat capacity measurements were made at each of seven unique molalities. One of the three values at the highest molality of 2.921 mol·kg^{-1} reported in the English language version of this journal, $c_{p,\mathrm{s}} = 0.7074$ cal·K^{-1}·g^{-1}, is presumably a misprint for 0.7374 cal·K^{-1}·g^{-1}.

and Archer's models give excellent and nearly equivalent representations of the available osmotic coefficients.

Analysis of Published Isopiestic Data and Direct Vapor Pressure Measurements

Isopiestic vapor pressure measurements have been reported for $Mg(NO_3)_2$(aq) at 298.15 K[18–26] and at (273.1$_5$ and 323.1$_5$) K.[27] These studies and other published thermodynamic studies involving $Mg(NO_3)_2$(aq) are summarized in Table 1. In this Table are listed the property that was measured, the investigated molality range, and the temperature or temperature range of each study.

In an isopiestic experiment, samples of a solution or solutions of interest, with nonvolatile solutes and a single solvent, are allowed to equilibrate with samples of one or more reference standard(s) by exchanging solvent through a common vapor phase under isothermal conditions until all solutions achieve the same water activity. The molalities of the solutions at isopiestic equilibrium are then measured. These equilibrium molalities can be used to calculate the osmotic coefficient ϕ of the solution or solutions of interest using the osmotic coefficient(s) of the reference standard(s) as described briefly below.

Robinson et al.[18] used KCl(aq) as the isopiestic reference standard for all of their experiments, as did Sadowska and Libuś[23] for experiments with $Mg(NO_3)_2$(aq) molalities $m \leq 2.1154$ mol·kg^{-1}. However, Sadowska and Libuś also used $Mg(ClO_4)_2$(aq) as a reference standard for additional measurements with $Mg(NO_3)_2(aq)$ molalities from $m = (1.2860$ to $4.9279)$ mol·kg^{-1}. Kümmel and Wilde[22] used NaCl(aq) as their reference standard for $Mg(NO_3)_2(aq)$ solutions having $m \leq 3.0027$ mol·kg^{-1} and $CaCl_2(aq)$ as the reference standard at higher molalities, whereas Biggs et al.[19] used $CaCl_2(aq)$ as the reference standard for all of their experiments. Platford[20] made isopiestic measurements for five of the six possible two-solute, common ion, ternary aqueous systems made by mixing $MgCl_2(aq)$, $Mg(NO_3)_2(aq)$, $CaCl_2(aq)$, and $Ca(NO_3)_2(aq)$ in various proportions. Most of Platford's isopiestic experiments also included samples of two of the limiting binary solutions, and the osmotic coefficients of $Mg(NO_3)_2(aq)$ could be calculated from its equilibrium molalities and from those of the $MgCl_2(aq)$, $CaCl_2(aq)$, or $Ca(NO_3)_2(aq)$ solutions that were also present by letting one of the other binary electrolyte solutions serve as the reference standard. Todorović and co-workers[24−26] used $KNO_3(aq)$ as their reference standard.

Chernykh et al.[27] did not report the equilibrium molalities of their LiCl(aq) and $H_2SO_4(aq)$ isopiestic reference standards, and Yakimov and Guzhavina[21] neither identified the reference standard or standards used nor reported their molalities. In these two studies, the isopiestic results were reported only as derived values of the water activities or vapor pressures, respectively, as a function of the $Mg(NO_3)_2(aq)$ solution composition.

The four most commonly used or traditional reference standards for isopiestic measurements involving aqueous electrolyte solutions are NaCl(aq), KCl(aq), $H_2SO_4(aq)$, and $CaCl_2(aq)$.[43,44] Their osmotic coefficients are well determined from a number of fairly concordant direct thermodynamic measurements, together with numerous isopiestic intercomparisons, with particularly numerous experimental results at 298.15 K.[16,45−47]

Five other electrolytes, $MgCl_2(aq)$, $Ca(NO_3)_2(aq)$, $Mg(ClO_4)_2(aq)$, LiCl(aq), and $KNO_3(aq)$, were used as nontraditional reference standards in some of the published isopiestic studies of $Mg(NO_3)_2(aq)$ described three paragraphs above.[20,23−27] There are relatively few thermodynamic studies for $KNO_3(aq)$ and $Mg(ClO_4)_2(aq)$ that determine their osmotic coefficients, and thus we do not believe that they are sufficiently well characterized at present to serve as isopiestic reference standards. Therefore, we do not reanalyze isopiestic measurements involving these electrolytes.[23−26] There is a fairly recent critical review of the thermodynamic properties of $Ca(NO_3)_2(aq)$,[11] but the authors did not discuss the uncertainty of the osmotic coefficients predicted by their model, which probably have significantly larger uncertainties than those of the four traditional standards. Furthermore, although the osmotic coefficients of $MgCl_2(aq)$ at $T = 298.15$ K are fairly well characterized,[48] at higher molalities they are based on those of $CaCl_2(aq)$, and thus their uncertainties must be larger than those of $CaCl_2(aq)$. Consequently, of Platford's[20] isopiestic measurements, only those with $CaCl_2(aq)$ as the reference standard were used here in the ion-interaction model parameter evaluations.

The molality-based stoichiometric ("practical") osmotic coefficients ϕ of $Mg(NO_3)_2(aq)$ were calculated with the fundamental equation for isopiestic equilibrium, which, for equilibrations involving only binary electrolyte solutions, is

$$\phi = \frac{\nu^* m^* \phi^*}{\nu m} \qquad (1)$$

where m denotes the equilibrium molality of $Mg(NO_3)_2(aq)$, $\nu = 3$ is its stoichiometric ionization number, and ν^*, m^*, and ϕ^* denote the corresponding quantities for the isopiestic reference standard. It was not necessary to correct the molalities reported in the published studies for changes in the accepted molar masses of $Mg(NO_3)_2$ and the reference standards because such corrections are an order of magnitude smaller than the typical precision of isopiestic molalities and because these corrections partially cancel out when ϕ values are calculated. For example, between 1942 when the first of these isopiestic studies was published and the present, the accepted values for the molar masses of $Mg(NO_3)_2$ and KCl have decreased by factors of (148.3148 g·mol^{-1}/148.34 g·mol^{-1}) = 0.99983 and (74.551 g·mol^{-1}/74.553 g·mol^{-1}) = 0.99997, respectively.

Values of ϕ^* for NaCl(aq) and KCl(aq) were calculated using the ion-interaction models and parameters presented in Archer's recent critical reviews.[16,45]

Rard and Clegg[46] critically assessed the available osmotic and activity coefficients of $CaCl_2(aq)$ at 298.15 K and evaluated the parameters of the standard form of Pitzer's ion-interaction model, extending this evaluation to several extended ion-interaction models with higher-order virial terms. They reported the parameters of one extended model that represents these activity data essentially to experimental accuracy over the full composition range from dilute solution to a molality of 10.77 mol·kg^{-1}, including measurements extending well into the supersaturated molality region. That particular model (their AEPEWHOVT model) is probably the most accurate one presently available for representing the osmotic and activity coefficients of $CaCl_2(aq)$ at 298.15 K. However, because their model formally includes $CaCl^+$ ion pairs, the calculation of ϕ^* values is complicated by the need for iterative calculations of the equilibrium ionic molalities and ionic activity coefficients at each stoichiometric molality.

Twenty years before the Rard and Clegg review,[46] Rard et al.[49] reported an empirical equation representing the osmotic coefficients of $CaCl_2(aq)$ at 298.15 K from infinite dilution to 9 mol·kg^{-1} as a function of the stoichiometric molality. The experimental results that constrained the empirical equation of Rard et al.[49] (R.H.S.) obviously do not include the more recently published thermodynamic data, and thus osmotic coefficients calculated with their equation are probably less accurate than those from the equation of Rard and Clegg[46] (R.C.). However, the earlier equation is much easier to use when calculating $\phi^*(CaCl_2)$ values. Values of the ratio of the osmotic coefficient calculated from the Rard and Clegg AEPEWHOVT equation to the value calculated with the equation of Rard et al.[49] at any fixed molality, $\phi^*(CaCl_2, R.C.)/\phi^*(CaCl_2, R.H.S.)$, vary between 1.0072 and 0.9990, and accurate values of this ratio may be estimated by interpolation. We therefore calculated values of $\phi^*(CaCl_2, R.H.S.)$ with the equation of Rard et al.[49] and corrected them graphically to yield values of $\phi^*(CaCl_2, R.C.)$.

El Guendouzi and Marouani[50] recently reported the results of vapor pressure measurements for $Mg(NO_3)_2(aq)$ at 298.15 K using a hygrometric method developed in their laboratory. This method involves the equilibrium, through the vapor phase, of a small droplet of a NaCl(aq) or LiCl(aq) standard against a much larger sample of $Mg(NO_3)_2(aq)$ or another aqueous electrolyte being investigated. These measurements could not be reanalyzed to make them consistent with Archer's thermodynamic evaluation[16] for NaCl(aq) because the authors did not report the molalities of the reference solutions. Their reported ϕ values are in approximate agreement with the more consistent isopiestic results,[19,20,22] exhibiting both positive and negative deviations. However, for solutions with $m \geq 2.5$ mol·kg^{-1}, the deviations are $\Delta\phi \leq 0.015$, but at lower molalities they become as large as $\Delta\phi = 0.03$. Because of this low precision, the hygrometric method results[50] were not included in the model parameter evaluations.

Osmotic coefficients can also be calculated from directly measured values of the saturation vapor pressure of the solvent above a solution, p_s, and the saturation vapor pressure of the pure solvent (in this case, water), p_w, at exactly the same temperature T. For a solution of a single electrolyte in water with a molality of m and with only water vapor being present in the vapor phase,[44]

$$\begin{aligned}\phi &= -\left(\frac{m_w}{\nu m}\right)\ln a_w \\ &\approx -\left(\frac{m_w}{\nu m R T}\right)\left\{RT\ln\left(\frac{p_s}{p_w}\right) + (B_2 - V_{m,w})(p_s - p_w)\right\} \qquad (2)\end{aligned}$$

Here, $m_w = (1/0.0180153$ kg·mol$^{-1}) = 55.5084$ mol·kg^{-1} is the molality of water, a_w is the water activity, $R = 8.31451$ J·K^{-1}·mol^{-1} is the ideal gas constant, B_2 is the second virial coefficient of $H_2O(g)$ at temperature T for the pressure series expansion form of the virial expansion, and $V_{m,w}$ is the partial molar volume of water (assumed to be incompressible) in the liquid solution. The maximum temperature for which there are measured saturation water vapor pressures for $Mg(NO_3)_2(aq)$ is 378.7_5 K (Table 1). At and below this temperature, the contributions from the third- and higher-order virial coefficients for $H_2O(g)$ are insignificant compared to the experimental measurement error. Similarly, the effect of the changing water vapor pressure on the activity of the liquid phase is negligible at these temperatures and pressures. That is, $(V_{m,w}/B_2) \leq 0.04$, and thus $(B_2 - V_{m,w}) \approx B_2$. Also, although $B_2(p_s - p_w)$ is small compared to $RT\ln(p_s/p_w)$, it was included in our calculations because this term is comparable in size to the measurement errors for higher-quality vapor pressure measurements. If the values of B_2 and $V_{m,w}$ are given in units of cm^3·mol^{-1} and p_s and p_w are in units of Pa, then $R = 8.31451 \times 10^6$ Pa·cm^3·K^{-1}·mol^{-1} in consistent units.

Values of B_2 were calculated using eq 27 of Rard and Platford.[44] Hill's equation of state[51] gives a very accurate representation of the saturation vapor pressures p_w above $H_2O(l)$, and Hill's equation would be suitable for the calculation of values of ϕ from directly measured water vapor pressures. However, the water vapor pressures assessed by Wexler and Greenspan[52] were selected instead because they were reported for both the IPTS-48 and IPTS-68 temperature scales. Unfortunately, none of the authors[28−30,32,33] of the direct vapor pressure studies for $Mg(NO_3)_2(aq)$ identified which temperature scale was used for their measurements. We therefore assume that the temperature scale used was the international temperature scale that was generally accepted when these studies were published. In the temperature range of interest here, the ITS-27 and IPTS-48 temperature scales are identical.[53]

Equation 2 was also used to calculate values of ϕ from the two isopiestic studies[21,27] that reported their results only as derived values of vapor pressures or water activities.

Preliminary comparisons of the recalculated osmotic coefficients of $Mg(NO_3)_2(aq)$ at 298.15 K, derived from isopiestic measurements,[18−23] were made graphically. In general, the ϕ values from the various isopiestic studies are in good agreement, except for those of Yakimov and Guzhavina,[21] which are considerably more scattered and are generally systematically higher by $\Delta\phi \approx 0.02$ to 0.04. Therefore, the Yakimov and Guzhavina ϕ values were given zero weight in the ion-interaction model fits that are described below. However, the derived ϕ values from the study of Robinson et al.[18] are somewhat scattered below 0.6 mol·kg^{-1} although they are more precise at higher molalities. The results of Sadowska and Libuś[23] are systematically higher by $\Delta\phi \approx 0.01$ above 1.0 mol·kg^{-1}, and those of Platford[20] are higher by $\Delta\phi \approx 0.01$ to 0.02 compared to those of Biggs et al.[19] and Kümmel and Wilde[22] at high molalities. Although there are some systematic differences among the osmotic coefficients from these isopiestic studies,[18−20,22,23] the ϕ values from each study overlap with ϕ values from one or more of the other studies, and no single set is clearly more accurate. Consequently, all of the more consistent isopiestic results at 298.15 K[18−20,22,23] were given equal weight when evaluating the parameters of Pitzer's model[12,14] and Archer's extended model.[15,16]

Osmotic coefficients at temperatures other than 298.15 K are available from isopiestic measurements[27] and from direct vapor pressure measurements.[28,30] A graphical comparison of the ϕ values derived from these three studies was made at 323.15 K, which is their only common experimental temperature. Values of ϕ from the studies of Ewing et al.[28] and of Chernykh et al.[27] are reasonably consistent within the $\Delta\phi \approx \pm(0.02$ to $0.05)$ imprecision typical of their measurements, although some of their ϕ values have significantly larger deviations. This imprecision is significantly larger than the imprecision for ϕ observed for the more consistent isopiestic results at 298.15 K. However, the vapor pressure results from Mashovets et al.[30] yield ϕ values at 323.15 K that are lower than those from the other two studies[27,28] by $\Delta\phi \approx 0.1$ to 0.2 at the higher molalities and are lower by $\Delta\phi \approx 0.6$ at the lowest molality, which is a significantly large discrepancy. Ewing et al.[28] made a single vapor pressure measurement at 298.15 K for an unsaturated solution of known molality, which yields an osmotic coefficient of $\phi = 2.452$ at 4.870 mol·kg^{-1}; this value is higher by $\Delta\phi \approx 0.1$ (4%) compared to the results from more consistent isopiestic studies.[19,20,22] Because of the low precision of vapor pressures determined in these three studies[27,28,30] and some significant discrepancies, these ϕ values were given zero weight when evaluating the ion-interaction model parameters.

Several of the published studies reported direct vapor pressure measurements for two-phase mixtures of presumably saturated solutions in direct contact with a solid phase of $Mg(NO_3)_2 \cdot xH_2O(s)$,[28,29,32,33,54] where the solid phase is not necessarily the equilibrium hydrate at the temperature of measurement. In three of these studies,[29,32,33] references are given to earlier, less precise measurements of this type. The molalities of the saturated solutions were not determined in these experiments, and thus these molalities must be taken from some other source if ϕ values are to be calculated. The accuracy of the derived osmotic coefficients from such measurements, ϕ(sat), is generally much less than for values of ϕ determined from isopiestic measurements, and they typically will be less accurate than values obtained from direct vapor pressure measurements involving solutions whose molalities have been measured. Factors contributing to these larger uncertainties are (1) the usually larger imprecision of direct vapor pressure measurements compared to that of isopiestic measurements; (2) the occasionally large variations between the molalities of saturated solutions, m(sat), determined in different laboratories for hydrated salts of type $Mg(NO_3)_2 \cdot xH_2O(s)$; and (3) the possibly insufficient duration of contact between the solid and solution phases, which may have been inadequate to produce a saturated solution after each temperature change.

Of the 29 vapor pressure measurements reported by Ewing et al.[28] as a function of temperature for presumably saturated solutions with $Mg(NO_3)_2{\cdot}6H_2O(s)$ as the initial solid phase, 8 were made in the thermodynamically stable ascending branch of the solubility polytherm, and the remaining 21 experiments were made in the descending branch. Only the experiments made within the thermodynamically stable temperature regions for $Mg(NO_3)_2{\cdot}6H_2O(s)$ and $Mg(NO_3)_2{\cdot}2H_2O(s)$ were further analyzed.

To avoid introducing uncertainties from different possible choices of values of $m(\mathrm{sat})$, a preliminary comparison of the direct vapor pressure results for presumably saturated solutions[28,29,32,33] was made using the function derived from eq 2:

$$m(\mathrm{sat})\,\phi(\mathrm{sat}) = -\left(\frac{m_w}{3}\right)\ln a_w(\mathrm{sat}) \tag{3}$$

Plots of $m(\mathrm{sat})\,\phi(\mathrm{sat})$ were made as a function of temperature to compare the consistency of the results from these four studies. Although these comparisons indicate that the values of $m(\mathrm{sat})\,\phi(\mathrm{sat})$ from all four of these studies are not in particularly good agreement, the results from the studies of Apelblat[32] and Apelblat and Korin[33] are in approximate agreement. However, their values are distinctly lower than the results from the studies of Ewing et al.[28] and Wexler and Hasegawa,[29] which are also in approximate agreement with each other. Furthermore, the values of $m(\mathrm{sat})\,\phi(\mathrm{sat})$ calculated from the measurements of Ewing et al. and Apleblat and Korin are more scattered than those from the other studies.

Values of $a_w(\mathrm{sat})$ from the study of Apelblat[32] increase with increasing temperature from 283.95 K to around 290 K and then regularly decrease with further increase in temperature. The results of Apelblat and Korin[33] show a similar trend but with the maximum occurring around 295 K. These trends conflict with the $a_w(\mathrm{sat})$ values of Wexler and Hasegawa[29] from (273.54 to 321.25) K, which decrease regularly with increasing temperature. Because the solubility of $Mg(NO_3)_2{\cdot}6H_2O(s)$ increases regularly with increasing temperature in this region,[37] $a_w(\mathrm{sat})$ is not expected to have a maximum.

A quantitative comparison of the results from these four studies was made at 298.15 K. Ewing et al.[28] reported the vapor pressure of a presumably saturated solution of $Mg(NO_3)_2(aq)$ in equilibrium with $Mg(NO_3)_2{\cdot}6H_2O(s)$, from which we calculated $a_w(\mathrm{sat}) = 0.5241$. Wexler and Hasegawa[29] reported vapor pressures for presumably saturated solutions at six temperatures, and they interpolated their results to yield values of $10^2(p_s/p_w)$ at various selected temperatures on the centigrade temperature scale. Their results at 298.15 K yield $a_w(\mathrm{sat}) = 0.534_4 \pm 0.006$. Similarly, Apelblat[32] and Apelblat and Korin[33] reported vapor pressures of such solutions at various temperatures, used least-squares fits to represent their results as functions of temperature, and reported derived values of $a_w(\mathrm{sat}) = 0.552$ and 0.546, respectively, at 298.15 K. In these measurements, most types of experimental error, such as the failure to equilibrate the solution adequately with the solid phase, will yield erroneously high values of $a_w(\mathrm{sat})$ rather than low values. In addition, Stokes and Robinson[54] measured $a_w(\mathrm{sat}) = 0.5286$ at 298.15 K using the isopiestic method with $H_2SO_4(aq)$ as the reference standard. This value[54] is essentially midway between values of $a_w(\mathrm{sat})$ from the studies of Ewing et al.[28] and Wexler and Hasegawa.[29] However, we have slightly less confidence in the results from Ewing et al.[28] because of the lower precision, and we believe the values of $a_w(\mathrm{sat})$ from the experiments of Wexler and Hasegawa[29] and Stokes and Robinson[54] to be the most reliable for $Mg(NO_3)_2(aq)$. On the basis of these comparisons, we accept the results from the studies of Ewing et al.,[28] Wexler and Hasegawa,[29] and Stokes and Robinson,[54] but we reject the experimental vapor pressures of Apelblat[32] and Apelblat and Korin[33] as being erroneously too high.

Ewing et al.[28] also reported vapor pressures for presumably saturated solutions of $Mg(NO_3)_2(aq)$, with $Mg(NO_3)_2{\cdot}2H_2O(s)$ as the solid phase, for the temperature range of (328.15 to 358.20) K. The derived values of the water activity, $a_w(\mathrm{sat}) = 0.037 \pm 0.001$, are both unexpectedly low and independent of temperature within the precision of the measurements. Because the solubility varies significantly over this temperature interval,[37] the constancy of $a_w(\mathrm{sat})$ is certainly not expected. In the absence of an independent study to confirm these rather unusual values of $a_w(\mathrm{sat})$, we do not consider these results any further.

Ha and Chan[55] reported the results from electrodynamic balance measurements at ambient temperature for $Mg(NO_3)_2(aq)$ and several other aqueous salts and mixtures. They reported an average ambient temperature of $(294.9_5 \pm 0.2)$ K for their $Mg(NO_3)_2(aq)$ experiments. Electrodynamic balance measurements involve the determination of the mass-to-charge ratio of a microscopic, electrically charged, liquid solution particle that is levitated between a pair of parabolic electrodes by adjusting the electrical field until the electrical and gravitational forces balance exactly. A series of vapor pressure measurements are made with each particle in which the relative humidity experienced by that suspended particle is varied and controlled externally. Because the initial solid particle may have been hydrated to some unknown degree rather than being anhydrous and because its dry mass is unknown, the molalities of the liquid particles are not obtained directly. Rather, these molalities are obtained by normalizing the composition−water activity scale to agree with some previous measurements in the overlapping molality region. The reported[55] electrodynamic balance measurements for $Mg(NO_3)_2(aq)$ were normalized to make their water activities agree with the smoothed isopiestic results tabulated by Robinson and Stokes[56] at 298.15 K, and thus they do not yield independent values of the water activities. We did not reanalyze these electrodynamic balance results but note that they extend nearly 3 $\mathrm{mol{\cdot}kg^{-1}}$ into the supersaturated molality region.

Analysis of Published Freezing Temperature Lowering Measurements

Data for the lowering of the freezing temperature of $Mg(NO_3)_2(aq)$ solutions of different molalities in contact with ice have been reported in several studies. Rivett[36] and Ewing et al.[37] reported the compositions of their solutions in units of mass % of $Mg(NO_3)_2$, and Jones and Stine[35] reported the "weights" of $Mg(NO_3)_2$ and H_2O used to prepare their solutions. We converted these reported compositions to molalities using the currently accepted molar mass of 148.3148 $\mathrm{g{\cdot}mol^{-1}}$ for $Mg(NO_3)_2$. In contrast, Jones and Pearce[34] reported their solution compositions in units of $\mathrm{mol{\cdot}L^{-1}}$ along with their specific gravities (i.e., densities relative to that of water), both at 293.15 K, and these concentrations were also converted by us to molalities. Timmermans[57] tabulated freezing temperature depressions from several other studies, including studies published in 1872 and 1899. Because the reported freezing temperature depressions in these studies are of inadequate precision, they were not analyzed in the present investigation.

The results from four studies[34−37] were compared graphically using the function $\{(273.15\ \mathrm{K} - T_f)/m\}$ plotted against the solution molality m, where T_f is the observed freezing temperature. The values of $\{(273.15\ \mathrm{K} - T_f)/m\}$ calculated from the results reported by Rivett[36] are very precise and increase smoothly with increasing molality. In contrast, values of $\{(273.15\ \mathrm{K} - T_f)/m\}$ calculated from the study of Jones and Pearce[34] exhibit a minimum around $m \approx 0.15$ mol·kg^{-1}. Values of $\{(273.15\ \mathrm{K} - T_f)/m\}$ from the study of Jones and Stine[35] have a dependence on molality similar to those from the study of Jones and Pearce;[34] this is to be expected for measurements from the same laboratory, but the results from these two studies are displaced by about 2%. Above $m \approx 0.15$ mol·kg^{-1} the values of $\{(273.15\ \mathrm{K} - T_f)/m\}$ of Jones and Stine show a trend parallel to the results of Rivett, whereas those from Jones and Pearce's study are 4−5% higher. Values of $\{(273.15\ \mathrm{K} - T_f)/m\}$ calculated from the results reported by Ewing et al.[37] at their two lowest molalities disagree considerably by ∼ −25% to ∼ +30%, and they are both skewed and lower at their higher molalities relative to those from the other three studies. Therefore, the results from the study of Ewing et al.[37] were rejected. In the absence of adequate calorimetric information, the freezing temperature depression results from the other three studies[34−36] cannot be compared for consistency with the accurate isopiestic results at 298.15 K. Consequently, we do not include the freezing temperature depression results when evaluating the ion-interaction model parameters.

Analysis of Published Enthalpies of Dilution and Heat Capacities

Enthalpies of dilution $\Delta_{\mathrm{dil}}H_{\mathrm{m}}$ of $\mathrm{Mg(NO_3)_2(aq)}$ have been reported at temperatures of 298.15 and 288.15 K.[38,39] These enthalpies of dilution are differences between the relative apparent molar enthalpies L_ϕ of the final and initial solutions, whose molalities are denoted by m_f and m_i, respectively. They are given by the relation

$$\Delta_{\mathrm{dil}}H_{\mathrm{m}} = L_\phi(m_\mathrm{f}) - L_\phi(m_\mathrm{i}) \tag{4}$$

Values of $\Delta_{\mathrm{dil}}H_{\mathrm{m}}$ could also be derived for $\mathrm{Mg(NO_3)_2(aq)}$ from differences between enthalpies of solution $\Delta_{\mathrm{sol}}H_{\mathrm{m}}$ measured for $\mathrm{Mg(NO_3)_2{\cdot}6H_2O(cr)}$[28,40] and other hydrates[28] in water at $T = 298.15$ K to yield solutions with two different final molalities, denoted here by m_1 and m_2:

$$\begin{aligned}\Delta_{\mathrm{dil}}H_{\mathrm{m}} &= \Delta_{\mathrm{sol}}H_{\mathrm{m}}(m_2) - \Delta_{\mathrm{sol}}H_{\mathrm{m}}(m_1)\\ &= L_\phi(m_2) - L_\phi(m_1)\end{aligned} \tag{5}$$

Ewing et al.[28] reported that they combined their enthalpy of solution measurements with the $\Delta_{\mathrm{dil}}H_{\mathrm{m}}$ reported by Lange and Streeck[38] at low concentrations to yield L_ϕ values, but they did not report their experimental $\Delta_{\mathrm{sol}}H_{\mathrm{m}}$ values. Although Milonjic et al.[40] reported the results of enthalpy of solution measurements with 11 different final solution molalities, the precision of their measurements is not sufficient for the derivation of meaningful values of $\Delta_{\mathrm{dil}}H_{\mathrm{m}}$. Unfortunately, the average value of the enthalpy of solution of $\mathrm{Mg(NO_3)_2{\cdot}6H_2O(cr)}$ to form an infinitely dilute solution at 298.15 K reported by Ewing et al.,[28] $\Delta_{\mathrm{sol}}H_{\mathrm{m}}^\circ = (18.150 \pm 0.010)$ kJ·mol^{-1}, and the values of $\Delta_{\mathrm{sol}}H_{\mathrm{m}}^\circ = (15.7$ and $16.0)$ kJ·mol^{-1} (depending on the method of extrapolation) reported by Milonjic et al.[40] are only in rough agreement, indicating that at least one of these two studies is not accurate. Apelblat[32] and Apelblat and Korin[33] reported values of $\Delta_{\mathrm{sol}}H_{\mathrm{m}}(\mathrm{sat}) = 26.1$ kJ·mol^{-1} and 26.5 kJ·mol^{-1}, respectively, for the dissolution of $\mathrm{Mg(NO_3)_2{\cdot}6H_2O(cr)}$ to form its saturated solution at 298.15 K, both based on the variation of the saturated solution molality and osmotic coefficient with temperature. However, these values cannot be compared directly to the $\Delta_{\mathrm{sol}}H_{\mathrm{m}}^\circ$ values at infinite dilution because $L_\phi(\mathrm{sat})$ is not available.

Mashovets et al.[30] measured the water vapor pressures of $m = (1.22$ to $9.93)$ mol·kg^{-1} $\mathrm{Mg(NO_3)_2(aq)}$ solutions at temperatures of (363.15, 368.15, and 373.15) K and used these results to calculate values of the relative partial molar enthalpy of water, $L_{\mathrm{m},1}$, at these three temperatures. However, because of low precision and systematic errors in their measurements described above, these derived $L_{\mathrm{m},1}$ values are probably inaccurate.

The reported values[28,38,39] of $\Delta_{\mathrm{dil}}H_{\mathrm{m}}$ or L_ϕ were recalculated for consistency using the current value for the molar mass of $\mathrm{Mg(NO_3)_2}$ to account for differences between international and absolute joules[28] and were converted from calories to joules,[38,39] as necessary, using the energy unit conversion factors given by Rossini.[58] The first two of these corrections are very small compared to the imprecision of the measurements.

Experimental heat capacities of aqueous solutions measured with "batch" calorimetry, which are commonly reported as the heat capacity per gram of solution, $c_{p,\mathrm{s}}$, are related to the apparent molar heat capacity of the solute, $C_{p,\phi}$, by

$$C_{p,\phi} = Mc_{p,\mathrm{s}} + \frac{(c_{p,\mathrm{s}} - c_{p,\mathrm{w}})(10^3\ \mathrm{g{\cdot}kg^{-1}})}{m} \tag{6}$$

where $c_{p,\mathrm{w}}$ is the heat capacity of the solvent (water). Here $c_{p,\mathrm{s}}$ and $c_{p,\mathrm{w}}$ are given in units of J·K^{-1}·g^{-1}, and M is the molar mass of the solute given in units of g·mol^{-1}. Heat capacities from measurements using flow calorimetry are generally reported as volumetric heat capacities σ_s and σ_w, where $\sigma_\mathrm{s} = c_{p,\mathrm{s}}\rho_\mathrm{s}$ and $\sigma_\mathrm{w} = c_{p,\mathrm{w}}\rho_\mathrm{w}$, and where ρ_s and ρ_w are the densities of the solution and of water, respectively.

The flow calorimetry measurements of Spitzer et al.[42] cover the range $m = (0.03774$ to $0.2455)$ mol·kg^{-1}, whereas the batch calorimetry results of Drakin et al.[41] cover the larger range $m = (0.215$ to $2.921)$ mol·kg^{-1}, with both studies performed at 298.15 K. Unfortunately, the duplicate values of $C_{p,\phi}$ derived from the measurements of Drakin et al.[41] at their lowest molality $m = 0.215$ mol·kg^{-1} differ by 34 J·K^{-1}·mol^{-1}, and their replicate measurements at their highest molality $m = 2.921$ mol·kg^{-1} are ∼20 J·K^{-1}·mol^{-1} more positive than obtained by extrapolation from their measurements at the five intermediate molalities. Furthermore, the extrapolation of a smooth curve drawn through the more consistent $C_{p,\phi}$ from the Drakin et al. measurements at the five intermediate molalities yields results that lie on a curve that is parallel to but is displaced by ∼20 J·K^{-1}·mol^{-1} from the experimental results of Spitzer et al.[42] The $C_{p,\phi}$ values of Spitzer et al. are much more precise and probably more accurate, but they are limited to $m \le 0.2455$ mol·kg^{-1}.

Equations for the Analysis of Thermodynamic Results Using the Standard (Pitzer) and Extended (Archer) Ion-Interaction Models

We represent the available thermodynamic information for $\mathrm{Mg(NO_3)_2(aq)}$ using the standard version of Pitzer's ion-interaction model[12−14] and also with the extended ion-interaction model of Archer[15,16] that uses an ionic-strength-dependent third virial coefficient. The relevant equations are given below. We use a superscript of either "P" for Pitzer or "A" for Archer for the various thermodynamic quantities and ion-interaction parameter symbols in these equations because the evaluated parameters will generally have different numerical values for these two model variants.

Pitzer's original ion-interaction model equation[12,14] may be written in the following general form for the molality-based osmotic coefficient ϕ of a binary solution of a strong electrolyte of stoichiometry $M_{\nu_M}X_{\nu_X}$:

$$\phi^{P} = 1/|z_M z_X|A_\phi I^{1/2} - (1 + bI^{1/2}) + (2\nu_M\nu_X/\nu)m\{\beta^{(0,P)}_{M,X} + \beta^{(1,P)}_{M,X}\exp(-\alpha_1 I^{1/2})\} + \{2(\nu_M\nu_X)^{3/2}/\nu\}m^2 C^{(\phi,P)}_{M,X} \quad (7)$$

where M denotes the cation and X denotes the anion; m is the stoichiometric molality; $b = 1.2\ \mathrm{kg^{1/2}{\cdot}mol^{-1/2}}$, independent of temperature and pressure; A_ϕ is the Debye−Hückel limiting law slope for ϕ; I is the stoichiometric, molality-based ionic strength; z_M and z_X are the signed valences of ions M and X; ν_M and ν_X are the number of M and X ions formed by the complete dissociation of one molecule of the solute; and $\nu = \nu_M + \nu_X$ is the total or stoichiometric ionization number of the electrolyte. The exponential coefficient α_1 is usually fixed at $\alpha_1 = 2.0\ \mathrm{kg^{1/2}{\cdot}mol^{-1/2}}$, independent of both temperature and pressure, for strong and nearly strong electrolytes.[14] The quantities $\beta^{(0,P)}_{M,X}$, $\beta^{(1,P)}_{M,X}$, and $C^{(\phi,P)}_{M,X}$ are ion-interaction parameters to be evaluated using experimental data. For this model, the mean activity coefficient $\gamma_\pm$ of the solute is given by

$$\ln \gamma_\pm{}^{P} = -|z_M z_X|A_\phi\{I^{1/2}/(1 + \mathrm{b}I^{1/2}) + (2/b)\ln(1 + bI^{1/2})\} + (2\nu_M\nu_X/\nu)m[2\beta^{(0,P)}_{M,X} + 2\{\beta^{(1,P)}_{M,X}/\alpha_1{}^2 I\}\{1 - (1 + \alpha_1 I^{1/2} - \alpha_1{}^2 I/2)\exp(-\alpha_1 I^{1/2})\}] + \{3(\nu_M\nu_X)^{3/2}/\nu\}m^2 C^{(\phi,P)}_{M,X} \quad (8)$$

Archer[15,16] described an extension of Pitzer's model for ϕ of a binary electrolyte solution that may be written in the following general form:

$$\phi^{A} = 1 - |z_M z_X|A_\phi I^{1/2}/(1 + bI^{1/2}) + (2\nu_M\nu_X/\nu)m\{\beta^{(0,A)}_{M,X} + \beta^{(1,A)}_{M,X}\exp(-\alpha_1 I^{1/2})\} + (4\nu_M{}^2\nu_X z_M/\nu)m^2\{C^{(0,A)}_{M,X} + C^{(1,A)}_{M,X}\exp(-\omega_1 I^{1/2})\} \quad (9)$$

where most of the symbols are the same as defined above but with the notation being closer to that of Clegg et al.[47] rather than to that of Archer.[15,16] As with the usual form of Pitzer's model, $\alpha_1 = 2.0\ \mathrm{kg^{1/2}{\cdot}mol^{-1/2}}$ for most electrolytes, and $\omega_1 = 2.5\ \mathrm{kg^{1/2}{\cdot}mol^{-1/2}}$ is commonly used for strong electrolytes.[16,47] However, for 2:2 charge-type electrolytes, smaller values of $\alpha_1 = 1.4\ \mathrm{kg^{1/2}{\cdot}mol^{-1/2}}$ and $\omega_1 \approx 1\ \mathrm{kg^{1/2}{\cdot}mol^{-1/2}}$ have been used.[59,60] For the Archer model, the mean activity coefficient $\gamma_\pm$ of the solute is given by

$$\ln \gamma_\pm{}^{A} = -|z_M z_X|A_\phi\{I^{1/2}/(1 + bI^{1/2}) + (2/b)\ln(1 + bI^{1/2})\} + (2\nu_M\nu_X/\nu)m[2\beta^{(0,A)}_{M,X} + 2\{\beta^{(1,A)}_{M,X}/\alpha_1{}^2 I\}\{1 - (1 + \alpha_1 I^{1/2} - \alpha_1{}^2 I/2)\exp(-\alpha_1 I^{1/2})\}] + (2\nu_M{}^2\nu_X z_M/\nu)m^2[3C^{(0,A)}_{M,X} + 4\{C^{(1,A)}_{M,X}/\omega_1{}^4 I^2\}\{6 - (6 + 6\omega_1 I^{1/2} + 3\omega_1{}^2 I + \omega_1{}^3 I^{3/2} - \omega_1{}^4 I^2/2)\exp(-\omega_1 I^{1/2})\}] \quad (10)$$

The corresponding standard Pitzer model expression for the relative apparent molar enthalpy L_ϕ is

$$L^{P}_\phi = \nu|z_M z_X|A_H\ln(1 + bI^{1/2})/(2b) - 2\nu_M\nu_X RT^2(mB^{(L,P)}_{M,X} + m^2\nu_M z_M C^{(L,P)}_{M,X}) \quad (11)$$

where A_H is the Debye−Hückel limiting law slope for enthalpy. The $B^{(L,P)}_{M,X}$ term in this expression is defined by

$$B^{(L,P)}_{M,X} = (\partial\beta^{(0,P)}_{M,X}/\partial T)_p + 2(\partial\beta^{(1,P)}_{M,X}/\partial T)_p\{1 - (1 + \alpha_1 I^{1/2})\exp(-\alpha_1 I^{1/2})\}/(\alpha_1{}^2 I) \quad (12)$$

and the $C^{(L,P)}_{M,X}$ term is defined by

$$C^{(L,P)}_{M,X} = \frac{(\partial C^{(\phi,P)}_{M,X}/\partial T)_p}{2|z_M z_X|^{1/2}} \quad (13)$$

Similarly, for Archer's extended ion-interaction model,

$$L^{A}_\phi = \nu|z_M z_X|A_H\ln(1 + bI^{1/2})/(2b) - 2\nu_M\nu_X RT^2(mB^{(L,A)}_{M,X} + m^2\nu_M z_M C^{(L,A)}_{M,X}) \quad (14)$$

$$B^{(L,A)}_{M,X} = (\partial\beta^{(0,A)}_{M,X}/\partial T)_p + 2(\partial\beta^{(1,A)}_{M,X}/\partial T)_p\{1 - (1 + \alpha_1 I^{1/2})\exp(-\alpha_1 I^{1/2})\}/(\alpha_1{}^2 I) \quad (15)$$

$$C^{(L,A)}_{M,X} = (\partial C^{(0,A)}_{M,X}/\partial T)_p + 4(\partial C^{(1,A)}_{M,X}/\partial T)_p\{6 - (6 + 6\omega_1 I^{1/2} + 3\omega_1{}^2 I + \omega_1{}^3 I^{3/2})\exp(-\omega_1 I^{1/2})\}(\omega_1{}^4 I^2) \quad (16)$$

The corresponding equations for the apparent molar heat capacity are

$$\mathrm{C}^{P}_{p,\phi} = \mathrm{C}^{o}_{p,\phi} + \nu|z_M z_X|A_C\ln(1 + bI^{1/2})/(2b) - 2\nu_M\nu_X RT^2(mB^{(C,P)}_{M,X} + m^2\nu_M z_M C^{(C,P)}_{M,X}) \quad (17)$$

and

$$C^{A}_{p,\phi} = C^{o}_{p,\phi} + \nu|z_M z_X|A_C\ln(1 + bI^{1/2})/(2b) - 2\nu_M\nu_X RT^2(mB^{(C,A)}_{M,X} + m^2\nu_M z_M C^{(C,A)}_{M,X}) \quad (18)$$

The expressions for $B^{(C,P)}_{M,X}$ and $B^{(C,A)}_{M,X}$ are essentially identical (except for the superscripts) for the two forms of the ion-interaction model

$$B^{(C,P)}_{M,X} = (\partial^2\beta^{(0,P)}_{M,X}/\partial T^2)_p + (2/T)(\partial\beta^{(0,P)}_{M,X}/\partial T)_p + 2[\{(\partial^2\beta^{(1,P)}_{M,X}/\partial T^2)_p + (2/T)(\partial\beta^{(1,P)}_{M,X}/\partial T)_p\}\{1 - (1 + \alpha_1 I^{1/2})\exp(-\alpha_1 I^{1/2})\}]/(\alpha_1{}^2 I) \quad (19)$$

$$B^{(C,A)}_{M,X} = (\partial^2\beta^{(0,A)}_{M,X}/\partial T^2)_p + (2/T)(\partial\beta^{(0,A)}_{M,X}/\partial T)_p + 2[\{(\partial^2\beta^{(1,A)}_{M,X}/\partial T^2)_p + (2/T)(\partial\beta^{(1,A)}_{M,X}/\partial T)_p\}\{1 - (1 + \alpha_1 I^{1/2})\exp(-\alpha_1 I^{1/2})\}]/(\alpha_1{}^2 I) \quad (20)$$

However, the corresponding equations for $C_{\mathrm{M,X}}^{(\mathrm{C,P})}$ and $C_{\mathrm{M,X}}^{(\mathrm{C,A})}$ are quite different:

$$C_{\mathrm{M,X}}^{(\mathrm{C,P})} = \{(\partial^2 C_{\mathrm{M,X}}^{(\phi,\mathrm{P})}/\partial T^2)_p + (2/T)(\partial C_{\mathrm{M,X}}^{(\phi,\mathrm{P})}/\partial T)_p\}/(2|z_\mathrm{M} z_\mathrm{X}|^{1/2}) \tag{21}$$

$$C_{\mathrm{M,X}}^{(\mathrm{C,A})} = (\partial^2 C_{\mathrm{M,X}}^{(0,\mathrm{A})}/\partial T^2)_p + (2/T)(\partial C_{\mathrm{M,X}}^{(0,\mathrm{A})}/\partial T)_p + 4\{(\partial^2 C_{\mathrm{M,X}}^{(1,\mathrm{A})}/\partial T^2)_p + (2/T)(\partial C_{\mathrm{M,X}}^{(1,\mathrm{A})}/\partial T)_p\}\{6 - (6 + 6\omega_1 I^{1/2} + 3{\omega_1}^2 I + {\omega_1}^3 I^{3/2})\exp(-\omega_1 I^{1/2})\}/({\omega_1}^4 I^2) \tag{22}$$

The usual three-parameter equations of Pitzer's standard model[12−14] may be recovered from eqs 9, 10, 14−16, 18, 20, and 22 by setting $C_{\mathrm{M,X}}^{(1,\mathrm{A})}$ and its first and second temperature derivatives equal to zero, along with using the relation $C_{\mathrm{M,X}}^{(\phi,\mathrm{P})} = 2z_\mathrm{M}(\nu_\mathrm{M}/\nu_\mathrm{X})^{1/2} C_{\mathrm{M,X}}^{(0,\mathrm{A})}$.

Values of the Debye−Hückel limiting law slope A_ϕ and its temperature derivatives A_H and A_C were calculated using the Chebychev series of Clegg et al.,[47] which is based on the critical evaluation of the relative permittivity (dielectric constant) of water by Archer and Wang,[61] together with Hill's equation of state for water.[51]

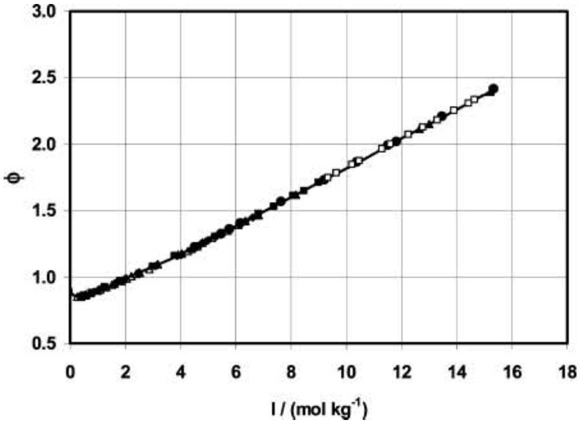

Figure 1. Osmotic coefficients ϕ of $Mg(NO_3)_2(aq)$ at $T = 298.15$ K. —, Smoothed values from three-parameter standard ion-interaction model (Pitzer model) using the second set of parameters from Table 2. Experimental values: ♦, Robinson et al.[18] with KCl(aq) as a reference standard; ●, Biggs et al.[19] with $CaCl_2(aq)$ as a reference standard; ▲, Platford[20] with $CaCl_2(aq)$ as a reference standard; ■, Kümmel and Wilde[22] with NaCl(aq) as a reference standard; □, Kümmel and Wilde[22] with $CaCl_2(aq)$ as a reference standard; △, Sadowska and Libuś[23] with KCl(aq) as a reference standard.

Evaluation of the Parameters of the Standard Pitzer Model and the Archer Model

The model parameters of the standard Pitzer and Archer models at the fixed temperature of 298.15 K were determined using the available osmotic coefficient, enthalpy of dilution, and apparent molar heat capacity property data sets listed in Table 1 by a least-squares error minimization procedure that can be applied simultaneously to all selected data sets of these types. The combined error measure that was minimized was defined as the average over all data sets of the weighted sum of the average square error for each data set. Relative property weights were assigned to the individual data sets for each type of thermodynamic property, and these weights are given in Table 1. The average square error for each data set was calculated from the squared difference between the fitted and measured values at each data point. In addition, an internal weight was applied to each data point of each data set. In this way, we could exclude individual erroneous data points (outliers) by setting their corresponding data-point weights equal to zero, along with excluding an entire set of erroneous data by setting its data-set weight equal to zero.

This error measure was minimized analytically in the standard way by setting its first derivative with respect to each unknown parameter equal to zero. This yielded a linear matrix equation for the unknown parameters that was programmed and solved within a Microsoft Excel spreadsheet using only in-cell formulas. Subsequently, the desired error statistics were evaluated for each set of fitted parameters.

As seen from the model equations given previously, eqs 7 through 22, the osmotic coefficient is a function of the standard Pitzer or Archer model parameters at the temperature of interest. In contrast, the enthalpy of dilution depends on the first temperature derivatives of these model parameters, whereas the apparent molar heat capacity depends on both their first and second derivatives at the temperature of interest. If the osmotic coefficients are known as a function of temperature, then obviously the first and second temperature derivatives of the model parameters must be consistent with this known temperature variation. However, for $Mg(NO_3)_2(aq)$, reliable values of the osmotic coefficients are available only at 298.15 K. Consequently, the fitting to obtain the standard Pitzer and Archer model parameters from osmotic coefficient data is independent of the fitting to obtain the first temperature derivative from the enthalpy of dilution and also from the fitting to obtain the first and second temperature derivatives from apparent molar heat capacity data. The latter two fits, however, are coupled to one another through the first temperature derivative, and their values are influenced by the relative (property) weights assigned to the two types of data. Exploratory calculations showed that using a relative weighting of unity for the latter two types of data sets was satisfactory. Therefore, because the osmotic coefficient fits were uncoupled from the enthalpy of dilution and apparent molar heat capacity fits, the data set property weights were set equal to unity for all included data sets of all types.

Osmotic Coefficient Model Parameter Evaluations. Figure 1 is a plot of the osmotic coefficients of $Mg(NO_3)_2(aq)$ at $T = 298.15$ K as a function of the molality. The initial fits were done using the commonly accepted value of $\alpha_1 = 2.0\ \mathrm{kg^{1/2}{\cdot}mol^{-1/2}}$ for both Pitzer and Archer models, eqs 7 and 9, and $\omega_1 = 2.5\ \mathrm{kg^{1/2}{\cdot}mol^{-1/2}}$ for Archer's model, as described above. The root-mean-square deviations for ϕ are $\sigma_\mathrm{rms}(\phi, \mathrm{Pitzer}) = 0.00830$ and $\sigma_\mathrm{rms}(\phi, \mathrm{Archer}) = 0.00376$. However, there are significant systematic deviations between experimental and model values, $\Delta\phi$, for the standard Pitzer model fit, typically amounting to $\Delta\phi = -0.01$ to -0.02 for $m < 0.5\ \mathrm{mol{\cdot}kg^{-1}}$ and $\Delta\phi = +0.01$ to $+0.02$ for $0.5\ \mathrm{mol{\cdot}kg^{-1}} < m < 2.1\ \mathrm{mol{\cdot}kg^{-1}}$, with the systematic deviations ranging from about $\Delta\phi = +0.02$ to -0.01 at higher molalities. Fixing $\alpha_1 = 2.0\ \mathrm{kg^{1/2}{\cdot}mol^{-1/2}}$ and choosing the value of ω_1 that yielded the second (deepest) minimum for $\sigma_\mathrm{rms}(\phi, \mathrm{Archer})$ gives $\omega_1 = 2.0\ \mathrm{kg^{1/2}{\cdot}mol^{-1/2}}$ with $\sigma_\mathrm{rms}(\phi, \mathrm{Archer}) = 0.00350$. The Archer model gives a significantly better representation of the experimental ϕ data than the standard Pitzer model at this value of α_1. Also, see the additional comments about the optimization of ω_1 given three paragraphs below, where the presence of three minima for $\sigma_\mathrm{rms}(\phi, \mathrm{Archer})$ as a function of ω_1 is discussed.

A commonly used approach to improve the quality of representation of experimental data with Pitzer model fits is to add additional ion-interaction model parameters. Filippov et al.[62] represented a subset of the available

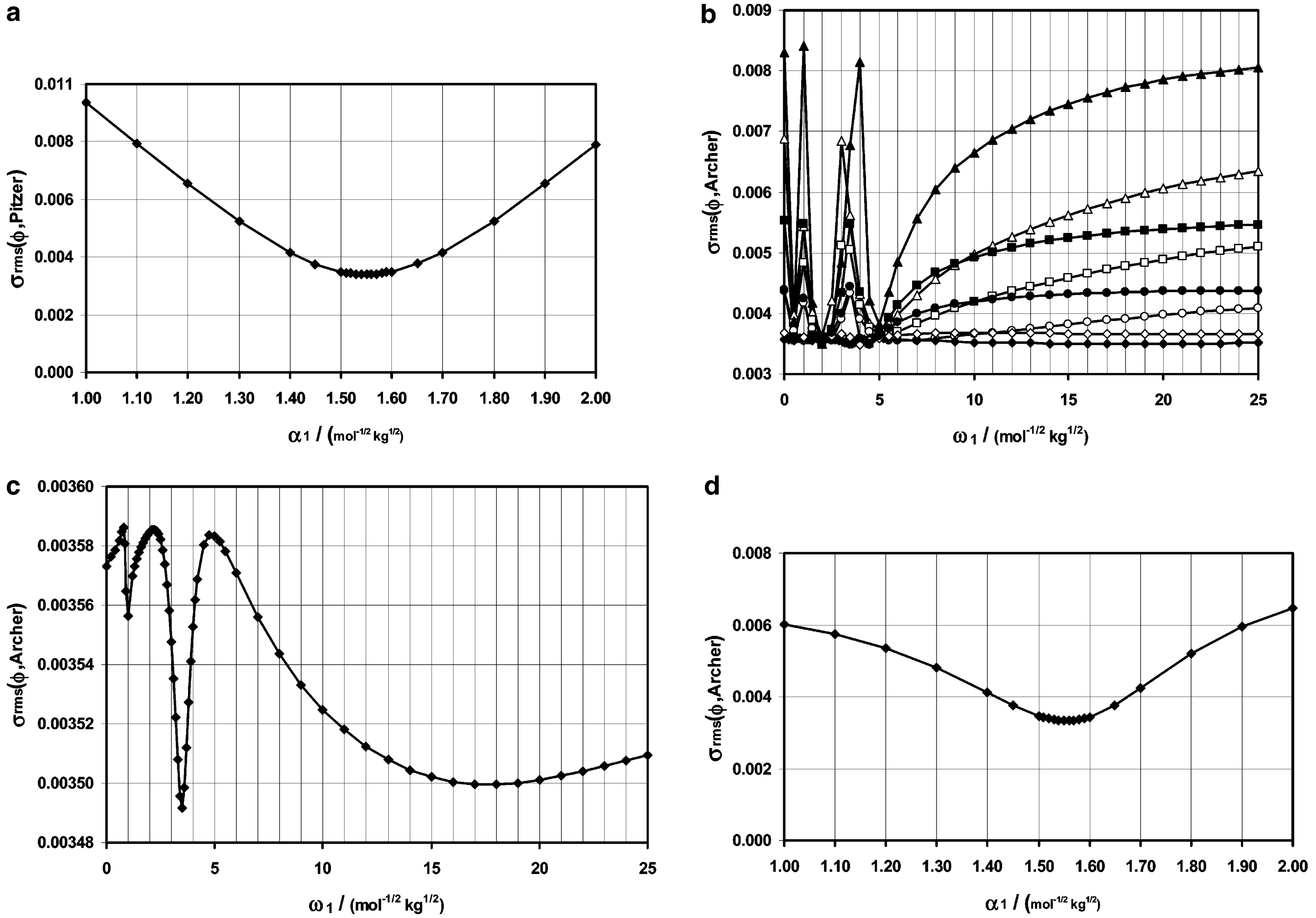

Figure 2. Root-mean-square deviations for standard Pitzer and Archer models for $Mg(NO_3)_2(aq)$ at $T = 298.15$ K. (a) Values of $\sigma_{rms}(\phi$, Pitzer) as a function of α_1. (b) Values of $\sigma_{rms}(\phi$, Archer) as a function of ω_1, plotted at various fixed values of α_1: △, $\alpha_1(m°)^{1/2} = 1.2$; □, $\alpha_1(m°)^{1/2} = 1.3$; ○, $\alpha_1(m°)^{1/2} = 1.4$; ♦, $\alpha_1(m°)^{1/2} = 1.55$; ◊, $\alpha_1(m°)^{1/2} = 1.6$; ●, $\alpha_1(m°)^{1/2} = 1.7$; ■, $\alpha_1(m°)^{1/2} = 1.8$; ▲, $\alpha_1(m°)^{1/2} = 2.0$. (c) Values of $\sigma_{rms}(\phi$, Archer) as a function of ω_1 when $\alpha_1 = 1.55$ $kg^{1/2}\cdot mol^{-1/2}$. (d) Values of $\sigma_{rms}(\phi$, Archer) as a function of α_1 when $\omega_1 = 3.5$ $kg^{1/2}\cdot mol^{-1/2}$.

osmotic coefficients for $Mg(NO_3)_2(aq)$ at 298.15 K (one experimental set of isopiestic ϕ values[23] and smoothed values of ϕ from two older reviews published in 1968 and 1979) using a form of Pitzer's standard model that includes the $\beta^{(2,P)}_{M,X}$ parameter. The $\beta^{(2,P)}_{M,X}$ parameter is related to an association constant and was used by Pitzer[14] only for higher-valence associated electrolytes that undergo association at low molalities followed by redissociation at higher molalities. Although the quality of the representation obtained by Fillipov for $Mg(NO_3)_2(aq)$ is fairly good, their resulting parameter value is $\beta^{(2,P)}_{M,X} = 0.30453$ $kg\cdot mol^{-1}$. As noted by Pitzer,[14] $\beta^{(2,P)}_{M,X}$ should have a negative value if it really represents ionic association. Thus, the obtained positive value implies that the improved representation is simply due to the inclusion of a fourth parameter rather than being the result of using a more realistic physicochemical model.

Pitzer recommended using a smaller value of the exponential coefficient, $\alpha_1 = 1.4$ $kg^{1/2}\cdot mol^{-1/2}$, for divalent metal sulfates and other 2:2 charge-type electrolytes that undergo some ionic association at low molalities;[14] similarly, Oakes et al.[63] found that using $\alpha_1 = 1.5$ $kg^{1/2}\cdot mol^{-1/2}$ gave a better representation than $\alpha_1 = 2.0$ $kg^{1/2}\cdot mol^{-1/2}$ for the 3:1 electrolyte $NdCl_3(aq)$. Therefore, we optimized the fits for the standard Pitzer model with respect to α_1 and found that $\alpha_1 = 1.55$ $kg^{1/2}\cdot mol^{-1/2}$ yielded the minimum root-mean-square error with $\sigma_{rms}(\phi$, Pitzer) = 0.00357, as shown in Figure 2a. Furthermore, as seen in Figure 3, the pattern of residuals of ϕ(experimental) − ϕ(model) is essentially completely random below $I = 10$ $mol\cdot kg^{-1}$ and very nearly random at higher ionic strengths.

We similarly optimized the exponential coefficients ω_1 of Archer's model, eq 9, at various values of α_1 in the range $\alpha_1 = (1.2$ to $2.0)$ $kg^{1/2}\cdot mol^{-1/2}$. Values of $\sigma_{rms}(\phi$, Archer) as a function of ω_1 at various fixed values of α_1 are plotted in Figure 2b. At the majority of selected values of α_1, $\sigma_{rms}(\phi$, Archer) exhibits three minima as a function of ω_1, with the second minimum generally being lower than the first. The first minimum occurs at $\omega_1 \approx (0.5$ to $1)$ $kg^{1/2}\cdot mol^{-1/2}$, the second minimum typically occurs at $\omega_1 \approx (2$ to $3)$ $kg^{1/2}\cdot mol^{-1/2}$, and the third minimum occurs at $\omega_1 \approx 5.0$ $kg^{1/2}\cdot mol^{-1/2}$. However, when $\alpha_1 = 1.55$ $kg^{1/2}\cdot mol^{-1/2}$ (the optimal value for the standard Pitzer model) and $\omega_1 = 3.5$ $kg^{1/2}\cdot mol^{-1/2}$ (the optimal Archer fit with this α_1 value), then the minima are much shallower than for comparable fits with other values of α_1.

Figure 2c gives an expanded plot of $\sigma_{rms}(\phi$, Archer) versus ω_1 when $\alpha_1 = 1.55$ $kg^{1/2}\cdot mol^{-1/2}$, and Figure 2d shows the variation of $\sigma_{rms}(\phi$, Archer) with respect to α_1 while ω_1 is fixed at its optimal value of $\omega_1 = 3.5$ $kg^{1/2}\cdot mol^{-1/2}$. For these fits with the standard Pitzer and Archer models, while fixing $\alpha_1 = 1.55$ $kg^{1/2}\cdot mol^{-1/2}$, $\sigma_{rms}(\phi$, Pitzer) − $\sigma_{rms}(\phi$, Archer) $\leq 8 \times 10^{-5}$. Thus, allowing the ionic-interaction $C_{M,X}$ term to have a dependence on ionic strength yields only a negligible improvement over the standard Pitzer model. That is, the standard Pitzer model and the Archer model give nearly identical and optimal quality of representation for $Mg(NO_3)_2(aq)$ osmotic coefficients at 298.15

Table 2. Parameters and Standard Errors for Pitzer's Ion-Interaction Model and Archer's Extended Model Applied to $Mg(NO_3)_2$(aq) and Debye−Hückel Limiting Law Slopes at $T = 298.15$ K, Where $m^\circ = 1$ mol·kg^{-1} and $T^\circ = 1$ K

parameter	parameter value[a,b]	parameter	parameter value[a,b]
$\beta^{(0,A)}_{M,X}(m^\circ)$	0.303227	$\beta^{(0,P)}_{M,X}(m^\circ)$	0.306728
$\beta^{(1,A)}_{M,X}(\mathrm{m}^\circ)$	1.423501	$\beta^{(1,P)}_{M,X}(m^\circ)$	1.257451
$C^{(0,A)}_{M,X}(m^\circ)^2$	-1.00982×10^{-3}	$C^{(\phi,P)}_{M,X}(m^\circ)^2$	-3.32923×10^{-3}
$C^{(1,A)}_{M,X}(m^\circ)^2$	-0.863310		
$\alpha_1(m^\circ)^{1/2}$	1.55	$\alpha_1(m^\circ)^{1/2}$	1.55
$\omega_1(m^\circ)^{1/2}$	3.5		
$A_\phi(m^\circ)^{1/2}$	0.391475	$A_\phi(m^\circ)^{1/2}$	0.391475
$\sigma_{rms}(\phi)$	0.00349	$\sigma_{rms}(\phi)$	0.00357
$(\partial\beta^{(0,A)}_{M,X}/\partial T)_p(m^\circ T^\circ)$	-4.06307×10^{-2}	$(\partial\beta^{(0,P)}_{M,X}/\partial T)_p(m^\circ T^\circ)$	-9.08354×10^{-3}
$(\partial\beta^{(1,A)}_{M,X}/\partial T)_p(m^\circ T^\circ)$	5.09829×10^{-2}	$(\partial\beta^{(1,P)}_{M,X}/\partial T)_p(m^\circ T^\circ)$	1.64225×10^{-2}
$(\partial C^{(0,A)}_{M,X}/\partial T)_p\{(m^\circ)^2 T^\circ\}$	2.37393×10^{-2}	$(\partial C^{(\phi,P)}_{M,X}/\partial T)_p\{(m^\circ)^2 T^\circ\}$	3.54586×10^{-2}
$(\partial C^{(1,A)}_{M,X}/\partial T)_p\{(m^\circ)^2 T^\circ\}$	0.204013		
$(\partial^2\beta^{(0,A)}_{M,X}/\partial T^2)_p\{(m^\circ)(T^\circ)^2\}$	1.21615×10^{-4}	$(\partial^2\beta^{(0,P)}_{M,X}/\partial T^2)_p\{(m^\circ)(T^\circ)^2\}$	-8.73390×10^{-6}
$(\partial^2\beta^{(1,A)}_{M,X}/\partial T^2)_p\{(m^\circ)(T^\circ)^2\}$	-2.32288×10^{-4}	$(\partial^2\beta^{(1,P)}_{M,X}/\partial T^2)_p\{(m^\circ)(T^\circ)^2\}$	1.37229×10^{-6}
$(\partial^2 C^{(0,A)}_{M,X}/\partial T^2)_p(m^\circ T^\circ)^2$	-1.05511×10^{-4}	$(\partial^2 C^{(\phi,P)}_{M,X}/\partial T^2)_p(m^\circ T^\circ)^2$	-1.14006×10^{-4}
$(\partial^2 C^{(1,A)}_{M,X}/\partial T^2)_p(m^\circ T^\circ)^2$	2.92540×10^{-4}		
$C^o_{P,\phi}$/J·K^{-1}·mol^{-1}	−158.74[c]	$C^o_{P,\phi}$/J·K^{-1}·mol^{-1}	−158.74[c]
A_H/RT	0.801844	A_H/RT	0.801844
A_C/R	3.83602	A_C/R	3.83602
$\sigma_{rms}(\Delta_{dil}H_m)$/J·mol^{-1}	16.9	$\sigma_{rms}(\Delta_{dil}H_m)$/J·mol^{-1}	17.3
$\sigma_{rms}(C_{p,\phi})$/J·K^{-1}·mol^{-1}	0.44	$\sigma_{rms}(C_{p,\phi})$/J·K^{-1}·mol^{-1}	0.51

[a] The values of $\sigma_{rms}(\phi)$, $\sigma_{rms}(\Delta_{dil}H_m)$, and $\sigma_{rms}(C_{p,\phi})$ are unweighted root-mean-square deviations. The maximum molality to which these parameters apply at 298.15 K is 5.123 mol·kg^{-1} for ϕ, 0.1007 mol·kg^{-1} for L_ϕ, and 0.2455 mol·kg^{-1} for $C_{p,\phi}$. For these model coefficient evaluations, 98 values of ϕ, 34 values of $\Delta_{dil}H_m$, and 8 values of $C_{p,\phi}$ were used. [b] For fits to obtain the parameters of the standard Pitzer model with the traditional value of $\alpha_1(m^\circ)^{1/2} = 2.0$, we obtain $\beta^{(0,P)}_{M,X}(m^\circ) = 0.328601$, $\beta^{(1,P)}_{M,X}(m^\circ) = 1.915868$, $C^{(\phi,P)}_{M,X}(m^\circ)^2 = -6.35368 \times 10^{-3}$, $(\partial\beta^{(0,P)}_{M,X}/\partial T)_p(m^\circ T^\circ) = -5.83890 \times 10^{-3}$, $(\partial\beta^{(1,P)}_{M,X}/\partial T)_p(m^\circ T^\circ) = 1.32506 \times 10^{-2}$, $(\partial C^{(\phi,P)}_{M,X}/\partial T)_p\{(m^\circ)^2 T^\circ\} = 3.07417 \times 10^{-2}$, $(\partial^2\beta^{(0,P)}_{M,X}/\partial T^2)_p\{(m^\circ)(T^\circ)^2\} = -1.19928 \times 10^{-5}$, $(\partial^2\beta^{(1,P)}_{M,X}/\partial T^2)_p\{(m^\circ)(T^\circ)^2\} = 6.16065 \times 10^{-6}$, and $(\partial^2 C^{(\phi,P)}_{M,X}/\partial T^2)_p(m^\circ T^\circ)^2 = -1.00460 \times 10^{-4}$, with $\sigma_{rms}(\phi$, Pitzer$) = 0.00830$. For fits to obtain the parameters of the Archer model with the traditional value $\alpha_1(m^\circ)^{1/2} = 2.0$ and optimized $\omega_1(m^\circ)^{1/2} = 2.0$, we obtain $\beta^{(0,A)}_{M,X}(m^\circ) = 0.302609$, $\beta^{(1,A)}_{M,X}(\mathrm{m}^\circ) = 1.546012$, $C^{(0,A)}_{M,X}(m^\circ)^2 = -9.78181 \times 10^{-4}$, $C^{(1,A)}_{M,X}(m^\circ)^2 = 0.327496$, $(\partial\beta^{(0,A)}_{M,X}/\partial T)_p(m^\circ T^\circ) = -1.75945 \times 10^{-2}$, $(\partial\beta^{(1,A)}_{M,X}/\partial T)_p(m^\circ T^\circ) = 2.67705 \times 10^{-2}$, $(\partial C^{(0,A)}_{M,X}/\partial T)_p\{(m^\circ)^2 T^\circ\} = -2.12546 \times 10^{-3}$, $(\partial C^{(1,A)}_{M,X}/\partial T)_p\{(m^\circ)^2 T^\circ\} = 9.00817 \times 10^{-2}$, $(\partial^2\beta^{(0,A)}_{M,X}/\partial T^2)_p\{(m^\circ)(T^\circ)^2\} = 6.09775 \times 10^{-6}$, $(\partial^2\beta^{(1,A)}_{M,X}/\partial T^2)_p\{(m^\circ)(T^\circ)^2\} = -6.86261 \times 10^{-5}$, $(\partial^2 C^{(0,A)}_{M,X}/\partial T^2)_p(m^\circ T^\circ)^2 = -6.17606 \times 10^{-6}$, and $(\partial^2 C^{(1,A)}_{M,X}/\partial T^2)_p(m^\circ T^\circ)^2 = 2.24349 \times 10^{-5}$ with $\sigma_{rms}(\phi$, Archer$) = 0.00351$. [c] This value was fixed at the sum of the recommended ionic standard partial molar heat capacities from Table 2 of Criss and Millero.[64]

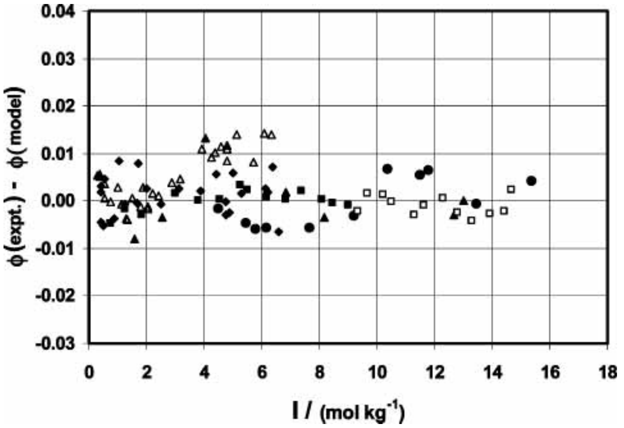

Figure 3. Deviations of the critically assessed experimental osmotic coefficients at $T = 298.15$ K for $Mg(NO_3)_2$(aq) as a function of the ionic strength from the three-parameter standard ion-interaction model (Pitzer model) using the second set of parameters from Table 2. Experimental values: ◆, Robinson et al.[18] with KCl(aq) as a reference standard; ●, Biggs et al.[19] with $CaCl_2$(aq) as a reference standard; ▲, Platford[20] with $CaCl_2$(aq) as a reference standard; ■, Kümmel and Wilde[22] with NaCl(aq) as a reference standard; □, Kümmel and Wilde[22] with $CaCl_2$(aq) as a reference standard; △, Sadowska and Libuś[23] with KCl(aq) as a reference standard.

K when $\alpha_1 = 1.55$ kg$^{1/2}$·mol$^{-1/2}$. Fits of good and nearly equivalent quality were obtained with Archer's model with all investigated values of α_1, although the best agreement occurs when $\alpha_1 = 1.55$ kg$^{1/2}$·mol$^{-1/2}$ and $\omega_1 = 3.5$ kg$^{1/2}$·mol$^{-1/2}$ with nearly equal values of $\sigma_{rms}(\phi$, Archer) and $\sigma_{rms}(\phi$, Pitzer). Therefore, the use of the simpler three-parameter Pitzer model with $\alpha_1 = 1.55$ kg$^{1/2}$·mol$^{-1/2}$ is recommended for this system at this temperature.

We note that these optimal values of α_1 and ω_1 were evaluated only at 298.15 K, and it is not clear whether they will be adequate to represent higher-temperature measurements once they become available. We also note that the value of $\alpha_1 = 1.55$ kg$^{1/2}$·mol$^{-1/2}$ for $Mg(NO_3)_2$(aq) is smaller than the value of $\alpha_1 = 2.0$ kg$^{1/2}$·mol$^{-1/2}$ used for most strong electrolytes but is similar in value to $\alpha_1 = 1.4$ kg$^{1/2}$·mol$^{-1/2}$ for divalent metal sulfates and other 2:2 charge-type electrolytes that undergo some ionic association.[14] The smaller value of $\alpha_1 = 1.55$ kg$^{1/2}$·mol$^{-1/2}$ is probably the result of partial ionic association in $Mg(NO_3)_2$(aq) solutions.

Table 2 lists the evaluated parameters for $Mg(NO_3)_2$(aq) at 298.15 K both for the standard Pitzer ion-interaction model[14] and for Archer's extended model.[15,16]

Enthalpy and Heat Capacity Model Parameter Evaluations. For the determination of the enthalpy and heat capacity parameters of the standard Pitzer and Archer models, the exponential coefficients were set at the recommended optimal values found for the osmotic coefficient models, $\alpha_1 = 1.55$ kg$^{1/2}$·mol$^{-1/2}$ and $\omega_1 = 3.5$ kg$^{1/2}$·mol$^{-1/2}$, and they were held fixed. Initially, both the lower-molality enthalpies of dilution of Lange and Streeck[38] and the higher-molality relative apparent molar enthalpies of Ewing et al.[28] were included in the evaluation of the param-

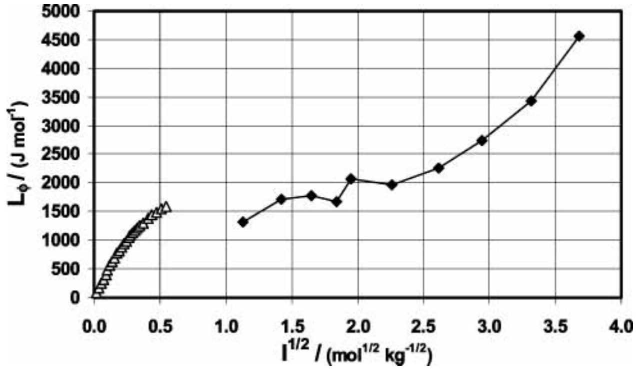

Figure 4. Relative apparent molar enthalpies L_ϕ of $Mg(NO_3)_2$(aq) at $T = 298.15$ K plotted against the square root of the ionic strength. Experimental values: △, Lange and Streeck;[38] ♦, Ewing et al.[28]

eters of eqs 11 through 16. However, when both data sets were given equal weight in these fits, the less precise results of Ewing et al. were represented reasonably well, whereas there were significant systematic deviations from the more precise results of Lange and Streeck. Increasing the weight given to the data of Lange and Streeck and reevaluating the model parameters reduced the size of the systematic deviations between the models and their data, but the representation of the Ewing et al. data became poorer.

The origin of this difficulty can be seen in Figure 4. Ewing et al.[28] reported that they measured the enthalpies of solution of $Mg(NO_3)_2$ hydrates in water at $T = 298.15$ K and used the enthalpies of dilution from Lange's laboratory to extrapolate their results to infinite dilution to extract their reported values of $L_\phi(m)$. As can be clearly seen from Figure 4, the $L_\phi(m)$ values from Ewing et al. are very scattered below $I \approx 5$ mol·kg^{-1}. There is also a gap between the lowest molality studied by Ewing et al. ($m \geq 0.474$ mol·kg^{-1}) and the highest molality studied by Lange and Streeck[38] ($m \leq 0.1007$ mol·kg^{-1}), and it is not clear if the data from these two studies are consistent. Unfortunately, Ewing et al. did not report their actual experimental results, so it is not possible to refine their derived results; consequently, their reported $L_\phi(m)$ values were rejected as being unreliable.

Similar problems were encountered while trying to represent the apparent molar heat capacities of Spitzer et al.[42] as determined by flow microcalorimetry and the results of Drakin et al.[41] as determined by batch calorimetry. As can be seen from Figure 5, the extrapolated trends of these two data sets disagree by ~20 J·K^{-1}·mol^{-1} on average, with the Drakin et al. results being much less precise and probably less accurate. Consequently, the Drakin et al. results were rejected as being unreliable.

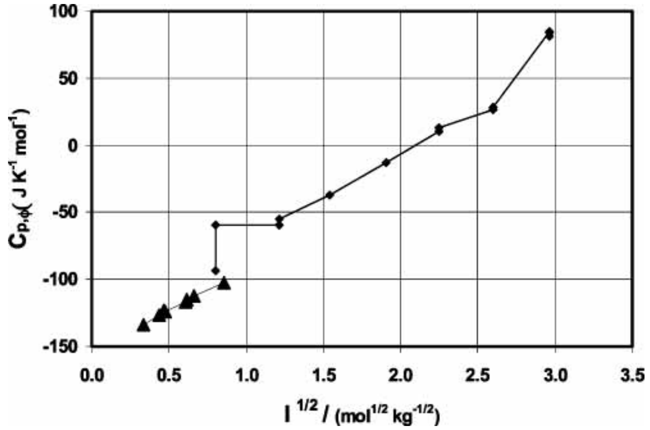

Figure 5. Apparent molar heat capacities $C_{p,\phi}$ of $Mg(NO_3)_2$(aq) at $T = 298.15$ K plotted against the square root of the ionic strength. Experimental values: ♦, Drakin et al.;[41] ▲, Spitzer et al.[42]

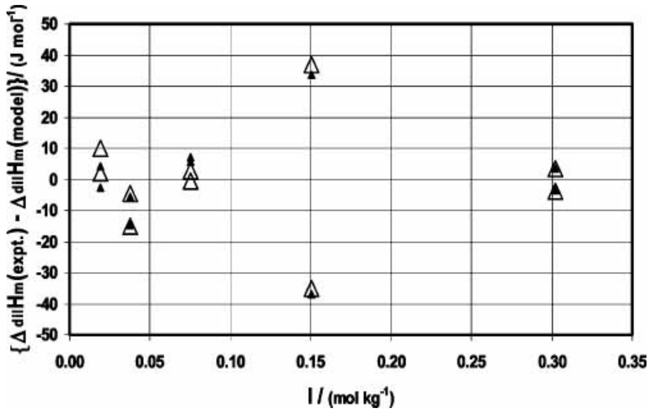

Figure 6. Deviations of the critically assessed experimental enthalpies of dilution of Lange and Streeck[38] for $Mg(NO_3)_2$(aq) at $T = 298.15$ K as a function of the ionic strength of the initial solution from the three-parameter standard ion-interaction model (Pitzer model), △, and the four-parameter ion-interaction model (Archer model), ▲, using the parameters from Table 2.

Equations 17 and 18 also contain an additional term, the standard partial molar heat capacity of $Mg(NO_3)_2$(aq) at infinite dilution, $C^{o}_{P,\phi}$. Initially, we allowed its values to be determined as additional parameters, which resulted in $C^{o}_{P,\phi} \approx -159.0$ J·K·mol^{-1} for both the Pitzer and Archer models. This value is very close to the sum of the ionic standard partial molar hear capacities listed in Table 2 of Criss and Millero,[64] $C^{o}_{P,\phi} = -158.74$ J·K·mol^{-1}, which is a "best value" based on the use of data for several different magnesium salts and nitrate salts. We then reduced the number of model parameters by fixing $C^{o}_{P,\phi} = -158.74$ J·K·mol^{-1} and evaluated the first and second temperature derivatives reported in Table 2. As anticipated from the fits to osmotic coefficients described above and because of the more restricted molality ranges for the usable enthalpy and heat capacity data, including the $(\partial C^{(1,A)}_{M,X}/\partial T)_p$ and $(\partial^2 C^{(1,A)}_{M,X}/\partial T^2)_p$ terms yielded only minor improvements in the representation of the relative apparent molar enthalpies and apparent molar heat capacities; therefore, the use of the standard Pitzer model with the parameters of Table 2 is recommended. Figures 6 and 7 show the residuals for the optimized Pitzer and Archer models for the enthalpies of dilution and apparent molar heat capacities, respectively.

In Table 3, we give values of ϕ, a_w, $\gamma_\pm$, L_ϕ, and $C_{p,\phi}$ at various molalities that were calculated using the standard Pitzer model parameters reported in Table 2.

Rard and Wijesinghe[65] described a method for directly converting the parameters of Archer's model and of an extended form of Archer's model to those of the standard Pitzer model. They then applied this conversion methodology to several test systems, including $Ca(NO_3)_2$(aq). Because the available thermodynamic data for $Ca(NO_3)_2$(aq) extend to very high ionic strengths, a five-parameter extended Pitzer model[11] was required to represent these results adequately. When the five-parameter model was converted to the three-parameter standard Pitzer model[65] using the traditional value $\alpha_1 = 2.0$ kg$^{1/2}$·mol$^{-1/2}$, there was a significant decline in the accuracy of the representation of the source data. In view of the significant improvement observed in this study for the accuracy of representation

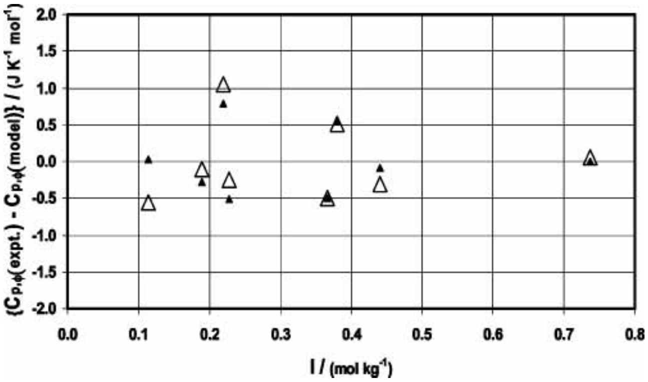

Figure 7. Deviations of the critically assessed experimental apparent molar heat capacities $C_{p,\phi}$ of Spitzer et al.[42] for $Mg(NO_3)_2$(aq) at $T = 298.15$ K as a function of the ionic strength from the three-parameter standard ion-interaction model (Pitzer model), △, and the four-parameter ion-interaction model (Archer model), ▲, using the parameters from Table 2.

of the osmotic coefficients of $Mg(NO_3)_2$(aq) with Pitzer's standard model when a smaller (optimum) value of α_1 was selected instead, we believe it is likely that a similar improvement could be obtained for $Ca(NO_3)_2$(aq) if the parameter conversions described by Rard and Wijesinghe[65] were repeated using a smaller α_1 value. We plan to examine this possibility in a future publication.

Evaluation of the Thermodynamic Solubility Product for $Mg(NO_3)_2 \cdot 6H_2O$(s)

The isopiestic data used to evaluate the parameters of Pitzer's model extend to 5.123 mol·kg^{-1}; this molality is close to and probably slightly exceeds the equilibrium solubility of $Mg(NO_3)_2 \cdot 6H_2O$(s) at 298.15 K. Thus, eqs 7 and 8, together with the evaluated parameters of Table 2, may be used to calculate the standard ("thermodynamic") solubility product provided a reliable value of the molality of the saturated solution m(sat) is available. The reaction describing the equilibrium between $Mg(NO_3)_2 \cdot 6H_2O$(s) and its saturated solution is

$$Mg(NO_3)_2 \cdot 6H_2O(s) = Mg^{2+}(aq) + 2NO_3^{-}(aq) + 6H_2O(l) \tag{23}$$

The standard (thermodynamic) solubility product is thus given by

$$\begin{aligned} K_s &= m(Mg^{2+}, \text{sat})\, m(NO_3^{-}, \text{sat})^2\, \gamma(Mg^{2+}, \text{sat}) \times \\ &\qquad \gamma(NO_3^{-}, \text{sat})^2\, a_w(\text{sat})^6 \\ &= 4m(\text{sat})^3\, \gamma_{\pm}(\text{sat})^3\, a_w(\text{sat})^6 \end{aligned} \tag{24}$$

Linke[66] recommended a value of 0.421 for the mass fraction of $Mg(NO_3)_2$ in a saturated solution in equilibrium with $Mg(NO_3)_2 \cdot 6H_2O$(s) at 298.15 K based on "closely agreeing results" from two concordant studies, which corresponds to $m(\text{sat}) = 4.902_5$ mol·kg^{-1}. However, a careful examination of Linke's recommended results at various temperatures indicates that only the solubilities at higher and lower temperatures are compromise values from the two studies, whereas from (274.15 to 358.15) K the recommended results were taken solely from a single study. At 298.15 K, the other closely agreeing study[37] reported a mass fraction of 0.425, which yields $m(\text{sat}) = 4.983_5$ mol·kg^{-1}. Linke also cited other solubility determinations that yield $m(\text{sat}) = (5.064$ and $5.684)$ mol·kg^{-1}. The last value is presumably an outlier, but the other three values show considerable variation between studies. Filippov et al.[62] reported $m(\text{sat}) = 5.020$ mol·kg^{-1}.

Table 3. Smoothed Values of ϕ, a_w, $\gamma_{\pm}$, L_{ϕ}, and $C_{p,\phi}$ for $Mg(NO_3)_2$(aq) at 298.15 K and at Selected Molalities Using the Second Set of Parameters of Table 2 for the Three-Parameter Standard Pitzer Model

m				L_{ϕ}	$C_{p,\phi}$
(mol·kg^{-1})	ϕ	a_w[a]	$\gamma_{\pm}$	(J·mol^{-1})	(J·K^{-1}·mol^{-1})
		$T = 298.15$ K			
0.01	0.9046	$0.999\,511_2$	0.7235	793	−144.4
0.02	0.8829	0.999 046	0.6577	1031	−139.3
0.05	0.8594	0.997 680	0.5704	$1410._5$	−129.8
0.1	0.8538	0.995 396	0.5131	1640	−119.6
0.2	0.8682	0.990 659	0.4720		−106.4
0.3	0.8904	0.985 667	0.4593		
0.4	0.9148	0.980 418	0.4576		
0.5	0.9402	0.974 913	0.4618		
0.6	0.9664	0.969 15	0.4700		
0.7	0.9931	0.963 13	0.4812		
0.8	1.0204	0.956 84	0.4949		
0.9	1.0483	0.950 29	0.5109		
1.0	1.0766	0.943 47	0.5291		
1.2	1.1346	0.929 06	0.5715		
1.4	1.1944	0.913 59	0.6222		
1.6	1.2555	0.897 12	0.6815		
1.8	1.3179	0.879 67	0.7502		
2.0	1.3813	0.861 30	0.8292		
2.5	1.5430	0.811 82	1.080		
3.0	1.7079	0.758 12	1.427		
3.5	1.8742	0.701 51	1.902		
4.0	2.0407	0.643 29	2.553		
4.5	2.2068	0.584 67	3.440		
4.99[b]	2.3684	0.527 96	4.619		
5.0	2.3717	0.526 82	4.647		
5.123	2.4120	0.512 82	5.004		

[a] The values of a_w are reported to the minimum number of figures required to reproduce the tabulated values of ϕ to ≤ 0.0001. [b] Selected molality for the saturated solution. The two higher molalities are for supersaturated solutions.

As discussed above, we assessed the water activity of a saturated solution in equilibrium with $Mg(NO_3)_2 \cdot 6H_2O$(s) as falling in the range of $a_w(\text{sat}) = 0.524$ to 0.534 at 298.15 K based on measurements of the vapor pressures of saturated solutions of unknown molalities.[28,29,54] Equation 7 and the recommended Pitzer model parameters yield values of a_w(sat) in this range provided that we assume that $m(\text{sat}) = (4.93$ to $5.02)$ mol·kg^{-1}. The only solubility values cited in the previous paragraph that fall in this range are $m(\text{sat}) = 4.983_5$ mol·kg^{-1} from the determination by Ewing et al.[37] and $m(\text{sat}) = 5.020$ mol·kg^{-1} from Fillipov et al.[62] Although these values of m(sat) may be the best choice from the viewpoint of thermodynamic consistency among the various types of thermodynamic measurements, clearly the available information is not adequate to make an unambiguous selection.

For want of a definitive value, we provisionally accept the average $m(\text{sat}) = (4.9925 \pm 0.1341)$ mol·kg^{-1} of the four values cited two paragraphs above while excluding the outlying value, where this uncertainty is the 95% confidence limit. Because of this large uncertainty, we round this average value to $m(\text{sat}) = (4.99 \pm 0.13)$ mol·kg^{-1} for the calculation of K_s. The Pitzer model parameters of Table 2 then yield $a_w(\text{sat}) = 0.527\,96$ and $\gamma_{\pm}(\text{sat}) = 4.619$; therefore, $K_s = 1061$ at 298.15 K. The calculated value of a_w(sat) falls within the range assessed for saturated solutions, agreeing best with the experimental results of Stokes and Robinson,[54] $a_w(\text{sat}) = 0.5286$, and agreeing with results of Wexler and Hasegawa[29] to nearly within their reported uncertainty limits: $a_w(\text{sat}) = 0.534_4 \pm 0.006$. No uncertainty is assigned to our derived value of K_s because

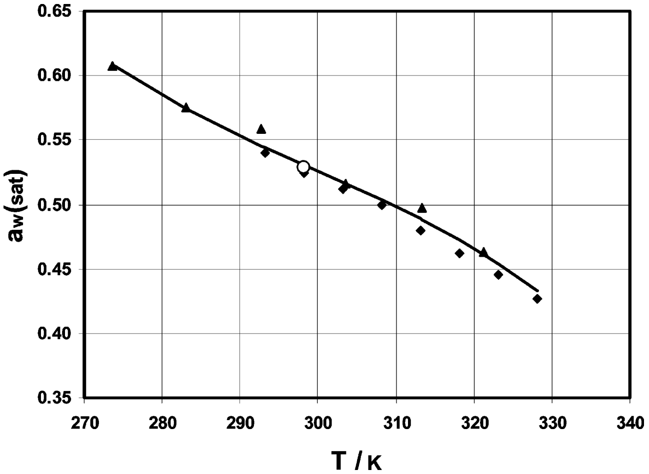

Figure 8. Variation of the values of a_w(sat) as a function of the temperature for saturated solutions in contact with a solid phase of composition $Mg(NO_3)_2 \cdot 6H_2O(s)$. —, Smoothed values calculated from eq 25. Experimental values: ◆, Ewing et al.;[28] ▲, Wexler and Hasegawa;[29] ○, Stokes and Robinson.[54]

of the large uncertainty for the selected value of m(sat), but it is probably in the range of 10 to 15%.

Representation of the Water Activities of Saturated Solutions with Temperature-Dependent Functions

We represented the more reliable of the critically assessed water activities of saturated solutions,[28,29,54] a_w(sat), with the following reference-temperature-centered expression

$$a_w(\text{sat}) = a_1 + a_2(T - T_r) + a_3(T^2 - T_r^{\,2}) + a_4(T^3 - T_r^{\,3}) \tag{25}$$

where the reference temperature was chosen to be T_r = 298.15 K, 273.54 K ≤ T ≤ 328.20 K and with $Mg(NO_3)_2 \cdot 6H_2O(s)$ as the solid phase. Figure 8 is a plot of the variation of a_w(sat) with temperature. The resulting least-squares fitted parameters are $a_1 = 0.53090$, $a_2 = -0.19398$ K^{-1}, $a_3 = 6.3999 \times 10^{-4}$ K^{-2}, and $a_4 = -7.1368 \times 10^{-7}$ K^{-3} with $\sigma_{rms}(a_w(sat)) = 0.0066$. These parameters yield a_w(sat) = 0.5309 ± 0.0066 at 298.15 K, which agrees well with our assessment given above. The coefficients of eq 25 were obtained by fitting them to the relevant a_w(sat) data in an independent least-squares error minimization that was implemented within the same Microsoft Excel spreadsheet described above.

Suggestions for Future Research

The survey and critical analysis of the published thermodynamic data for $Mg(NO_3)_2$(aq) given in the present paper indicate that its thermodynamic characterization at temperatures other than 298.15 K is quite inadequate. Measurements of the isopiestic molalities, enthalpies of dilution, and heat capacities at higher and lower temperatures are necessary to improve this characterization. Although three isopiestic chambers are available at Lawrence Livermore National Laboratory,[67] these chambers and their associated thermostatically controlled water bath were designed for use around 298.15 K and are not suitable for measurements at significantly higher or lower temperatures. Even at 298.15 K, more extensive and precise enthalpy of dilution, heat capacity, and solubility measurements from low molalities to saturation are needed to supplement the present incomplete data. We hope that some readers of this paper will perform these needed measurements.

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