Isopiestic Investigation of the Osmotic and Activity Coefficients of $\{y\text{MgCl}_2 + (1 − y)\text{MgSO}_4\}$(aq) and the Osmotic Coefficients of $\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4$(aq) at 298.15 K

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Abstract Isopiestic vapor-pressure measurements were made for $\{y\text{MgCl}_2 + (1 − y)\text{MgSO}_4\}$(aq) solutions with MgCl$_2$ ionic strength fractions of $y = (0, 0.1997, 0.3989, 0.5992, 0.8008,$ and $1)$ at the temperature 298.15 K, using KCl(aq) as the reference standard. These measurements for the mixtures cover the ionic strength range $I = 0.9794$ to 9.4318 mol·kg^{-1}. In addition, isopiestic measurements were made with NaCl(aq) as reference standard for mixtures of $\{x\text{Na}_2\text{SO}_4 + (1 − x)\text{MgSO}_4\}$(aq) with the molality fraction $x = 0.5000$ that correspond to solutions of the evaporite mineral bloedite (astrakanite), Na$_2$Mg(SO$_4$)$_2$·4H$_2$O(cr). The total molalities, $m_\text{T} = m(\text{Na}_2\text{SO}_4) + m(\text{MgSO}_4)$, range from $m_\text{T} = 1.4479$ to 4.4312 mol·kg^{-1} ($I = 5.0677$ to 15.509 mol·kg^{-1}), where the uppermost concentration is the highest oversaturation molality that could be achieved by isothermal evaporation of the solvent at 298.15 K. The parameters of an extended ion-interaction (Pitzer) model for MgCl$_2$(aq) at 298.15 K, which were required for an analysis of the $\{y\text{MgCl}_2 + (1 − y)\text{MgSO}_4\}$(aq) mixture results, were evaluated up to $I = 12.075$ mol·kg^{-1} from published isopiestic data together with the six new osmotic coefficients obtained in this study. Osmotic coefficients of $\{y\text{MgCl}_2 + (1 − y)\text{MgSO}_4\}$(aq) solutions from the present study, along with critically-assessed values from previous studies, were used to evaluate the mixing parameters of the extended ion-interaction model.

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1 Introduction

Seawater is an aqueous multicomponent electrolyte mixture with the predominant ions being, in their decreasing order of molality: Cl^-, Na^+, Mg^{2+}, SO_4^{2-}, Ca^{2+}, and K^+. These ions are also the predominant ones found in most brines that are derived from seawater and in many other natural waters, and salts derived from various combinations of these ions are commonly found in evaporite deposits.

The six predominate seawater ions can be combined to yield the seven soluble salts NaCl, Na_2SO_4, KCl, K_2SO_4, $MgCl_2$, $MgSO_4$, and $CaCl_2$, and the sparingly soluble $CaSO_4$. These seven soluble salts can be mixed to yield (excluding mixtures with $CaSO_4$) 18 soluble binary salt mixtures, 23 soluble ternary salt mixtures, etc. Even at a single temperature, a considerable amount of experimental data is required to adequately characterize the thermodynamic properties of all of these systems because mixtures with several different mole ratios of the salts need to be studied.

Because of this large number of possible aqueous mixtures, there has been considerable interest in the thermodynamic modeling of these solutions with an emphasis on developing methods for predicting the properties of multicomponent mixtures from those of the simpler (usually binary) mixtures. The ion-interaction model developed by Pitzer [1] has proven to be especially valuable for thermodynamic modeling of natural brines [2–5]. For extremely concentrated electrolyte solutions, especially those encountered in atmospheric aerosols where the concentrations are not limited by heterogeneous nucleation, analogous equations based on the mole-fraction composition scale [6, 7] are capable of representing the entire composition range. However, these mole-fraction composition-based equations have not been widely used in geochemical modeling, at least in part because of their more complicated functional forms.

The assumptions of Pitzer's ion-interaction model [1] lose their validity at high ionic strengths where the solvent-to-ion mole ratio falls below that required by the hydration needs of the individual ions, ionic atmospheres overlap, and solvent-sharing ion pairs must therefore be present. The standard form of Pitzer's equation for the osmotic coefficient of an individual electrolyte contains a third-virial coefficient $C_{M,X}^\phi$ that formally represents simultaneous short-range interactions between three ions, and which was assumed to be independent of the ionic strength. The standard form of Pitzer's model gives a good representation of thermodynamic properties of many electrolytes for ionic strengths of $I \leq 6$ mol·kg^{-1} [1], but has also been shown to be adequate for modeling the solubilities of many brines at much higher ionic strengths [1–5].

To improve the accuracy of Pitzer's ion-interaction model for representing thermodynamic properties of more soluble electrolytes, Archer [8] replaced the constant $C_{M,X}^\phi$ parameter with an ionic strength-dependent function with two parameters having the form $C_{M,X}^{(0)} + C_{M,X}^{(1)} \exp(-\omega_{M,X} I^{1/2})$. Clegg et al. [9] have extended Archer's extended ion-interaction model to include mixed electrolyte solutions of arbitrary complexity, including those like H_2SO_4(aq) that undergo self-association.

A more generalized form of the ion-interaction model described by Pitzer et al. [10] is capable of representing thermodynamic data of extremely soluble single electrolytes. However, so far it has been applied to very few systems, e.g., $CaCl_2$(aq) and $MgCl_2$(aq) at 298.15 K [10] and $MgCl_2$(aq) over a wide temperature range [11].

In order to evaluate reliable values of the parameters of these thermodynamic models, accurate experimental thermodynamic data are required. For the excess Gibbs energy, the most widely available experimental results are activity coefficients obtained from Emf measurements and osmotic coefficients from isopiestic measurements, with isopiestic results being

available for the largest number of systems [12]. Such experimental results are not always available at temperatures far removed from 298.15 K, and thus solubility measurements have also been used to evaluate the parameters of ion-interaction models [3–5]. However, the most accurate parameter values will be obtained when the experimental thermodynamic data used for their evaluations span the full composition range.

For the seawater-based subsystems at 298.15 K, particularly extensive isopiestic measurements are available for $NaCl + MgCl_2 + H_2O$ [13, 14], $NaCl + Na_2SO_4 + H_2O$ [15], and $KCl + MgCl_2 + H_2O$ [16–18]. Isopiestic data are also available for other seawater-based mixtures at 298.15 K, e.g., the results reported in [19–26].

The seawater-based subsystem $MgCl_2 + MgSO_4 + H_2O$ has not been as thoroughly studied by the isopiestic method. Two studies are available at 298.15 K [21, 25] but are not in very good agreement, and at 323.15 K [27] mixing parameters were reported but the experimental data were not given. Enthalpies of mixing of $MgCl_2(aq)$ and $MgSO_4(aq)$ are also available at 298.15, 303.15, and 373.15 K [28–30]. Similarly, available isopiestic data for $Na_2SO_4 + MgSO_4 + H_2O$ at 298.15 K are fairly limited. Wu et al. [21] reported isopiestic results for 15 compositions at 298.15 K. Additional results of Reznik, cited in [31], are not readily available. Rard and Miller [32] reported numerous isopiestic results at 298.15 K for the equal molar mixtures ranging from $m_T = 0.62562$ to 4.046 $mol \cdot kg^{-1}$ that extend very close to saturation [22]. Enthalpies of mixing of $Na_2SO_4(aq)$ and $MgSO_4(aq)$ are also available at 298.15, 303.15, and 373.15 K [28–30].

To supplement the limited amount of published thermodynamic data for the $MgCl_2 + MgSO_4 + H_2O$ and $Na_2SO_4 + MgSO_4 + H_2O$ systems, isopiestic data were measured for both systems at 298.15 K. These results are reported here, and the available isopiestic data for $MgCl_2 + H_2O$ and $MgCl_2 + MgSO_4 + H_2O$ were analyzed with an extended ion-interaction model. The new measurements for $Na_2SO_4 + MgSO_4 + H_2O$ extend the earlier results [32] to beyond saturation and to the highest concentration that could be achieved during isothermal evaporation of the solvent.

2 Experimental Section

2.1 Experiments at the University of Belgrade

The isopiestic apparatus and experimental procedure used in the part of this work done at the University of Belgrade are essentially the same as described previously [33]. Duplicate samples of each of the $\{yMgCl_2 + (1 - y)MgSO_4\}(aq)$ mixed electrolyte solutions, the $KCl(aq)$ reference solution, and the single salt solutions $MgCl_2(aq)$ and $MgSO_4(aq)$ were equilibrated at 298.15 ± 0.01 K in gold-plated silver cups for appropriate times that ranged from 3 to 18 days, with the longer times being required at lower molalities. The ionic strengths of duplicate pairs of solutions at isopiestic equilibrium agreed to $\pm 2 \times 10^{-3}$ $mol \cdot kg^{-1}$ or better, with the average molality being accepted. Buoyancy corrections were made for all weighings. The $KCl(aq)$ and $MgCl_2(aq)$ stock solutions are the same as those used by Miladinović et al. [18] and are also described below.

The reference $KCl(aq)$ stock solution was prepared from Sigma-Aldrich Suprapure grade KCl (reported mass fraction 0.99999) and double-distilled, deionized water. The $KCl(aq)$ molality was determined gravimetrically by dehydration of six solution mass aliquots, followed by heating of the residues between 523 and 573 K, and also by mass titration with standardized $AgNO_3(aq)$. The resulting average molality of this stock solution is 4.7990 ± 0.0006 $mol \cdot kg^{-1}$, assuming the molar mass of KCl to be 74.5513 $g \cdot mol^{-1}$.

The $MgCl_2 + MgSO_4 + H_2O$ solutions were prepared by mixing known masses of the $MgCl_2$(aq) and $MgSO_4$(aq) stock solutions. This $MgCl_2$(aq) solution was prepared from Sigma-Aldrich Suprapure grade $MgCl_2 \cdot 6H_2O$ (reported mass fraction 0.99995) and double-distilled, deionized water. Its molality was determined by mass titration with standardized $AgNO_3$(aq) and by conversion of mass aliquots to anhydrous $MgSO_4$(s) by slow evaporation of the solutions with excess H_2SO_4 followed by further drying of the residue at 723 K in a furnace. The resulting average molality of this stock solution is 5.6440 ± 0.0008 mol·kg^{-1}, assuming the molar mass of $MgCl_2$ to be 95.2114 g·mol^{-1}.

The $MgSO_4$(aq) stock solution was prepared from Sigma-Aldrich Suprapure grade $MgSO_4 \cdot 7H_2O$ (reported mass fraction 0.9999) and double-distilled, deionized water. The molality of this stock solution was determined in triplicate by two methods: gravimetrically as $BaSO_4$(s) by precipitation of mass aliquots with $BaCl_2$(aq) and by dehydration analysis of acidified mass aliquots at 773 K and then at 848 K. The resulting average molality value is 2.9750 ± 0.0011 mol·kg^{-1} assuming the molar mass of $MgSO_4$ to be 120.3676 g·mol^{-1}.

2.2 Experiments at Lawrence Livermore National Laboratory

The isopiestic experiments performed at Lawrence Livermore National Laboratory (LLNL), at the temperature $298.15 \pm 0.00_5$ K (IPTS-68), were done using the apparatus described by Rard [34] but modified to include passive stirring of the vapor phase [35]. The sample cups containing solutions were made of tantalum metal that had been heat treated in air to produce a protective surface layer of Ta_2O_5. Some additional details of this isopiestic apparatus are described by Rard and Platford [12], who also give a very detailed general description of the isopiestic method with an emphasis on experimental aspects.

The NaCl(aq) isopiestic reference standard stock solution was prepared by combining appropriate masses of previously fused NaCl(s) and purified H_2O. This water was purified by deionization followed by distillation in a Barnstead still. The stock solution's molality calculated from the masses of NaCl and H_2O is 1.9995_9 mol·kg^{-1}. This stock solution's concentration was checked by evaporating three mass aliquots to dryness followed by further drying of the residues at 773 K; this analysis yielded a molality of $1.9999_3 \pm 0.0003_9$ mol·kg^{-1}, which is in excellent agreement with the value from direct weighing. The average of these two values, $m(\text{NaCl}) = 1.9997_6$, was accepted for molality calculations.

The aqueous $Na_2SO_4 + MgSO_4$ stock solution was prepared by combining appropriate masses of standardized Na_2SO_4(aq) and $MgSO_4$(aq) stock solutions. The two stock solutions were prepared by dissolving recrystallized Mallinckrodt analytical reagent $MgSO_4$ or recrystallized Baker Analyzed Na_2SO_4 in purified water, followed by filtration to remove any insoluble material. The purity of this recrystallized $MgSO_4$, as determined by direct current arc optical emission spectroscopy, is 0.99995, on a mass fraction basis [32]. The molality of each stock solution was determined by measuring the mass of anhydrous residue, after thermal dehydration at 773 K, of three mass aliquots slightly acidified with H_2SO_4. These analyses yielded $m(\text{Na}_2\text{SO}_4) = 1.4275_4 \pm 0.0001_4$ mol·kg^{-1} and $m(\text{MgSO}_4) = 2.8577_2 \pm 0.0004_0$ mol·kg^{-1}, where the uncertainties are "$n-1$" standard deviations. The assumed molar masses for the molality calculations are 58.443 g·mol^{-1} for NaCl, 142.037 g·mol^{-1} for Na_2SO_4, 120.363 g·mol^{-1} for $MgSO_4$, and 18.0153 g·mol^{-1} for H_2O. The mixed electrolyte stock solution used for isopiestic measurements contained 0.95149_5 mol·kg^{-1} Na_2SO_4 and 0.95149_8 mol·kg^{-1} $MgSO_4$ and thus $x = 0.50000$.

All apparent masses were converted to masses using buoyancy corrections. The isopiestic equilibration times ranged from 16 to 46 days and the molalities of duplicate pairs of solutions at isopiestic equilibrium agreed to $\pm 0.082\%$ or better, with the average molality being accepted.

2.3 Results and Calculation of Osmotic Coefficients

Osmotic coefficients of the $\{y\text{MgCl}_2 + (1 - y)\text{MgSO}_4\}(\text{aq})$ and $\{\text{Na}_2\text{SO}_4 + \text{MgSO}_4\}(\text{aq})$ solutions at 298.15 K were calculated from the experimental isopiestic molalities using the fundamental equation for isopiestic equilibrium:

$$\phi = \nu_R m_R \phi_R \Big/ \sum_i \nu_i m_i = 2 m_R \phi_R \Big/ \sum_i \nu_i m_i \tag{1}$$

where ν_i is the stoichiometric ionization number of the electrolyte i $\{\nu_1 = 3$ for MgCl$_2$ and Na$_2$SO$_4$, and $\nu_2 = 2$ for MgSO$_4\}$, m_i is the molality of electrolyte i, and ϕ is the osmotic coefficient of the mixed electrolyte solution based on the use of stoichiometric molalities and ionization numbers. Corresponding quantities for the isopiestic reference standards KCl(aq) or NaCl(aq) are denoted with a subscript R. The osmotic coefficient of each NaCl(aq) and KCl(aq) reference solution at 298.15 K was calculated using the ion-interaction (Pitzer) models and parameters reported by Archer [8, 36].

The experimental results for $\{y\text{MgCl}_2 + (1 - y)\text{MgSO}_4\}(\text{aq})$ solutions are given in Table 1. Quantities reported are the isopiestic molalities of the reference solution KCl(aq), m_R; the total ionic strength, I, of the mixtures; the "stoichiometric" osmotic coefficients (i.e., those calculated assuming complete dissociation of the electrolyte), ϕ, of $\{y\text{MgCl}_2 + (1 - y)\text{MgSO}_4\}(\text{aq})$ at 298.15 K; and the ionic strength fraction y of MgCl$_2$. Figure 1 is a plot of our experimental ϕ values at constant values of y as a function of I. The ϕ curves at the four mixture ratios are intermediate between those of the limiting single electrolytes. Table 2 gives the isopiestic results for $\{\text{Na}_2\text{SO}_4 + \text{MgSO}_4\}(\text{aq})$ solutions where the concentrations of the mixtures are reported as the total molality m_T.

3 Relations Between Different Molality-Based Composition Scales

The isopiestic results for $\{y\text{MgCl}_2 + (1 - y)\text{MgSO}_4\}(\text{aq})$ solutions, given in Table 1, are reported in units of the molality-based ionic strengths, I, whereas those for $\{\text{Na}_2\text{SO}_4 + \text{MgSO}_4\}(\text{aq})$ solutions, given in Table 2, are in units of the total molality m_T. The calculations of osmotic coefficients from the isopiestic molalities via Eq. 1 involve the total ionic molality of the solution $\sum_i \nu_i m_i$ and Pitzer's model equations for mixtures [1] include the equivalent ionic molality denoted by Pitzer as Z. We now give equations relating these different composition scales.

For $\{y\text{MgCl}_2 + (1 - y)\text{MgSO}_4\}(\text{aq})$ and $\{y\text{Na}_2\text{SO}_4 + (1 - y)\text{MgSO}_4\}(\text{aq})$ solutions let m_1 denote the molality of MgCl$_2$ or Na$_2$SO$_4$ and m_2 the molality of MgSO$_4$. Then

$$m_T = m_1 + m_2, \tag{2}$$

$$I = (1/2) \sum_i m_i \{(z_i)\}^2 = 3m_1 + 4m_2 = (4 - x)m_T, \tag{3}$$

$$y = \frac{3m_1}{3m_1 + 4m_2} = \frac{3m_1}{I} = \frac{3x}{4 - x}, \tag{4}$$

$$\sum_i \nu_i m_i = 3m_1 + 2m_2 = (2 + x)m_T = \left(\frac{1 + y}{2}\right)I \tag{5}$$

Table 1 Isopiestic molalities m_R of the reference standard solution KCl(aq),[a] isopiestic ionic strengths I and osmotic coefficients ϕ of {$yMgCl_2 + (1-y)MgSO_4$}(aq) at 298.15 K, and the ionic strength fraction y of $MgCl_2$ from experiments at the University of Belgrade

$\dfrac{m_R}{\text{mol·kg}^{-1}}$	$\dfrac{I}{\text{mol·kg}^{-1}}$	ϕ	$\dfrac{I}{\text{mol·kg}^{-1}}$	ϕ	$\dfrac{I}{\text{mol·kg}^{-1}}$	ϕ	$\dfrac{I}{\text{mol·kg}^{-1}}$	ϕ	$\dfrac{I}{\text{mol·kg}^{-1}}$	ϕ	$\dfrac{I}{\text{mol·kg}^{-1}}$	ϕ
	$y = 0.0$		$y = 0.1997$		$y = 0.3989$		$y = 0.5992$		$y = 0.8008$		$y = 1.0$	
3.21095	12.5600	0.9669	9.4318	1.0732	7.4043	1.1724	6.1371	1.2374	5.2546	1.2834	4.5936	1.3218
1.95990	9.5492	0.7508	6.7394	0.8868	5.2355	0.9790	4.2953	1.0438	3.6431	1.0929	3.1680	1.1316
1.40865	7.7876	0.6542	5.3289	0.7969	4.0930	0.8898	3.3358	0.9550	2.8036	1.0091	2.4384	1.0447
0.93120	5.8360	0.5736	3.8663	0.7217	2.9350	0.8153	2.3762	0.8809	2.0017	0.9286	1.7301	0.9674
0.63777	4.2872	0.5347	2.8060	0.6809	2.1212	0.7725	1.7144	0.8361	1.4425	0.8824	1.2462	0.9197
0.41800	2.8888	0.5219	1.8992	0.6618	1.4401	0.7484	1.1639	0.8100	0.9794	0.8550	0.8466	0.8905

[a]Osmotic coefficients of the KCl(aq) reference standard were calculated with the equations and parameters reported by Archer [36]

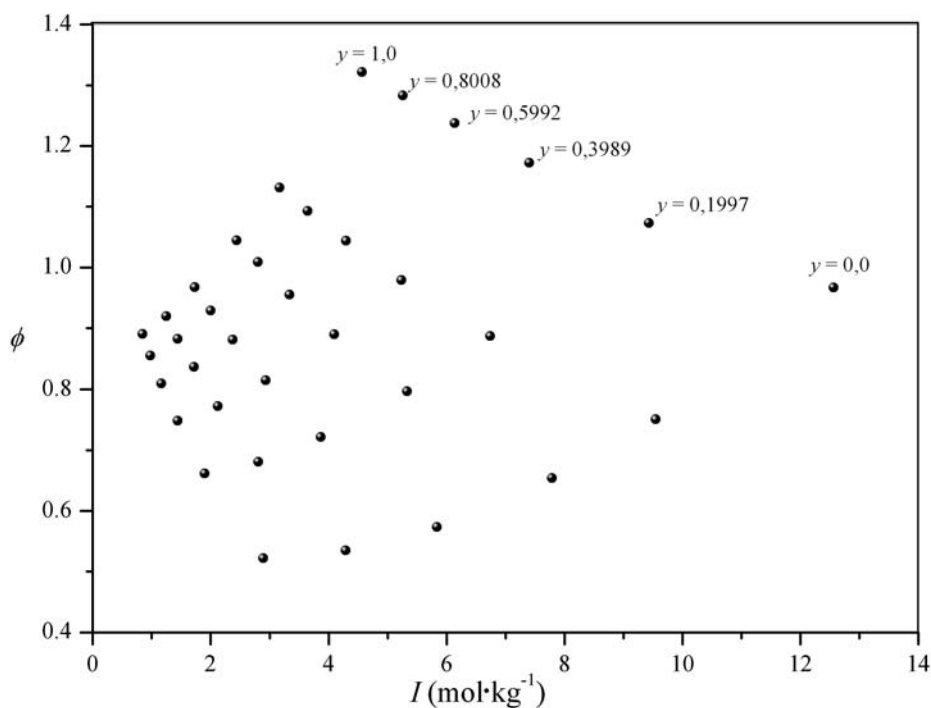**Fig. 1** Experimental osmotic coefficients ϕ of the $\{y\mathrm{MgCl_2} + (1-y)\mathrm{MgSO_4}\}(\mathrm{aq})$ system at 298.15 K from Table 1 plotted against the total ionic strength I at fixed values of the $\mathrm{MgCl_2}$ ionic strength fraction y

Table 2 Isopiestic molalities m_R of the NaCl(aq) reference standard solution, total molalities m_T and osmotic coefficients ϕ of equal molar $\{\mathrm{Na_2SO_4} + \mathrm{MgSO_4}\}(\mathrm{aq})$ mixtures at $T = 298.15$ K from experiments at the Lawrence Livermore National Laboratory

$m_R/\mathrm{mol\cdot kg^{-1}}$	$m_T/\mathrm{mol\cdot kg^{-1}}$	ϕ	$m_R/\mathrm{mol\cdot kg^{-1}}$	$m_T/\mathrm{mol\cdot kg^{-1}}$	ϕ
2.8978 ± 0.0005	3.1099 ± 0.0010	0.7767	2.9216 ± 0.0005	3.1290 ± 0.0012	0.7795
2.9749 ± 0.0004	3.1721 ± 0.0019	0.7855	2.5866 ± 0.0003	2.8562 ± 0.0010	0.7404
3.0500 ± 0.0004	3.2303 ± 0.0023	0.7946	2.2806 ± 0.0009	2.5892 ± 0.0007	0.7069
3.1876 ± 0.0002	3.3326 ± 0.0015	0.8120	1.9607 ± 0.0016	2.2903 ± 0.0005	0.6743
3.4413 ± 0.0006	3.5195 ± 0.0017	0.8435	1.7295 ± 0.0005	2.0585 ± 0.0010	0.6532
3.7037 ± 0.0002	3.7072 ± 0.0024	0.8765	1.5622 ± 0.0006	1.8793 ± 0.0008	0.6405
3.9680 ± 0.0001	3.8910 ± 0.0016	0.9100	1.4091 ± 0.0004	1.7092 ± 0.0004	0.6301
4.2597 ± 0.0012	4.0862 ± 0.0026	0.9478	1.1841 ± 0.0003	1.4479 ± 0.0006	0.6182
4.5580 ± 0.0009	4.2821 ± 0.0012	0.9865	2.0279 ± 0.0006	2.3542 ± 0.0013	0.6811
4.7920 ± 0.0015	4.4312^{a}	1.0739			

[a]Single sample because of crystallization in the other sample cup. Osmotic coefficients of the NaCl(aq) reference standard were calculated with the equations and parameters reported by Archer [8]. Rard and Miller [32] reported their isopiestic molalities as $m(\mathrm{Na_2SO_4}$–$\mathrm{MgSO_4})$, whereas ours are reported as the total molality $m_T = m_1 + m_2 = 2m(\mathrm{Na_2SO_4}$–$\mathrm{MgSO_4})$

and

$$Z = \sum_i m_i |z_i| = 4(m_1 + m_2) = 4m_{\text{T}} = \left(\frac{3+y}{3}\right) I, \tag{6}$$

where z_i is the valence (with sign) of ion i and $x = m_1/m_{\text{T}}$ is the molality fraction of MgCl$_2$ or Na$_2$SO$_4$.

4 Extended Ion-Interaction Model Equations for Solutions of Single Electrolytes and Parameter Evaluation for MgCl$_2$(aq) at 298.15 K

Archer's [8] extended form of Pitzer's ion-interaction model [1] was chosen to represent the osmotic and activity coefficients of MgCl$_2$(aq) at 298.15 K, because it is generally able to represent these properties more accurately than the original three-parameter model for higher valence and more soluble electrolytes. Including the $\beta_{\text{M,X}}^{(2)} \exp(-\alpha_2 I^{1/2})$ term that is needed for 2:2 electrolytes such as MgSO$_4$(aq), the equation can be written in the general form [37] for the osmotic coefficient

$$\begin{aligned}
\phi = 1 &- |z_{\text{M}} z_{\text{X}}| A_\phi \left(\frac{I^{1/2}}{1 + bI^{1/2}}\right) + \left(\frac{2\nu_{\text{M}} \nu_{\text{X}}}{\nu}\right) m\{\beta_{\text{M,X}}^{(0)} \\
&+ \beta_{\text{M,X}}^{(1)} \exp(-\alpha_{1,\text{M,X}} I^{1/2}) + \beta_{\text{M,X}}^{(2)} \exp(-\alpha_{2,\text{M,X}} I^{1/2})\} \\
&+ \left(\frac{4\nu_{\text{M}}^2 \nu_{\text{X}} z_{\text{M}}}{\nu}\right) m^2 \{C_{\text{M,X}}^{(0)} + C_{\text{M,X}}^{(1)} \exp(-\omega_{1,\text{M,X}} I^{1/2})\},
\end{aligned} \tag{7}$$

where A_ϕ is the Debye-Hückel limiting-law slope for water; M denotes the cation and X the anion; z_{M} and z_{X} are the valences (with sign) of the anion and cation; ν_{M} and ν_{X} are the stoichiometric ionization numbers of the anion and cation; $\nu = \nu_{\text{M}} + \nu_{\text{X}}$; $b = 1.2 \text{ mol}^{-1/2} \cdot \text{kg}^{1/2}$ for all aqueous electrolytes; and the $\beta_{\text{M,X}}^{(i)}$ and $C_{\text{M,X}}^{(i)}$ are model parameters whose values are determined empirically using experimental data. The corresponding equation for the mean (molality-based) activity coefficient is

$$\begin{aligned}
\ln \gamma_\pm = &-|z_{\text{M}} z_{\text{X}}| A_\phi \left\{ \left(\frac{I^{1/2}}{1 + bI^{1/2}}\right) + \left(\frac{2}{b}\right) \ln(1 + bI^{1/2}) \right\} + \left(\frac{2\nu_{\text{M}} \nu_{\text{X}}}{\nu}\right) m \Bigg[2\beta_{\text{M,X}}^{(0)} \\
&+ \left(\frac{2\beta_{\text{M,X}}^{(1)}}{\alpha_{1,\text{M,X}}^2 I}\right) \left\{ 1 - \left(1 + \alpha_{1,\text{M,X}} I^{1/2} - \frac{\alpha_{1,\text{M,X}}^2 I}{2}\right) \exp(-\alpha_{1,\text{M,X}} I^{1/2}) \right\} \\
&+ \left(\frac{2\beta_{\text{M,X}}^{(2)}}{\alpha_{2,\text{M,X}}^2 I}\right) \left\{ 1 - \left(1 + \alpha_{2,\text{M,X}} I^{1/2} - \frac{\alpha_{2,\text{M,X}}^2 I}{2}\right) \exp(-\alpha_{2,\text{M.X}} I^{1/2}) \right\} \Bigg] \\
&+ \left(\frac{2\nu_{\text{M}}^2 \nu_{\text{X}} z_{\text{M}}}{\nu}\right) m^2 \Bigg[3C_{\text{M,X}}^{(0)} + \left(\frac{4C_{\text{M,X}}^{(1)}}{\omega_{\text{M,X}}^4 I^2}\right) \left\{ 6 - \left\{ 6 + 6\omega_{\text{M,X}} I^{1/2} \right. \right. \\
&\left. \left. + 3\omega_{\text{M,X}}^2 I + \omega_{\text{M,X}}^3 I^{3/2} - \left(\frac{\omega_{\text{M,X}}^4 I^2}{2}\right) \right\} \exp(-\omega_{\text{M,X}} I^{1/2}) \right\} \Bigg].
\end{aligned} \tag{8}$$

Archer and Rard [37] reported the parameters of Eqs. 7 and 8 for a MgSO$_4$(aq) model that is valid over wide ranges of molality and temperature. The parameters at 298.15 K given in their errata are listed in our Table 3, and were used to calculate values of ϕ at

Table 3 Parameter values of the extended ion-interaction (Pitzer) models for $MgCl_2(aq)$, $MgSO_4(aq)$, and $\{yMgCl_2 + (1-y)MgSO_4\}(aq)$ at 298.15 K[a]

Parameter	Value	Parameter	Value	Parameter	Value
$\beta^{(0)}_{Mg,Cl}$	0.68723	$\beta^{(0)}_{Mg,SO_4}$	−0.03089	θ_{Cl,SO_4}	−0.14077[b]
$\beta^{(1)}_{Mg,Cl}$	1.56760	$\beta^{(1)}_{Mg,SO_4}$	3.7687	ψ_{Mg,Cl,SO_4}	−0.014774[b]
		$\beta^{(2)}_{Mg,SO_4}$	−37.3659	I	9.4318
$C^{(0)}_{Mg,Cl}$	−0.007594	$C^{(0)}_{Mg,SO_4}$	0.016406	$\sigma(\phi)$	0.0039[b]
$C^{(1)}_{Mg,Cl}$	−0.35497	$C^{(1)}_{Mg,SO_4}$	0.34549		
$\alpha_{1,Mg,Cl}$	3.0	α_{1,Mg,SO_4}	1.4		
		α_{2,Mg,SO_4}	12.0	$^S\theta_{Cl,SO_4}$	−0.07122[c]
$\omega_{Mg,Cl}$	1.0	ω_{Mg,SO_4}	1.0	ψ_{Mg,Cl,SO_4}	−0.038505[c]
m	4.0251	m	3.6176	I	9.4318
$\sigma(\phi)$	0.00234	$\sigma(\phi)$		$\sigma(\phi)$	0.0049[c]

[a]Units of $\beta^{(0)}_{M,X}$, $\beta^{(1)}_{M,X}$, $\beta^{(2)}_{M,X}$, $\theta_{X,X'}$, and $^S\theta_{X,X'}$ are $kg \cdot mol^{-1}$; of $C^{(0)}_{M,X}$, $C^{(1)}_{M,X}$ and $\psi_{M,X,X'}$ are $kg^2 \cdot mol^{-2}$; and of $\alpha_{1,M,X}$, $\alpha_{2,M,X}$, and $\omega_{M,X}$ are $kg^{1/2} \cdot mol^{-1/2}$. The quantities m and I are the maximum molality and total ionic strength, respectively, of the experimental osmotic coefficients used for evaluation of these parameters and $\sigma(\phi)$ is the standard deviation of the model fit. The assumed value of the Debye-Hückel limiting-law slope for aqueous solutions at 298.15 K is $A_\phi = 0.391475 \ mol^{-1/2} \cdot kg^{1/2}$ [9, 44]. Values of the parameters for $MgCl_2(aq)$ were evaluated using the critically-assessed database and weights described in Table 5 whereas those for $MgSO_4(aq)$ are the revised values reported by Archer and Rard [37]

[b]These parameters were evaluated without including the higher-order electrostatic effects

[c]These parameters were evaluated while including the higher-order electrostatic effects

the six experimental concentrations reported in Table 1. Table 4 compares these calculated values of ϕ for $MgSO_4(aq)$ with the experimental ones; both positive and negative deviations are observed with a mean absolute deviation of $MAD(\phi) = 0.0013$. Because of this very good agreement, we accept the Archer and Rard parameter values for our mixed electrolyte solution calculations.

The standard three-parameter form of Pitzer's model is not able to represent the osmotic coefficients of $MgCl_2(aq)$ at 298.15 K to their full experimental accuracy, although the generalized model of Pitzer et al. [10] with six parameters was able to represent these data over the full molality range with moderate systematic cyclic deviations of $\Delta\phi \approx 0.003$ in some regions. A similar model [11] representing thermodynamic data over a large temperature range had larger systematic deviations at 298.15 K, but this reduced accuracy is at least partly a consequence of the inclusion of data up to $m = 25 \ mol \cdot kg^{-1}$ at high temperatures where the solubility of aqueous $MgCl_2$ is considerably larger.

We reevaluated the parameters of the extended ion-interaction model for $MgCl_2(aq)$ at 298.15 K, Eqs. 7 and 8 with $\beta^{(2)}_{M,X} = 0$, using available isopiestic data [13, 16–19, 21, 24, 32, 38–41] and generally followed the recommendations of Rard and Miller [41], but supplemented with more recent isopiestic data and the freezing temperature depression results of Gibbard and Gossmann [42] converted to osmotic coefficients at 298.15 K (given in Table VII of [41]). The various isopiestic studies are based on use of four different isopiestic reference standards: $NaCl(aq)$, $KCl(aq)$, $CaCl_2(aq)$, and $H_2SO_4(aq)$. The osmotic coefficients from the available isopiestic studies at 298.15 K [13, 16–19, 21, 24, 32, 38–41] were recalculated for consistency using the up-to-date ion-interaction models for these reference

Table 4 Osmotic coefficients of $MgCl_2(aq)$ and $MgSO_4(aq)$ at $T = 298.15$ K from the University of Belgrade experiments compared with values calculated from the accepted extended Pitzer models

$I/\text{mol·kg}^{-1}$	$m/\text{mol·kg}^{-1}$	$\phi(\text{exp.})$[a]	$\phi(\text{calc.})$[b]	$\Delta\phi$[c]
$MgCl_2(aq)$				
4.5936	1.5312	1.3218	1.3229	−0.0011
3.1680	1.0560	1.1316	1.1326	−0.0010
2.4384	0.8128	1.0447	1.0459	−0.0012
1.7301	0.5767	0.9674	0.9699	−0.0025
1.2462	0.4154	0.9197	0.9236	−0.0039
0.8466	0.2822	0.8905	0.8902	+0.0003
$MgSO_4(aq)$				
12.5600	3.1400	0.9669	0.9701	−0.0032
9.5492	2.3873	0.7508	0.7497	+0.0011
7.7876	1.9469	0.6542	0.6528	+0.0014
5.8360	1.4590	0.5736	0.5739	−0.0003
4.2872	1.0718	0.5347	0.5346	+0.0001
2.8888	0.7222	0.5219	0.5201	+0.0018

[a] Values of $\phi(\text{exp.})$ were calculated from the experimental equilibrium molalities reported in Table 1

[b] Values of $\phi(\text{calc.})$ were obtained from our model and parameters for $MgCl_2(aq)$ and the revised model parameters of Archer and Rard for $MgSO_4(aq)$ [37], which are reported in Table 3

[c] $\Delta\phi = \phi(\text{exp.}) - \phi(\text{calc.})$. Mean absolute deviation $\text{MAD}(\Delta\phi) = 0.0017$ for $MgCl_2(aq)$ and $\text{MAD}(\Delta\phi) = 0.0013$ for $MgSO_4(aq)$

standards [8–10, 36], where the $CaCl_2(aq)$ models of Pitzer et al. [10] are based on refitting of results from the critical assessment of Rard and Clegg [43]. Pitzer et al. reported several different models for $CaCl_2(aq)$ with different numbers of parameters that are valid over different molality regions and we accepted their "np = 7 model". Rard and Miller [32, 41] generally used two or three isopiestic standards in their isopiestic measurements and the average value of the osmotic coefficient for $MgCl_2(aq)$ was accepted for each equilibration.

The value of the Debye-Hückel limiting-law slope for aqueous solutions at 298.15 K, $A_\phi = 0.391475 \ \text{mol}^{-1/2}·\text{kg}^{1/2}$, was taken from Archer and Wang's evaluation [44] as represented by the Chebychev polynomial of Clegg et al. [9]. When the parameters of Eqs. 7 and 8 (with $\beta_{\text{M,X}}^{(2)} = 0$) were evaluated using the complete osmotic coefficient database extending to $m = 5.9188 \ \text{mol·kg}^{-1}$, the resulting fit exhibited systematic cyclic deviations of $\Delta\phi \approx \pm 0.01$ from the experimental data. This model over the full molality range was considered to be not accurate enough for our analysis of the mixture results.

Because our mixture results reported in Table 1 do not extend to saturation, we repeated the fit while restricting the molality range of the osmotic coefficients being fitted to $m \leq 4.0251 \ \text{mol·kg}^{-1}$ ($I \leq 12.075 \ \text{mol·kg}^{-1}$). As shown in Fig. 2, which is a plot of differences between the experimental and calculated osmotic coefficients, this new model gives an excellent representation of the experimental osmotic coefficients with an essentially random distribution of the residuals. The parameters of this model fit for $MgCl_2(aq)$ were accepted and are reported in Table 3. Table 5 summarizes the experimental studies, their molality ranges, number of data points, and weights used for the model parameter evaluations. Experimental osmotic coefficients with deviations $> 2.5\sigma(\phi)$ were weighted zero in
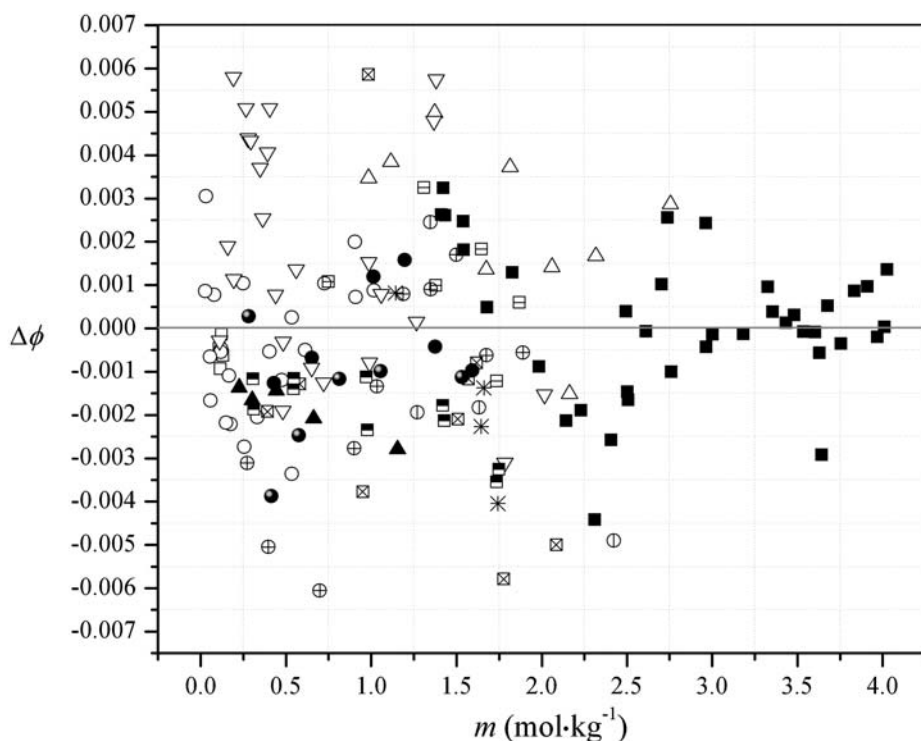
Fig. 2 Differences between the experimental osmotic coefficients of the $MgCl_2(aq)$ system at 298.15 K from those calculated with the extended ion-interaction model, using the parameters reported in Table 3. The data included in the model parameter evaluations are summarized in Table 5. *Plotting symbols*: ■, Rard and Miller [41]; □, Rard and Miller [32]; △, Platford [13]; ▲, Wu et al. [21]; ○, Gibbard and Gossmann [42]; ●, Padova and Saad [16]; ✳, Stokes [39]; ▽, Robinson and Stokes [38]; ⊟, Kuschel and Seidel [17]; ⊕, Miladinović, et al. [18]; ◑, this study (Table 1); ⊕, Frolov et al. [40]; ⊠, Saad et al. [24]; ⬛, Robinson and Bower [19]

these fits that corresponds approximately to rejecting values exceeding the 99% confidence limit.

Rodil and Vera [45] reported values of the mean activity coefficients $\gamma_\pm$ of $MgCl_2(aq)$ from $m = 0.01$ to 3.0 mol·kg^{-1} at 298.15 K from Emf measurements using so-called ion-selective electrodes. Their reported values of $\gamma_\pm$ agree to within 2 to 5% of those obtained from our evaluated model over most of this molality range, with the larger uncertainties being in the Emf results because of the need to estimate the liquid junction potentials.

5 Extended Ion-Interaction Model Equations and Calculations for $MgCl_2 + MgSO_4 + H_2O$ Solutions

The general equations for the extended ion-interaction model for mixed electrolytes are given in Appendix I of [9]. For the $\{yMgCl_2 + (1 - y)MgSO_4\}(aq)$ system, the osmotic coefficient equation is

$$\phi = 1 + \left(\frac{2}{m_{\mathrm{Mg}} + m_{\mathrm{Cl}} + m_{\mathrm{SO_4}}}\right)\left[\left(\frac{-A_\phi I^{3/2}}{1 + bI^{1/2}}\right) + m_{\mathrm{Mg}}m_{\mathrm{Cl}}(B_{\mathrm{Mg,Cl}}^\phi + ZC_{\mathrm{Mg,Cl}}^{\mathrm{T},\phi})\right.$$

$$\left. + m_{\mathrm{Mg}}m_{\mathrm{SO_4}}(B_{\mathrm{Mg,SO_4}}^\phi + ZC_{\mathrm{Mg,SO_4}}^{\mathrm{T},\phi}) + m_{\mathrm{Cl}}m_{\mathrm{SO_4}}\{\Phi_{\mathrm{Cl,SO_4}}^\phi + m_{\mathrm{Mg}}\psi_{\mathrm{Mg,Cl,SO_4}}\}\right], \quad (9)$$

where Z, defined by Eq. 6, is given by

$$Z = 2m_{\mathrm{Mg}} + m_{\mathrm{Cl}} + 2m_{\mathrm{SO_4}}, \quad (10)$$

$$B_{\mathrm{M,X}}^\phi = \beta_{\mathrm{M,X}}^{(0)} + \beta_{\mathrm{M,X}}^{(1)}\exp(-\alpha_{1,\mathrm{M,X}}I^{1/2}) + \beta_{\mathrm{M,X}}^{(2)}\exp(-\alpha_{2,\mathrm{M,X}}I^{1/2}) \quad (11)$$

and

$$C_{\mathrm{M,X}}^{\mathrm{T},\phi} = C_{\mathrm{M,X}}^{(0)} + C_{\mathrm{M,X}}^{(1)}\exp(-\omega_{1,\mathrm{M,X}}I^{1/2}). \quad (12)$$

Table 5 Summary of available studies yielding osmotic coefficients of $MgCl_2(aq)$ at 298.15 K that were used in the ion-interaction model parameter evaluation

$\dfrac{m}{\mathrm{mol \cdot kg^{-1}}}$	Number of data points[a]	Type of measurement	Relative weight[b]	Reference
0.1120–2.016	27	Isopiestic	1.0 (2)	Robinson and Stokes [38]
1.143–2.050	5	Isopiestic	1.0 (1)	Stokes [39]
0.3061–1.7475	11	Isopiestic	0.5	Robinson and Bower [19]
0.9852–2.7551	9	Isopiestic	1.0	Platford [13]
0.2256–1.1547	5	Isopiestic	1.0	Wu et al. [21]
1.097–2.423	6	Isopiestic	0.5 (2)	Frolov et al. [40]
0.3927–2.0853	10	Isopiestic	0.5 (1)	Saad et al. [24]
0.4301–1.9964	8	Isopiestic	1.0 (2)	Padova and Saad [16]
1.4099–4.0251	38	Isopiestic	1.0	Rard and Miller [41]
0.1090–0.1310	4	Isopiestic	1.0	Rard and Miller [32]
0.7479–1.8690	6	Isopiestic	1.0	Kuschel and Seidel [17]
0.2728–1.8899	10	Isopiestic	1.0	Miladinović et al. [18]
0.2822–1.5312	6	Isopiestic	1.0	This study, Table 1
0.0280–1.0161	22	f.t.d.[c]	1.0	Gibbard and Gossmann [42]

[a]The studies of Rard and Miller [41] and Stokes [39] include isopiestic data at higher molalities that were not analyzed because they occur above the upper molality limit of our model; the listed number of data points is only for those solutions with $m \leq 4.0251$ mol·kg^{-1} that were considered in the model parameter evaluations. Osmotic coefficients were also determined at higher molalities in the investigations of Robinson and Bower [19], and Gibbard and Gossmann [42], and at lower molalities by Platford [13], but they are not included here for reasons described by Rard and Miller [41]

[b]These are the relative weights given to the individual osmotic coefficients calculated from the reported isopiestic molalities; the numbers given in parentheses are the numbers of osmotic coefficients from that study given zero weight in the model parameter evaluations, based on a $2.5\sigma(\phi)$ rejection criterion. The molalities of the rejected points are $m = 0.5293$ and 1.713 mol·kg^{-1} from Robinson and Stokes [38], $m = 2.050$ mol·kg^{-1} from Stokes [39], $m = 1.097$ and 2.193 mol·kg^{-1} from Frolov et al. [40], $m = 1.2003$ mol·kg^{-1} from Saad et al. [24], and $m = 1.8630$ and 1.9964 mol·kg^{-1} from Padova and Saad [16]

[c]Freezing temperature depressions

The term $m_{\text{Cl}}m_{\text{SO}_4}\{\Phi^\phi_{\text{Cl,SO}_4} + m_{\text{Mg}}\psi_{\text{Mg,Cl,SO}_4}\}$ of Eq. 9 accounts for the mixing of the two electrolytes where $\psi_{\text{Mg,Cl,SO}_4}$ is an empirical (adjustable) parameter representing the interaction of three different kinds of ions. Pitzer [46] reported equations describing higher-order electrostatic contributions for the unsymmetrical mixing of two ions of like sign but different charge. If these higher-order contributions are considered, then

$$\Phi^\phi_{\text{Cl,SO}_4} = \Phi_{\text{Cl,SO}_4} + I\Phi'_{\text{Cl,SO}_4} = {}^S\theta_{\text{Cl,SO}_4} + {}^E\theta(I) + I\{{}^E\theta'(I)\}, \tag{13}$$

where ${}^E\theta(I)$ and ${}^E\theta'(I)$ are known functions [1, 46] of the Debye-Hückel limiting-law slope, the charges of the ions are of like sign, and the total ionic strength; ${}^S\theta_{\text{Cl,SO}_4}$ is an adjustable parameter; and

$$\Phi'_{\text{Cl,SO}_4} = \left(\frac{\partial \Phi_{\text{Cl,SO}_4}}{\partial I}\right)_{T,p} = {}^E\theta'(I). \tag{14}$$

If these higher-order electrostatic effects are neglected, then $\Phi^\phi_{\text{Cl,SO}_4}$ is replaced by the adjustable parameter $\theta_{\text{Cl,SO}_4}$. The empirical representation of the J function, required to calculate values of the ${}^E\theta(I)$ and ${}^E\theta'(I)$ functions, is that given by Pitzer's Eq. 47 and his second set of Table III coefficients [46], and was also used in our earlier work [9, 15, 18].

The corresponding expressions for the ionic activity coefficients are:

$$\ln\gamma_{\text{Mg}} = 4F + m_{\text{Cl}}(2B_{\text{Mg,Cl}} + ZC^T_{\text{Mg,Cl}}) + m_{\text{SO}_4}(2B_{\text{Mg,SO}_4} + ZC^T_{\text{Mg,SO}_4})$$
$$+ 2m_{\text{Mg}}m_{\text{Cl}}C^T_{\text{Mg,Cl}} + 2m_{\text{Mg}}m_{\text{SO}_4}C^T_{\text{Mg,SO}_4} + m_{\text{Cl}}m_{\text{SO}_4}\psi_{\text{Mg,Cl,SO}_4}, \tag{15}$$

$$\ln\gamma_{\text{Cl}} = F + m_{\text{Mg}}(2B_{\text{Mg,Cl}} + ZC^T_{\text{Mg,Cl}}) + m_{\text{Mg}}m_{\text{Cl}}C^T_{\text{Mg,Cl}} + m_{\text{Mg}}m_{\text{SO}_4}C^T_{\text{Mg,SO}_4}$$
$$+ m_{\text{SO}_4}(2\Phi_{\text{Cl,SO}_4} + m_{\text{Mg}}\psi_{\text{Mg,Cl,SO}_4}), \tag{16}$$

$$\ln\gamma_{\text{SO}_4} = 4F + m_{\text{Mg}}(2B_{\text{Mg,SO}_4} + ZC^T_{\text{Mg,SO}_4}) + 2m_{\text{Mg}}m_{\text{Cl}}C^T_{\text{Mg,Cl}}$$
$$+ 2m_{\text{Mg}}m_{\text{SO}_4}C^T_{\text{Mg,SO}_4} + m_{\text{Cl}}(2\Phi_{\text{Cl,SO}_4} + m_{\text{Mg}}\psi_{\text{Mg,Cl,SO}_4}), \tag{17}$$

where

$$F = -A_\phi\left\{\frac{I^{1/2}}{1 + bI^{1/2}} + \left(\frac{2}{b}\right)\ln(1 + bI^{1/2})\right\} + m_{\text{Mg}}m_{\text{Cl}}\left(B'_{\text{Mg,Cl}} + \frac{ZC^{T'}_{\text{Mg,Cl}}}{2}\right)$$
$$+ m_{\text{Mg}}m_{\text{SO}_4}\left(B'_{\text{Mg,SO}_4} + \frac{ZC^{T'}_{\text{Mg,SO}_4}}{2}\right) + m_{\text{Cl}}m_{\text{SO}_4}\Phi'_{\text{Cl,SO}_4}, \tag{18}$$

$$B_{\text{M,X}} = \beta^{(0)}_{\text{M,X}} + 2\beta^{(1)}_{\text{M,X}}\left[\frac{\{1 - (1 + \alpha_{1,\text{M,X}}I^{1/2})\exp(-\alpha_{1,\text{M,X}}I^{1/2})\}}{\alpha^2_{1,\text{M,X}}I}\right]$$
$$+ 2\beta^{(2)}_{\text{M,X}}\left[\frac{\{1 - (1 + \alpha_{2,\text{M,X}}I^{1/2})\exp(-\alpha_{2,\text{M,X}}I^{1/2})\}}{\alpha^2_{2,\text{M,X}}I}\right], \tag{19}$$

$$C^T_{\text{M,X}}$$
$$= C^{(0)}_{\text{M,X}} + 4C^{(1)}_{\text{M,X}}\left[\frac{\{6 - (6 + 6\omega_{1,\text{M,X}}I^{1/2} + 3\omega^2_{1,\text{M,X}}I + \omega^3_{1,\text{M,X}}I^{3/2})\exp(-\omega_{1,\text{M,X}}I^{1/2})\}}{\omega^4_{1,\text{M,X}}I^2}\right],$$
$$\tag{20}$$

$$B'_{M,X} = \left(\frac{\partial B_{M,X}}{\partial I} \right)_{T,p} \qquad (21)$$

and

$$C^{T'}_{M,X} = \left(\frac{\partial C^{T'}_{M,X}}{\partial I} \right)_{T,p}. \qquad (22)$$

The explicit functional relations for the ionic strength derivatives $B'_{M,X}$ and $C^{T'}_{M,X}$ are given in Appendix I of Clegg et al. [9].

There are two published sets of isopiestic data for the $\{yMgCl_2 + (1 - y)MgSO_4\}$(aq) system at 298.15 K [21, 25] along with the 24 values reported in Table 1 (0.1997 ≤ y ≤ 0.8008). Osmotic coefficients were calculated at the 14 compositions (0.2461 ≤ y ≤ 0.7516) reported by Wu et al. [21] using Archer's model [8] for the osmotic coefficients of the NaCl(aq) reference standard. Filippov and Cheremnykh [25] reported isopiestic results at 26 compositions oven a wider ionic strength range. Because Filippov and Cheremnykh did not report the molalities of the isopiestic reference standards, their results could not be recalculated and their reported osmotic coefficients were accepted.

Initial fits of the mixing parameters of Eq. 9 were made using both published sets of isopiestic data [21, 25] and our results of Table 1. Including the higher-order electrostatic effects terms $^E\theta(I)$ and $^E\theta'(I)$, and fixing the parameter $^S\theta_{Cl,SO_4}$ at its value for the NaCl + Na$_2$SO$_4$ + H$_2$O system [15], $^S\theta_{Cl,SO_4} = +0.01236$ kg·mol^{-1}, resulted in $\psi_{Mg,Cl,SO_4} = -0.081047$ kg^2·mol^{-2} with $\sigma(\phi) = 0.0202$. However, there were large systematic deviations, all negative and ranging up to $\Delta\phi \approx -0.02$ below $I = 6$ mol·kg^{-1}, and all positive ranging up to $\Delta\phi \approx +0.07$ at higher ionic strengths. Allowing both mixing parameters to be optimized yielded $^S\theta_{Cl,SO_4} = -0.088624$ kg·mol^{-1} and $\psi_{Mg,Cl,SO_4} = -0.022159$ kg^2·mol^{-2} with $\sigma(\phi) = 0.0067$. Although the two-parameter fit was considerably better than the one-parameter fit, similar deviations were still present but their magnitudes were reduced significantly to $\Delta\phi \approx -0.01$ to $+0.02$.

We carefully examined the deviations of the different data sets from the model fits and observed the following. The values of ϕ from Table 1 and the recalculated results of Wu et al. [21] are fairly consistent, $\Delta\phi \approx 0.001$ to 0.002 at lower values of y and $\Delta\phi \approx 0.003$ to 0.004 at higher values of y. In contrast, the results of Filippov and Cheremnykh [25] are much more scattered and typically systematically lower. Filippov and Cheremnykh also reported ϕ values for MgCl$_2$(aq) and MgSO$_4$(aq) in that study and their values are uniformly lower that those calculated using the extended Pitzer model parameters reported in Table 3. Because of their lesser precision and apparent negative systematic bias, the ϕ values of Filippov and Cheremnykh [25] for $\{yMgCl_2 + (1 - y)MgSO_4\}$(aq) were rejected.

Using our isopiestic results and those of Wu et al. [21] and including the $^E\theta(I)$ and $^E\theta'(I)$ terms resulted in $^S\theta_{Cl,SO_4} = -0.07122$ kg·mol^{-1} and $\psi_{Mg,Cl,SO_4} = -0.038505$ kg^2·mol^{-2} with $\sigma(\phi) = 0.0049$. Repeating the calculation without the higher-order $^E\theta(I)$ and $^E\theta'(I)$ terms gave $\theta_{Cl,SO_4} = -0.14077$ kg·mol^{-1} and $\psi_{Mg,Cl,SO_4} = -0.014774$ kg^2·mol^{-2} with $\sigma(\phi) = 0.0039$. These parameters are included in Table 3 along with those of the single salt solutions. Figure 3 is a plot of the differences between the experimental osmotic coefficients and those calculated with the parameters obtained with the higher-order mixing effects; systematic differences are not large, $\Delta\phi \approx -0.007$ to $+0.013$, but exceed the likely experimental error.

Figure 4 is a plot of the corresponding $\Delta\phi$ differences using the first set of mixing parameters of Table 3, i.e., without the higher-order electrostatic effects. The fit is even better than the previous one, especially for $I < 6.2$ mol·kg^{-1} where there are comparable numbers
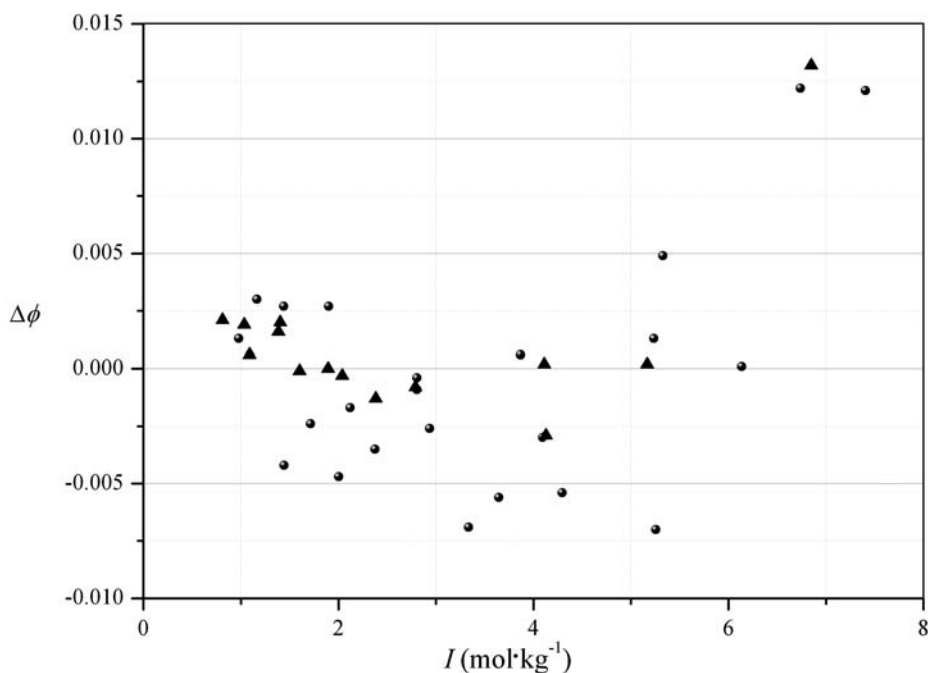
Fig. 3 Differences between the experimental osmotic coefficients of the $\{y\text{MgCl}_2 + (1 - y)\text{MgSO}_4\}$(aq) mixtures at 298.15 K and those calculated using the parameters reported in Table 3 for the model including higher-order electrostatic effects. *Plotting symbols*: ●, this study (Table 1); ▲, Wu et al. [21]

of positive and negative deviations. The positive deviations observed around $I \approx 7$ mol·kg^{-1} are possibly a consequence of the small number of data points at high ionic strengths and their restricted ionic-strength fraction range, $y < 0.4$, being insufficient to constrain the model parameters at these higher ionic strengths. We recommend that these parameters be accepted for solutions with $I < 6.2$ mol·kg^{-1}. However, we note that there is a tendency for the $\Delta\phi$ differences to be positive at low values of y and negative at high values of y, which implies that although Pitzer's two-parameter mixing function [1] gives a nearly quantitative representation of the mixing effects for $\{y\text{MgCl}_2 + (1 - y)\text{MgSO}_4\}$(aq) at 298.15 K, some minor details may be missed.

Table 6 lists calculated values of the osmotic coefficients and mean activity coefficients of MgCl$_2$, $\gamma_\pm(\text{MgCl}_2)$, and of MgSO$_4$, $\gamma_\pm(\text{MgSO}_4)$, as a function of y at selected values of I that were calculated with the parameters $\theta_{\text{Cl,SO}_4} = -0.14077$ kg·mol^{-1} and $\psi_{\text{Mg,Cl,SO}_4} = -0.014774$ kg^2·mol^{-2}. Figure 5 is a plot of $\gamma_\pm(\text{MgCl}_2)$ and Fig. 6 is that of $\gamma_\pm(\text{MgSO}_4)$ as a function of the ionic strength at equal intervals of y. The activity coefficients of MgCl$_2$ in the mixtures are always higher than those of MgSO$_4$ as also occurs for the corresponding single electrolyte solutions. The activity coefficients of MgCl$_2$ decrease regularly as the ionic strength fraction of MgSO$_4$ increases, whereas those of MgSO$_4$ increase regularly as the ionic strength fraction of MgCl$_2$ increases, which is normal behavior for such electrolyte mixtures.

We found that when the ϕ values for MgCl$_2$(aq) and MgSO$_4$(aq) at 298.15 K were represented by Archer-type extended ion-interaction models then $\theta_{\text{Cl,SO}_4} = -0.14077$ kg·mol^{-1} if higher-order electrostatic effects are not included and $^S\theta_{\text{Cl,SO}_4} = -0.07122$ kg·mol^{-1} if they are, which is a difference of 0.06955 kg·mol^{-1}. Values of these parameters are also available
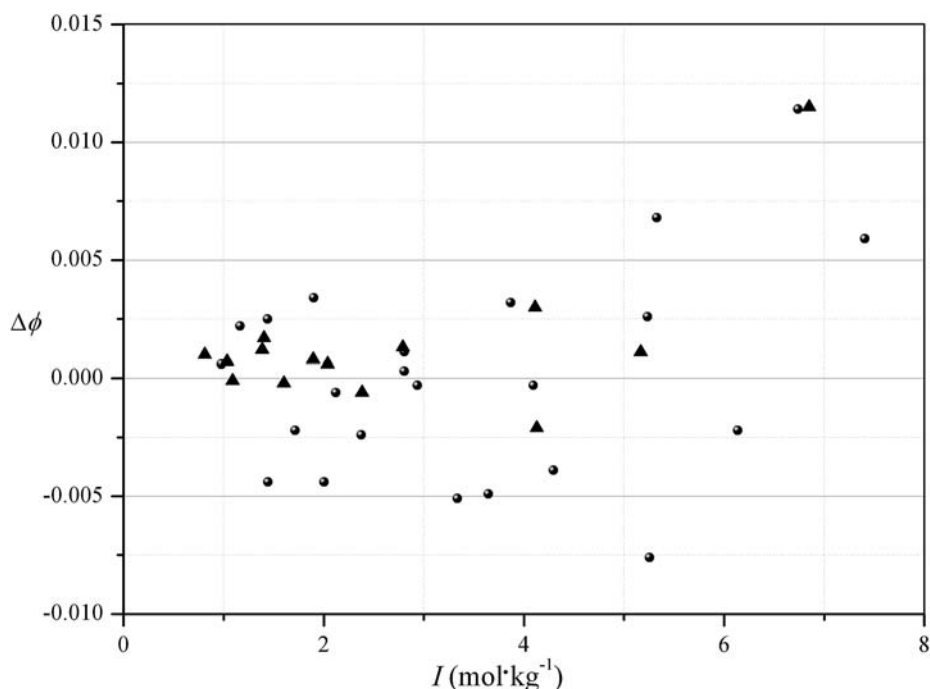
Fig. 4 Differences between the experimental osmotic coefficients of the $\{y\text{MgCl}_2 + (1 − y)\text{MgSO}_4\}$(aq) mixtures at 298.15 K and those calculated using the parameters reported in Table 3 for the model that does not include higher-order electrostatic effects. *Plotting symbols*: ●, this study (Table 1); ▲, Wu et al. [21]

for the standard three-parameter form of Pitzer's ion-interaction model: $\theta_{\text{Cl,SO}_4} = −0.02$ to $−0.056$ kg·mol^{-1} [1, 25] and $^S\theta_{\text{Cl,SO}_4} = +0.02$ to $+0.07$ kg·mol^{-1} [1–4, 26, 47]. Irrespective of whether the thermodynamic properties of the single electrolyte solutions are represented by the extended or standard forms of the ion-interaction model, including the higher-order electrostatic effects causes the value of θ to be shifted in the positive direction by similar amounts.

In this section and in Table 3 the mixing parameters of the extended ion-interaction model are reported to more decimal places than are justified by their accuracy. However, these values are instead reported to the number of figures needed to reproduce both the osmotic coefficients used in their evaluation, and the smoothed osmotic and activity coefficients of Table 6 to the reported number of figures.

Scatchard [48] proposed his neutral electrolyte model that contains up to six mixing parameters and is capable of representing accurately the osmotic coefficients of many ternary electrolyte solutions. For the $\{y\text{MgCl}_2 + (1 − y)\text{MgSO}_4\}$(aq) system, Scatchard's equation can be written in the form:

$$\phi\left(\frac{1+y}{2}\right) = y\phi_1^* + \left(\frac{1-y}{2}\right)\phi_2^* + y(1-y)(b_{01}I + b_{02}I^2 + b_{03}I^3)$$

$$+ y(1-y)(2y-1)(b_{12}I^2 + b_{13}I^3) + y(1-y)(2y-1)^2 b_{23}I^3, \quad (23)$$

where ϕ_1^* and ϕ_2^* are the osmotic coefficients of MgCl$_2$(aq) and MgSO$_4$(aq), respectively, evaluated at the total ionic strength of the mixture and the b_{ij} are adjustable mixing para-

Table 6 Calculated values of the osmotic coefficients ϕ of $\{yMgCl_2 + (1 - y)MgSO_4\}$(aq) solutions and of the mean activity coefficients of the individual salts $\gamma_\pm(MgCl_2)$ and $\gamma_\pm(MgSO_4)$, at rounded values of the ionic strength I and ionic strength fraction y of $MgCl_2$, at $T = 298.15$ K based on the parameters of Table 3 for the mixture model without higher-order electrostatic effects

$I/$ mol·kg^{-1}	y	$\gamma_\pm(MgCl_2)$	$\gamma_\pm(MgSO_4)$	ϕ
1.0	0.0	0.3835[a]	0.1073	0.5487
1.5	0.0	0.3603[a]	0.0876	0.5326
2.0	0.0	0.3481[a]	0.0758	0.5241
2.5	0.0	0.3421[a]	0.0679	0.5203
3.0	0.0	0.3401[a]	0.0622	0.5204
3.5	0.0	0.3411[a]	0.0580	0.5236
4.0	0.0	0.3445[a]	0.0548	0.5298
4.5	0.0	0.3500[a]	0.0523	0.5386
5.0	0.0	0.3573[a]	0.0504	0.5499
5.5	0.0	0.3664[a]	0.0490	0.5635
6.0	0.0	0.3771[a]	0.0480	0.5793
1.0	0.2	0.4028	0.1105	0.6541
1.5	0.2	0.3849	0.0915	0.6537
2.0	0.2	0.3784	0.0803	0.6603
2.5	0.2	0.3783	0.0730	0.6714
3.0	0.2	0.3827	0.0680	0.6862
3.5	0.2	0.3907	0.0644	0.7040
4.0	0.2	0.4018	0.0618	0.7245
4.5	0.2	0.4157	0.0601	0.7475
5.0	0.2	0.4323	0.0589	0.7727
5.5	0.2	0.4516	0.0582	0.8000
6.0	0.2	0.4737	0.0580	0.8293
1.0	0.4	0.4216	0.1132	0.7352
1.5	0.4	0.4094	0.0950	0.7484
2.0	0.4	0.4089	0.0846	0.7681
2.5	0.4	0.4156	0.0781	0.7923
3.0	0.4	0.4274	0.0739	0.8201
3.5	0.4	0.4438	0.0712	0.8509
4.0	0.4	0.4642	0.0696	0.8844
4.5	0.4	0.4887	0.0688	0.9204
5.0	0.4	0.5173	0.0686	0.9586
5.5	0.4	0.5502	0.0691	0.9989
6.0	0.4	0.5877	0.0701	1.0409
1.0	0.6	0.4397	0.1154	0.8007
1.5	0.6	0.4335	0.0981	0.8258
2.0	0.6	0.4396	0.0887	0.8571
2.5	0.6	0.4537	0.0832	0.8929
3.0	0.6	0.4741	0.0801	0.9323
3.5	0.6	0.5002	0.0785	0.9748

Table 6 (*Continued*)

I/ mol·kg^{-1}	y	$\gamma_{\pm}(MgCl_2)$	$\gamma_{\pm}(MgSO_4)$	ϕ
4.0	0.6	0.5320	0.0781	1.0202
4.5	0.6	0.5696	0.0787	1.0682
5.0	0.6	0.6134	0.0801	1.1185
5.5	0.6	0.6640	0.0823	1.1709
6.0	0.6	0.7220	0.0852	1.2251
1.0	0.8	0.4571	0.1171	0.8555
1.5	0.8	0.4571	0.1009	0.8910
2.0	0.8	0.4703	0.0927	0.9326
2.5	0.8	0.4926	0.0884	0.9786
3.0	0.8	0.5226	0.0866	1.0284
3.5	0.8	0.5600	0.0865	1.0816
4.0	0.8	0.6053	0.0879	1.1378
4.5	0.8	0.6589	0.0904	1.1986
5.0	0.8	0.7217	0.0940	1.2583
5.5	0.8	0.7950	0.0987	1.3220
6.0	0.8	0.8800	0.1045	1.3878
1.0	1.0	0.4737	0.1183[b]	0.9024
1.5	1.0	0.4801	0.1033[b]	0.9472
2.0	1.0	0.5008	0.0964[b]	0.9978
2.5	1.0	0.5320	0.0936[b]	1.0529
3.0	1.0	0.5728	0.0935[b]	1.1119
3.5	1.0	0.6233	0.0955[b]	1.1746
4.0	1.0	0.6845	0.0991[b]	1.2406
4.5	1.0	0.7575	0.1043[b]	1.3097
5.0	1.0	0.8441	0.1112[b]	1.3816
5.5	1.0	0.9462	0.1196[b]	1.4560
6.0	1.0	1.0665	0.1299[b]	1.5327

[a]Trace activity coefficient of $MgCl_2$ in a solution of $MgSO_4(aq)$

[b]Trace activity coefficient of $MgSO_4$ in a solution of $MgCl_2(aq)$

meters. We calculated the values of ϕ_1^* and ϕ_2^* at the total ionic strengths of the mixtures using the extended ionic interaction model parameters of Table 3, and evaluated the b_{ij} by a least-squares method using our isopiestic results and those of Wu et al. [21].

Table 7 summarizes the resulting b_{ij} parameter values. The one-parameter model with b_{01} gives a fit comparable in accuracy to that of the "pure" extended ion-interaction models of Table 3, whereas two-parameter models that include the b_{01} term give slightly better representations (but the two-parameter model without b_{01} has about twice the standard deviation of the "pure" ion-interaction model without higher-order electrostatic effects). Including all three mixing terms that are symmetrical in the ionic-strength fractions of the two solutes (i.e., b_{01}, b_{02}, and b_{03}) yields a standard deviation of $\sigma(\phi) = 0.0020$ that is about one half that of the "pure" ion-interaction model without higher-order electrostatic effects, $\sigma(\phi) = 0.0039$. The six-parameter model with three asymmetrical mixing terms in addition to the symmetrical ones is only slightly better, $\sigma(\phi) = 0.0015$, indicating that the
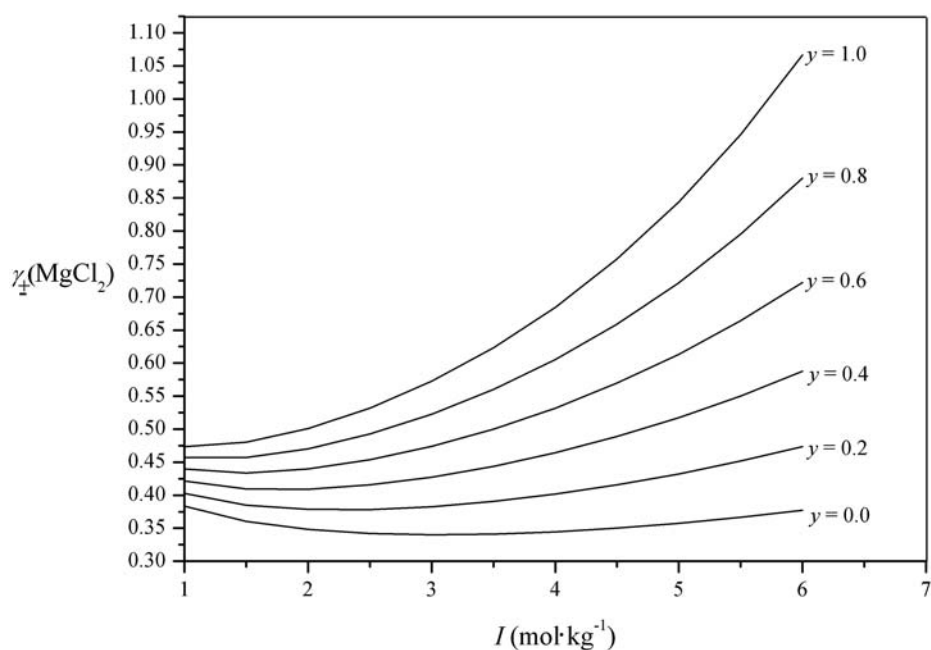
Fig. 5 Mean activity coefficients of MgCl$_2$ in {yMgCl$_2$ + (1 − y)MgSO$_4$}(aq) mixtures at 298.15 K using the parameters reported in Table 3 for the model that does not include higher-order electrostatic effects
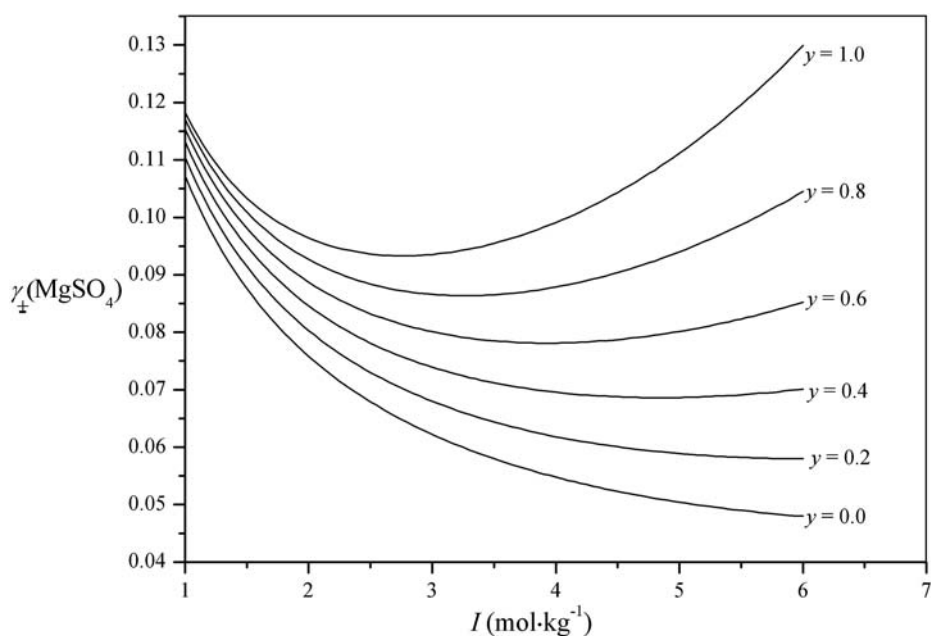

Fig. 6 Mean activity coefficients of MgSO$_4$ in {yMgCl$_2$ + (1 − y)MgSO$_4$}(aq) mixtures at 298.15 K using the parameters reported in Table 3 for the model that does not include higher-order electrostatic effects

Table 7 Mixing parameter values of Scatchard's equation for $\{y\mathrm{MgCl_2} + (1 - y)\mathrm{MgSO_4}\}$(aq) mixtures at 298.15 K, using the extended ion-interaction (Pitzer) model parameters for the single electrolytes $\mathrm{MgCl_2}$(aq) and $\mathrm{MgSO_4}$(aq) reported in Table 3

$b_{01}/\mathrm{kg \cdot mol^{-1}}$	$b_{02}/\mathrm{kg^2 \cdot mol^{-2}}$	$b_{03}/\mathrm{kg^3 \cdot mol^{-3}}$	$b_{12}/\mathrm{kg^2 \cdot mol^{-2}}$	$b_{13}/\mathrm{kg^3 \cdot mol^{-3}}$	$b_{23}/\mathrm{kg^3 \cdot mol^{-3}}$	$\sigma(\phi)$
−0.040114						0.0447
−0.033544	−0.0011451					0.0042
−0.035836		−0.00011277				0.0032
	−0.012121	0.00081159				0.0027
−0.045319	0.0036252	−0.00041108				0.0087
−0.033111	−0.0012608					0.0020
			−0.00014279			0.0032
−0.04561	0.004138	−0.00049533	−0.00048942	−0.000094123	−0.00016026	0.0015

mixing contributions to ϕ of the $\{y\mathrm{MgCl_2} + (1 - y)\mathrm{MgSO_4}\}$(aq) system are predominantly symmetrical within the framework of Scatchard's model.

For most practical applications the extended ion-interaction models of Table 3 will be adequate. For greater accuracy the three-parameter Scatchard model of Table 7 with b_{01}, b_{02}, and b_{03} should be used, but the differences between the models are not large, i.e., $\Delta\sigma(\phi) \approx$ 0.002–0.003.

6 Comments on the Na₂SO₄ + MgSO₄ + H₂O System

The isopiestic results of Rard and Miller [32] for the equal molar $\mathrm{Na_2SO_4} + \mathrm{MgSO_4} + \mathrm{H_2O}$ mixtures were recalculated using Archer's [36] model to calculate the osmotic coefficients of the KCl(aq) reference standard. A comparison of their results to those reported in Table 2 with NaCl(aq) as reference standard indicates essentially complete agreement of the osmotic coefficients over most of the molality range but with slight differences of $\approx$0.2% at the highest overlapping molalities. This slight difference is within the uncertainties of the reference standards and thus the agreement between the two sets of measurements is excellent.

Wu et al. [21] reported isopiestic results at 15 compositions for this system at 298.15 K. However, their osmotic coefficients for $\mathrm{Na_2SO_4}$(aq) are discrepant from most other studies as noted in [32, 49]; thus it is likely that the Wu et al. osmotic coefficients for $\mathrm{Na_2SO_4} + \mathrm{MgSO_4} + \mathrm{H_2O}$ mixtures are skewed as a function of y. As noted in the introduction, the results cited in [31] were not available to us. Mounir et al. [50] reported osmotic coefficients at 24 compositions having $y = 0.2$, 0.5, or 0.8 using their "hygrometric" method. Obviously, there is a need for more extensive isopiestic measurements for this system. The measurements reported in Table 2 were not extended to other solute molar ratios because the Isopiestic Laboratory at Lawrence Livermore National Laboratory has been closed.

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