Osmotic and Activity Coefficients of the {xZnCl2 + (1 - x)ZnSO4}(aq) System at 298.15 K

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Rozalija Ninković · Jelena Miladinović · Milica Todorović · Snežana Grujić · Joseph A. Rard

Abstract Isopiestic vapor pressure measurements were made for $\{x\text{ZnCl}_2 + (1 - x)\text{ZnSO}_4\}$(aq) solutions with ZnCl_2 molality fractions of $x = (0, 0.3062, 0.5730, 0.7969,$ and 1) at the temperature 298.15 K, using KCl(aq) as the reference standard. These measurements cover the water activity range $0.901–0.919 \leq a_\text{w} \leq 0.978$. The experimental osmotic coefficients were used to evaluate the parameters of an extended ion-interaction (Pitzer) model for these mixed electrolyte solutions. A similar analysis was made of the available activity data for ZnCl_2(aq) at 298.15 K, while assuming the presence of equilibrium amounts of ZnCl^+(aq) ion-pairs, to derive the ion-interaction parameters for the hypothetical pure binary electrolytes $(\text{Zn}^{2+},2\text{Cl}^-)$ and $(\text{ZnCl}^+,\text{Cl}^-)$. These parameters are required for the analysis of the mixture results. Although significant concentrations of higher-order zinc chloride complexes may also be present in these solutions, it was possible to represent the osmotic coefficients accurately by explicitly including only the predominant complex ZnCl^+(aq) and the completely dissociated ions. The ionic activity coefficients and osmotic coefficients were calculated over the investigated molality range using the evaluated extended Pitzer model parameters.

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1. Introduction

Zinc is a technologically important metal that is a component of common metal alloys such as brass that have been known since antiquity, and is used for electroplating (galvanizing) coatings to protect more reactive metals such as iron. Paints containing zinc dust are sometimes applied to metals as a substitute for galvanizing. This zinc metal serves as a sacrificial anode, for example, for protecting metal pipelines and ship hulls. Zinc alloys are used in die casting, especially Zn-Al alloys [1]. Zinc is an essential element for humans and other animals that is necessary for the proper functioning of the immune system, for the healing of wounds, for the synthesis of DNA, and for the normal functioning of the senses of taste and smell [2].

Zinc metal is used in several types of rechargeable storage batteries, including alkaline batteries (containing KOH) with $NiOOH$, MnO_2 or MnO_2-BiO_x and the Zn-O_2 battery; the aqueous zinc-bromine battery that usually has a tetraalkyl ammonium bromide present as a supporting electrolyte to improve the electrical conductivity; and the aqueous zinc-chlorine battery that contains aqueous $ZnCl_2$ and solid chlorine hydrate $Cl_2\cdot6H_2O$ along with a supporting electrolyte that is typically KCl [3,4]. The zinc-chlorine battery has been extensively studied for load leveling of electrical energy, *i.e.*, for the electrochemical storage of electricity produced in excess of usage such as at night, so that it can be used at other times when the usage exceeds the generating capacity. The zinc-chlorine battery has the advantages of a high open circuit potential of about 2.12 V, a low overpotential, and a high energy capacity per unit mass because of the low equivalent masses of the reactants [4]. However, because of the complex design of the flow arrangement needed by the zinc-chlorine battery, it is no longer extensively used. The Clark saturated standard cell, cell A, which was used as an potential standard for electrochemical measurements in the past, contains a saturated solution of $ZnSO_4$(aq):

Pt(cr)|Zn–Hg(two phase)|ZnSO$_4$·7H$_2$O(cr)|ZnSO$_4$(aq, satd.)|ZnSO$_4$·7H$_2$O(cr)|Hg$_2$SO$_4$(cr)|Hg(l)|Pt(cr)

(A)
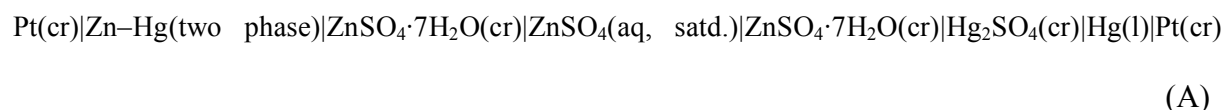
At least 55 zinc minerals are known, but the ones of greatest commercial importance are sphalerite, ZnS; hemimorphite (also known as calamine), Zn$_4$Si$_2$O$_7$(OH)$_2$·H$_2$O; smithsonite, ZnCO$_3$; hydrozincite, Zn$_5$(OH)$_6$(CO$_3$)$_2$; zincite, ZnO; willemite, Zn$_2$SiO$_4$; and franklinite, (Zn,Fe,Mn)(Fe,Mn)$_2$O$_4$. Of these, sphalerite is currently the predominant mineral source of zinc [1].

The most common way of extracting zinc from sphalerite is by burning the ZnS in air ("roasting") to yield ZnO + SO$_2$, followed by dissolution of the ZnO in a H$_2$SO$_4$ solution to form ZnSO$_4$. Alternately, the ZnS may be solubilized by the reaction

$$ZnS(s) + Fe_2(SO_4)_3(aq) \rightarrow ZnSO_4(aq) + 2FeSO_4(aq) + S(s) \qquad (1)$$
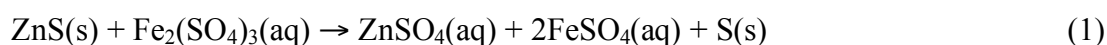
The FeSO$_4$ produced by this process is re-oxidized to Fe$_2$(SO$_4$)$_3$ by O$_2$ in the presence of H$_2$SO$_4$(aq), which is then recycled in reaction (1). Zinc that is present in pyrite cinders can be converted into a soluble form by chlorine roasting, yielding an aqueous Zn(II)/Fe(III)/Cl$^-$/SO$_4^{2-}$ solution. The zinc present in this solution as the ZnCl$_4^{2-}$ ion can be extracted with a secondary amine and then stripped with water [1,5].

Clearly, thermodynamic data and models for ZnSO$_4$(aq), ZnCl$_2$(aq), their mixtures, and their mixtures with other electrolytes are required for a quantitative understanding of the hydrometallurgical extraction of zinc from its ores and for predicting the Emf of several important cells and batteries under various operating conditions.

Goldberg [6] compiled and compared available thermodynamic activity data for ZnCl$_2$(aq) at 298.15 K, as have Rard and Miller [7] who also reported new isopiestic results from 0.3136 to 13.134 mol·kg^{-1} at this temperature. Osmotic coefficients of ZnCl$_2$(aq) have been reported from isopiestic vapor-pressure measurements, direct vapor-pressure

measurements and freezing temperature depressions. As noted by Rard and Miller [7], vapor pressure measurements at 298.15 K yield osmotic coefficients that are 11 to 24 % lower than the ones from isopiestic measurements and are erroneous, and available calorimetric data (enthalpies of dilution and heat capacities) are not adequate to convert vapor pressures at other temperatures [8,9] to yield activities at 298.15 K. Goldberg found that freezing-temperature depressions did not provide any usable thermodynamic results for $ZnCl_2$(aq) [6].

Isopiestic data are available from several investigations but are restricted to 298.15 K. Early isopiestic data from Robinson and Stokes [10] and Farrelly [11] were used by Stokes [12] to produce the recommended osmotic coefficients for $ZnCl_2$(aq) at 298.15 K. The more recent isopiestic data of Rard and Miller [7] and Miladinović *et al*. [13], both involving $ZnCl_2$ of very high purity, essentially confirm the earlier isopiestic results [10,11], and the combined results from these four independent isopiestic studies yield an accurate characterization of the osmotic coefficients from 0.1 mol·kg^{-1} to very high molalities. Osmotic coefficients from the isopiestic results of Pan and Argersinger [14] are somewhat high by up to 0.7 %.

Values of the Emf have been reported as a function of molality from several different cells containing $ZnCl_2$(aq), with most studies at 298.15 K. Some of these Emf studies involved the chloride ion reversible silver/silver chloride electrode whereas others used a mercury/mercurous chloride (calomel) electrode. The cation-responsive electrode was either the two-phase zinc amalgam, a single-phase zinc amalgam, or zinc metal. The cells used for most of the Emf measurements are:

Zn–Hg(two phase)|$ZnCl_2$(aq, *m*)|AgCl(s)|Ag(cr)   (B)

Zn–Hg(single phase)|$ZnCl_2$(aq, *m*)|AgCl(s)|Ag(cr)   (C)

Zn(cr)|$ZnCl_2$(aq, *m*)|AgCl(s)|Ag(cr)   (D)

Zn–Hg(two phase)|$ZnCl_2$(aq, *m*)| Hg_2Cl_2(s)|Hg(l)   (E)

Zn–Hg(single phase)|$ZnCl_2$(aq, *m*)|Hg_2Cl_2(s)|Hg(l)   (F)
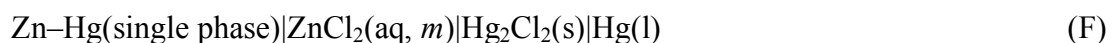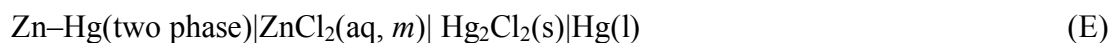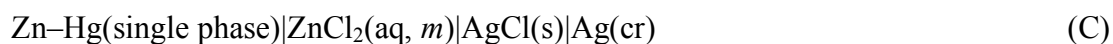
See, for example, the Emf studies reported in references [9,10,15–19].

Dissolution of AgCl(s) increases with increasing $ZnCl_2$(aq) molality because of the formation of aqueous complexes such as $AgCl^0$(aq) and $AgCl_2^-$(aq). An even larger number of complexes is produced by the dissolution of Hg_2Cl_2(s) in concentrated chloride solutions. Rard and Clegg [20] noted that in the presence of $CaCl_2$(aq) at various molalities, the amount of excess chloride produced by dissolution of the Hg_2Cl_2(s) electrode material makes insignificant contributions to the Emf of cells containing this electrolyte, and also that the contributions from dissolution of a AgCl(s) electrode to the Emf of cells are probably slightly smaller. Because $ZnCl_2$(aq) is a partially associated electrolyte, the activity of the chloride ion at any particular molality should be lower than in $CaCl_2$(aq) solutions and thus the effect of electrode dissolution on the Emfs should be even smaller. Consequently, the effect of electrode dissolution may be neglected when analyzing Emfs of cells containing $ZnCl_2$(aq).

Rard and Miller [7] critically compared available Emf measurements for cells (B) through (F) at 298.15 K. Several studies were found to be unreliable, presumably because of electrode failure. However, they identified seven concordant studies with highly consistent molality dependences of the Emfs, after adjustments were made for differences in E^o for the different electrode systems used, which yielded accurate mean activity coefficients for $ZnCl_2$(aq).

Lutfullah *et al*. [18] reported very precise Emfs for cell (B) at very closely spaced molalities over a wide range from 4.3×10^{-4} to 0.8766 mol·kg^{-1} at 298.15 K, and this study probably provides the most accurate set of Emfs (and thus activity coefficients) for a cell containing $ZnCl_2$(aq). They concluded that in the dilute molality region below 0.008 mol·kg^{-1}, $ZnCl_2$(aq) behaves as a completely dissociated electrolyte, whereas in the more concentrated region from 0.01 to 0.88 mol·kg^{-1} the $ZnCl^+$ complex is an important species that needs to be taken into account when extrapolating the Emfs to obtain E^o. They approximated the activity

coefficients by an extended Debye-Hückel equation with the addition of a $B_{ij}I$ term that is linear in the ionic strength I. Lutfullah et al. allowed E^o, the B_{11} and B_{21} coefficients and the association constant for formation of $ZnCl^+$, K_1^o, to be least-squares variables while systematically varying the Debye-Hückel ion-size parameters $\mathring{a}_{11}$ and $\mathring{a}_{21}$, where subscripts 11 denote $(ZnCl^+,Cl^-)$ and 21 denote (Zn^{2+},Cl^-) interactions, respectively. Their calculations yielded a recommended average value of $E° = 984.28 \pm 0.15$ mV for a physically reasonable range of ion size values, but the resulting values of K_1^o were very sensitive to the choice of ion sizes. The analysis of Lutfullah et al. required the iterative calculation of the equilibrium molalities of $ZnCl^+$, Zn^{2+} and Cl^- based on this assumed speciation, which were obtained by the method of successive approximations. Their recommended value of the thermodynamic association constant at 298.15 K is $K_1^o = 4.5$, which corresponds to ion-size parameters of $\mathring{a}_{11}$ $= 4.0 \times 10^{-10}$ m and $\mathring{a}_{21} = 4.5 \times 10^{-10}$ m.

Albright et al. [21] reported extensive isopiestic measurements for $ZnSO_4(aq)$ at 298.15 K using well characterized $ZnSO_4$ with a mole-fraction purity of 0.9993. Their measurements extend to supersaturated molalities and included solubilities. They compared their osmotic coefficients to those from previous isopiestic studies [22–25] and noted that systematic differences occurred among all of these studies. These differences must arise either from differences in sample purity (none of these previous studies provide information about the purity of their $ZnSO_4$), or errors in their molality analyses, or direct experimental error. Miladinović et al. [26,27] subsequently reported isopiestic measurements using high-purity $ZnSO_4$ that yielded osmotic coefficients in essential agreement with those of Albright et al. [21], and the combined results from these three isopiestic studies yield an accurate characterization of the osmotic coefficients from 0.1 mol·kg^{-1} to supersaturated molalities. Miladinović et al. [27] list values of the isopiestic equilibrium molalities from these studies, along with derived osmotic coefficients that were recalculated for consistency with the best

current values of the osmotic coefficients of the NaCl(aq) and KCl(aq) reference standards [28,29]. Recent measurements by the hygrometric method [30] are of significantly lesser precision.

Malatesta and Zamboni [31] reported Emf measurements for $ZnSO_4$(aq) at 298.15 K using a complex liquid membrane cell arrangement that also contained solutions of K_2SO_4(aq) and KCl(aq). Thus, their evaluation of the mean activity coefficients of $ZnSO_4$(aq) depended on assessed activity coefficients for these other two electrolytes. Stable potentials were obtained for $ZnSO_4$(aq) molalities from 8×10^{-5} to 1.5 mol·kg^{-1}. Because of the extremely low solubilities of the liquid membrane materials, no solubility corrections are required to the measured Emfs. In contrast to $ZnSO_4$(aq), a liquid membrane cell containing $ZnCl_2$(aq) showed appreciable time-dependent drifts of the measured Emf that they attributed to partial dissolution of the $ZnCl_2$ in the liquid membranes. According to the assessment by Albright *et al.* [21], the most reliable published Emfs for cells containing $ZnSO_4$(aq) have been obtained using the cell

Zn–Hg(two phase)|$ZnSO_4$(aq)|$PbSO_4$(cr)|Pb–Hg(two phase)　　　　　　　　　(G)
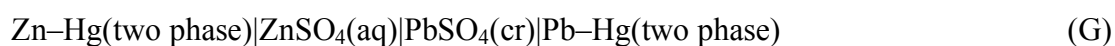
There is only limited data for the thermodynamic properties of mixed electrolyte solutions that contain $ZnCl_2$(aq). Farrelly [11] reported isopiestic results for equimolar mixtures corresponding to the compositions $CaZnCl_4$(aq) and $CoZnCl_4$(aq), Pan and Argersinger [14] presented isopiestic results for the $ZnCl_2$ + $BaCl_2$ + H_2O system, both studies at 298.15 K, and Kolàr *et al*. [32] reported vapor-liquid equilibrium data for the LiCl + $ZnCl_2$ + H_2O system at two mole ratios from 310 to 421 K. Pan and Argersinger [14] described the influence of $ZnCl_2$ on the osmotic and activity coefficients in the mixed $ZnCl_2$ + $BaCl_2$ + H_2O solution. According to these authors, the influence of $ZnCl_2$ on these properties is principally determined by ion association and ionic hydration. Anstiss and Pitzer [33] applied extended ion-interaction (Pitzer) equations to the analysis of NaCl solubility

measurements in $ZnCl_2$ + NaCl + H_2O solutions. The solubilities of Bouchacourt *et al.* [34] at 300.15 K and Filippov *et al.* [35] at 298.15 K were used to derive mixing parameters without correcting for the 2 K temperature difference between these studies.

The only previous thermodynamic investigation of the $ZnCl_2$ + $ZnSO_4$ + H_2O system that we located is the Emf study by Esparza *et al.* [36] for a concentration cell without transport that yields $ZnSO_4$ activity coefficients. They reported four experimental Emfs at 298.15 K for mixtures with total molalities $m_T \leq 1.0$ mol·kg^{-1}.

There is strong evidence for the occurrence of extensive complex formation in $ZnCl_2$(aq) solutions at moderate and high molalities. The transport number of Zn(II) was reported to change from positive values at low and moderate molalities to negative values when the concentration exceeded 2.0 mol·kg^{-1} based on Emf measurements for concentration cells with transference [17], which was confirmed by measurement of more accurate Hittorf transport numbers [19]. A negative "cation" transport number implies that a significant fraction of the Zn(II) is migrating to the anode rather than to the cathode, which can only happen if negatively charged chloro-zinc complexes are present that have a greater mobility than the cationic chloro-zinc complexes and uncomplexed Zn^{2+}(aq) that must also be present. Weingärtner *et al.* [37] measured the tracer diffusion of coefficients of Zn(II) and chloride in $ZnCl_2$(aq) solutions and found that they became nearly equal at 4 mol·L^{-1}. This indicates that the diffusive motions of these ions are strongly coupled at high concentrations and thus extensive complex formation must be present.

As was first pointed out by Weingärtner *et al.* [37] and confirmed by Rard and Miller [7], the osmotic coefficients ϕ of $ZnCl_2$(aq) at 298.15 K initially decrease but then have a plateau-like feature in the molality region around 0.1 to 0.4 mol·kg^{-1} that is followed by a further gradual decrease to reach a minimum at 1.6 mol·kg^{-1}. Beyond this minimum the values of ϕ regularly increase with increasing molality. This complicated behavior is uniquely

characteristic of $ZnCl_2(aq)$. However, Goldberg's [6] assessed ϕ values for $ZnBr_2(aq)$ also show a plateau-like region, but it is much broader and occurs on the opposite side of the osmotic coefficient minimum at higher molalities, between *ca.* 1.25 and 2.5 mol·kg^{-1}, implying that $ZnBr_2(aq)$ solutions are less complexed than $ZnCl_2(aq)$. No analogous anomalies are present for $ZnF_2(aq)$, probably because of its limited solubility.

Rard and Miller [38] subsequently reported that the mutual diffusion coefficients of $ZnCl_2(aq)$ have anomalies that parallel the behavior of the osmotic coefficients. Even more unusual, the thermodynamic diffusion coefficients (*i.e.,* corrected for the thermodynamic driving force) have two maxima; double maxima have not been observed for any other aqueous electrolyte. Miller and Rard [39] reported that the Hittorf transport numbers and several of the solvent-fixed Onsager transport coefficients, velocity correlation coefficients, and other types of transport coefficients show anomalies at ≈ 0.15 mol·L^{-1} that they attributed to the sudden onset of significant complex formation.

Mean-molal activity coefficients of $ZnSO_4(aq)$, $\gamma_{\pm}$, at low ionic strengths fall below the values predicted by the Debye-Hückel limiting law (DHLL), whereas the ion-size approximation is only capable of accounting for positive deviations. According to Malatesta and Zamboni [31], the negative deviations from the DHLL occur at molalities below 0.011 mol·kg^{-1} whereas positive deviations are found at higher concentrations. Negative deviations from the DHLL are normally observed for 2:2 and higher charge-type electrolytes. Bjerrum [40–42] was able to represent these negative deviations by assuming the formation of uncharged ion-pairs such as $ZnSO_4^0(aq)$. However, more rigorous theoretical calculations using Meyer's cluster expansion theory [43] and the non-linearized Poisson-Boltzmann equation [44] yield models that are able to represent activity coefficients in this low ionic strength region without assuming the presence of ion-pairing. This observation indicates that the initial negative deviations from the DHLL are an artefact of the linear approximation used

to solve the Poisson-Boltzmann equation in the Debye-Hückel approximation, and by themselves do not provide evidence for ion-pair formation. However, there is ample evidence for the existence of neutral ion pairs at higher concentrations, and a large number of determinations of the association constants have been reported [45–47]. As noted by Malatesta and Zamboni [31], Bjerrum's ion-pair model allows the representation of the negative deviations from the DHLL with much less computational effort than the other theoretical models because it avoids the detailed calculation of the radial distribution function for the primitive model (*i.e.*, the model based on use of the hard core potential) for a higher change electrolyte.

Pitzer and Mayorga [48] noted that although ionic association is present in solutions of 2:2 electrolytes including divalent metal sulfates, re-dissociation is expected to occur at higher molalities because of the ionic strength variation of the activity coefficient factor. Degrees of association, α, at 298.15 K determined by Raman spectroscopy [46] show only a gradual increase from $\alpha = 0.009$ at 0.034 mol·kg^{-1} to $\alpha = 0.12$ at 3.304 mol·kg^{-1}. However, as noted by these authors, their spectroscopic measurements detect only contact (inner-sphere) complexes and not solvent-separated (outer-sphere) ion-pairs that could well show a different trend with concentration. The degree of association predicted by some thermodynamic models increases rapidly across the range of low concentrations but become practically constant or decreases ("redissociation") for concentrated solutions. See, for example, the paper by Wasylkiewicz [47]. Pitzer and Mayorga [48] showed that the observed negative deviations from the Debye-Hückel limiting law at low ionic strengths could be represented within the framework of the ion-interaction model by including an additional second virial term with a $\beta^{(2)}$ coefficient. Their model predicts that as the concentration approaches infinite dilution, then $K_1^{\circ} = -2\beta^{(2)}$ where K_1° is the thermodynamic association constant (*i.e.*, extrapolated to infinite dilution) for formation of the neutral complex. An advantage of this approach is that

ion-pairing does not need to be considered explicitly, which eliminates the need for iterative calculations of the ionic molalities and ionic strength.

The initial negative deviations of ln $\gamma_\pm$ from the Debye-Hückel limiting law for ZnSO$_4$(aq) at very low molalities is not evident in the experimental osmotic coefficients due to the fact that this behavior occurs much below the lower molality limit of $\approx$0.1 mol·kg^{-1} for isopiestic measurements.

Our primary goal was to extend the meager amount of thermodynamic data for ZnCl$_2$ + ZnSO$_4$ + H$_2$O mixtures at 298.15 K by making isopiestic measurements, and to obtain an extension of Pitzer's ion-interaction model that will accurately represent the experimental results over the investigated molality range. In contrast to ZnSO$_4$(aq), the amount of association in ZnCl$_2$(aq) solutions increases regularly with increasing molality, and thus it was necessary to include explicitly the presence of equilibrium amounts of zinc-chloride complexes in order to obtain quantitative ion-interaction models for the thermodynamic properties of the ZnCl$_2$(aq) and ZnCl$_2$ + ZnSO$_4$ + H$_2$O systems. Modeling of the ZnCl$_2$(aq) system was done by treating it as a mixture containing the ZnCl$^+$ complex, and the derived parameters for (Zn^{2+},2Cl$^-$) and (ZnCl$^+$,Cl$^-$) interactions were then used for the subsequent modeling of the ZnCl$_2$ + ZnSO$_4$ + H$_2$O solutions.

2. Experimental section

The isopiestic apparatus and experimental procedure used in this work at the University of Belgrade are essentially the same as previously described [49]. Duplicate samples of each of the mixed electrolyte solutions, the KCl(aq) reference solution, and the single salt solutions ZnSO$_4$(aq) and ZnCl$_2$(aq) were equilibrated at 298.15 ± 0.01 K for appropriate times that ranged between 3 and 21 days, with the longer times being required at lower molalities. The molalities of duplicate pairs of solutions at isopiestic equilibrium agreed to ±2 × 10^{-3} mol·kg^{-1}

or better, with the average molality being accepted for each pair of solution samples. Buoyancy corrections were made for all weightings.

The ZnSO$_4$(aq) stock solution was prepared from Sigma-Aldrich suprapure grade ZnSO$_4\cdot$7H$_2$O (reported mass fraction 0.99999) and double-distilled, deionized water. The molality of this stock solution was determined by two gravimetric methods: 1) by addition of (NH$_4$)$_2$HPO$_4$ to aliquots of ZnSO$_4$(aq) to yield a precipitate of ZnNH$_4$PO$_4$, followed by calcining of the precipitate at 1173 to 1273 K to form Zn$_2$P$_2$O$_7$ [50]; and 2) from the masses of anhydrous ZnSO$_4$ obtained after dehydration of stock solution aliquots followed by heating of the residues at 673 to 723 K. The average molality of ZnSO$_4$(aq) for each method was determined using three samples. The combined average result from all of these analyses is 1.4319 ± 0.0025 mol·kg^{-1}. The assumed molar masses are 161.4526 g·mol^{-1} for ZnSO$_4$ and 304.7233 g·mol^{-1} for Zn$_2$P$_2$O$_7$.

The ZnCl$_2$(aq) stock solution was prepared from Sigma-Aldrich suprapure grade ZnCl$_2$ (reported mass fraction 0.99999) and double distilled, deionized water. Following the procedure of Rard and Miller [7], the initial stock solution was acidified as described in the next paragraph in order to avoid precipitation of zinc hydroxide or a hydrous oxy-chloride or hydroxy-chloride upon dilution.

The ZnCl$_2$(aq) stock solution was first acidified with just the minimum amount of concentrated analytical reagent grade HCl required so that dilution of a sample with water no longer resulted in precipitation. The slightly acidified solution was then heated to about 335 K in order to dissolve any residual precipitate or colloidal material. Water lost during heating was restored, the solution was rechecked for precipitation, and additional HCl was added if required. When dilution of an acidified sample did not cause precipitation after 2 days, the adjustment was considered to be complete. Solutions adjusted in this manner have the correct stoichiometric 2:1 ratio of chloride-to-zinc [7].

The molality of the $ZnCl_2$(aq) stock solution was determined gravimetrically by conversion of three samples to $ZnSO_4$ by addition of excess H_2SO_4 and evaporating the resulting solution, followed by drying of the residues between 673 and 723 K, and also in triplicate gravimetrically as $Zn_2P_2O_7$ by the same procedure as described above for $ZnSO_4$(aq). The average $ZnCl_2$(aq) molality from these analyses is 2.9125 ± 0.0008 mol·kg^{-1}, assuming the molar mass of $ZnCl_2$ to be 136.2960 g·mol^{-1}.

The reference KCl(aq) stock solution was prepared from Sigma-Aldrich suprapure grade KCl (mass fraction 0.9999) 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. The resulting average value is 4.0571 ± 0.0006 mol·kg^{-1}, assuming the molar mass of KCl to be 74.5513 g·mol^{-1}.

The three mixed $ZnCl_2 + ZnSO_4 + H_2O$ stock solutions were prepared by mixing known masses of the $ZnCl_2$(aq) and $ZnSO_4$(aq) stock solutions.

Osmotic coefficients of the $\{xZnCl_2 + (1 - x)ZnSO_4\}$(aq) solutions at 298.15 K were calculated from the isopiestic molalities using the fundamental equation for isopiestic equilibrium:

$$\phi = \nu_R m_R \phi_R \bigg/ \sum_i \nu(i)m_i = \nu_R m_R \phi_R \big/ (2 + x)m_T \tag{1}$$

where $\nu(i)$ is the stoichiometric ionization number of the electrolyte i $\{\nu(1) = 3$ for $ZnCl_2$ and $\nu(2) = 2$ for $ZnSO_4\}$, m_i is the molality of electrolyte i, x is the molality fraction of $ZnCl_2$, $m_T = m_1 + m_2$ is the total molality where m_1 is the stoichiometric molality of $ZnCl_2$ and m_2 is the stoichiometric molality of $ZnSO_4$, 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 standard KCl(aq) are denoted with a subscript R. The

osmotic coefficient of each KCl(aq) reference solution at 298.15 K was calculated using the ion-interaction (Pitzer) model and parameters reported by Archer [29].

The experimental results are given in Table 1. Quantities reported are the isopiestic molalities of the reference solution KCl(aq), m_R; the total isopiestic molalities, m_T, of the $\{xZnCl_2 + (1 - x)ZnSO_4\}$(aq) solutions; and the "stoichiometric" osmotic coefficients (*i.e.*, those calculated assuming complete dissociation), ϕ, of $\{xZnCl_2 + (1 - x)ZnSO_4\}$(aq) at 298.15 K along with the molality fraction x of $ZnCl_2$. Figure 1 is a plot of our experimental ϕ values at constant x as a function of m_T. The ϕ curves at the three mixture ratios are intermediate between those of the limiting binary electrolytes at lower molalities but are closer to the curve for $ZnCl_2$(aq). However, at higher values of m_T the ϕ curves of the mixtures are higher than those of both binary electrolytes.

3. Complex formation and association constants in ZnSO₄(aq) and ZnCl₂(aq) solutions

3.1. ZnSO₄(aq) solutions

As was discussed in the Introduction, the observed negative deviations of the activity coefficients from the DHLL at low molalities do not provide unambiguous evidence for complex formation because they can also be understood as resulting from the linearization approximation used for solving the Poisson-Boltzmann distribution. However, it has long been recognized that the electrical conductances of ZnSO₄(aq) and other aqueous divalent metal sulfates are significantly lower than those expected for strong electrolyte solutions, which may be explained by the partial formation of an uncharged complex [51]:

$$\text{Zn}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) \underset{\leftarrow}{\overset{\rightarrow}{}} \text{ZnSO}_4^0(\text{aq}) \tag{2}$$

Association constants for this reaction have been determined by electrical conductance measurements, spectrophotometry, isopiestic and freezing temperature measurements, Emf

measurements, and calorimetry. Wasylkiewicz [47] summarized published association constants at 298.15 K for reaction (2), which show a nearly three-fold variation from $K_1^\circ = 111$ to 309. Katayama [52] derived values of K_1° from electrical conductance measurements over the temperature range from 273.15 to 318.15 K that also yielded the enthalpy and entropy changes for this reaction.

Raman spectroscopic measurements by Rudolph *et al.* [46] yielded the equilibrium constant for the conversion of the outer-sphere sulfate complex $Zn(OH_2)_6(SO_4)$ to the inner-sphere sulfate complex $Zn(OH_2)_5(OSO_3)$, K_{12}°, whereas the association constants determined by the methods described in the previous paragraph yield K_1° for all of the complexes, both inner- and outer-sphere. That is,

$$K_{12}^\circ = a\big(Zn(OH_2)_5(OSO_3)\big)/a\big(Zn(OH_2)_6(SO_4)\big) \tag{3}$$

$$K_1^\circ = \{a\big(Zn(OH_2)_6(SO_4) + Zn(OH_2)_5(OSO_3)\big)\}/a\big(Zn(OH_2)_6^{2+}\big)a\big(SO_4^{2-}\big) \tag{4}$$

where $a(i)$ denotes the thermodynamic activity of species i. These authors wrote their chemical formulae with six inner sphere waters for the Zn(II) aquo ion as this coordination is well established, and assumed that only one water molecule would be displaced when the inner-sphere sulfate complex forms. As noted by Rudolph *et al.* [46], ultrasonic absorption measurements also allow the individual steps of the association reaction to be studied, but the results for K_{12}° obtained by this method do not agree well with those obtained by Raman specroscopy. However, for the analysis of macroscopic thermodynamic properties such as osmotic and activity coefficients, K_1° is the pertinent quantity. Normally, the equilibrium constant described by Eq. (4) is written without explicitly including the water molecules in the chemical formulae.

The rather large variation in the values of K_1° noted above, $K_1^\circ = 111$ to 309 at 298.15 K, will not impact the thermodynamic analysis by Pitzer's ion-interaction model because

complex formation is not included explicitly for divalent metal sulfates. However, the prediction that the $\beta^{(2)}$ parameter of this model is related to the association constant by $K_1^{\circ} = -2\beta^{(2)}$ [48] shall be tested by comparing its value with the published values of K_1°.

3.2. ZnCl₂(aq) solutions

As described in the Introduction, there is a large amount of evidence for complex formation in the ZnCl₂(aq) system from thermodynamic and transport property measurements. For example, osmotic coefficients, mutual diffusion coefficients, and Hittorf transport numbers at 298.15 K show anomalies around 0.15 mol·kg^{-1} that were attributed to the sudden onset of complex formation [7,37–39], and that the Hittorf transport numbers for Zn(II) becoming negative above 2.0 mol·kg^{-1} was attributed to the formation of negatively changed zinc-chloro complexes [17,19]. There is more direct evidence for the nature of these complexes that will now be described.

Irish *et al.* [53] performed Raman spectroscopic measurements for ZnCl₂(aq) at 298 K and concentrations of $c(ZnCl_2)$ = 2.19, 7.61, and 13.0 mol·dm^{-3}, along with several solutions having added chloride ion with Cl$^-$/Zn(II) molar ratios ranging up to 8.71. Based on these measurements, they were able to identify and assign Raman frequencies to the various chemical species that were present in different concentration regions: $Zn(OH_2)_6^{2+}$ when $c(ZnCl_2)$ < 13 mol·dm^{-3}, ZnCl$^+$(aq) when $c(ZnCl_2)$ < 4 mol·dm^{-3}, $ZnCl_2^0$(aq) when $c(ZnCl_2)$ > 4 mol·dm^{-3}, and $ZnCl_4(OH_2)_2^{2-}$ when $c(ZnCl_2)$ < 10 mol·dm^{-3}. The complex $ZnCl_3(OH_2)_3^-$ was not identified in this study. They also reported Raman frequencies when $c(ZnCl_2)$ > 10 mol·dm^{-3} that were attributed to the formation of polynuclear aggregates. The authors also referenced previous, less detailed, Raman spectroscopic studies with sometimes contradictory assignments of the bands.

Maciel *et al.* [54] reported Fourier transform NMR measurements at 300 K for ^{67}Zn(II) in ZnCl₂(aq) and in mixtures containing 12 mol·dm^{-3} HCl. Based on these

measurements they identified the four monomeric chloro-complexes of the type $ZnCl_n^{2-n}$ where n = 1 to 4, but the numbers of coordinated water molecules were not specified. Their Fig. 2, which is a speciation diagram for 0.5 mol·dm^{-3} Zn(II) in the presence of variable amounts of chloride, indicates that for ZnCl$_2$(aq) ≈ 60% of the Zn(II) is present as the un-complexed aquo ion, ≈ 15% each of ZnCl$^+$ and $ZnCl_2^0$, and ≈ 5% each of $ZnCl_3^-$ and $ZnCl_4^{2-}$. Darbari *et al.* [55] reported ultrasonic absorption and velocity measurements for ZnCl$_2$(aq) at temperatures between 258 and 298 K, for frequencies from 5 to 250 MHz and concentrations from 0.5 to 12 mol·dm^{-3}, and for some solutions containing KCl or HCl with higher Cl$^-$/Zn(II) ratios. Only a single relaxation process was observed over this entire concentration range, which they suggested always involved $ZnCl_4^{2-}$.

There are several studies that report the number of water molecules directly coordinated to the Zn(II) ion, the primary hydration number n_W. Dreier and Rabe [56] used extended X-ray fine structure (EXAFS) measurements to deduce that n_W = 6 to 7 at c(ZnCl$_2$) = 0.1 to 0.5 mol·kg^{-1}, but its value gradually decreased to n_W = 4.2 at m(ZnCl$_2$) = 2 mol·kg^{-1}, to n_W = 2.8 at m(ZnCl$_2$) = 5 mol·kg^{-1}, and to n_W = 2.0 at m(ZnCl$_2$) = 30 mol·kg^{-1}. The corresponding average number of chlorides directly coordinated to the Zn(II) increased from n_{Cl} = 0.9 at m(ZnCl$_2$) = 1 mol·kg^{-1} to n_{Cl} = 2.5 ± 0.1 at m(ZnCl$_2$) = 10 to 30 mol·kg^{-1}, with the total coordination number having values of n_W + n_{Cl} ≈ 5 when m(ZnCl$_2$) ≥ 5 mol·kg^{-1} and n_W + n_{Cl} ≈ 6 to 7 when m(ZnCl$_2$) ≤ 2 mol·kg^{-1}. The value n_{Cl} = 2.5 at m(ZnCl$_2$) = 30 mol·kg^{-1} exceeds the maximum value of n_{Cl} = 2 possible for monomeric complexes and implies that chloride ions and presumably the water molecules are being shared between the primary coordination spheres of Zn(II). Salmon [57] combined published neutron diffraction results with stability constants for the four monomeric chloride complexes to yield values of n_W ≈ 4.8 at c(ZnCl$_2$) = 0.27 mol·dm^{-3} and n_W ≈ 3.0 to 3.5 at c(ZnCl$_2$) = 1.07 to 3.83 mol·dm^{-3}, where a wide range of stability constant values was used in their calculations. These two sets of n_W

values [56,57] are approximately consistent. Matsubara and Waseda [58] reported anomalous X-ray scattering results of $n_W = 5.7 \pm 0.7$ at $c(ZnCl_2) = 0.98$ mol·dm^{-3} and $n_W = 6.2 \pm 0.2$ at $c(ZnCl_2) = 2.85$ mol·dm^{-3}, which are equal within their uncertainty limits. It should be noted that their value $n_W = 6.2 \pm 0.2$ at $c(ZnCl_2) = 2.85$ mol·dm^{-3} is significantly larger than $n_W \approx 3$ to 4 from the two other cited studies [56,57]. Ohtaki and Radnai [59] reviewed structural data for various hydrated hydrated ions including Zn(II). They cited an X-ray diffraction study that yielded values of $n_W = 1.7$ to 0.2 for $m(ZnCl_2) = 9.0$ to 31 mol·kg^{-1}. The lower values of n_W obtained at higher concentrations of ZnCl$_2$(aq) are quite reasonable because the increasing amounts of complex formation should cause water molecules to be displaced from the primary hydration sphere of the Zn(II) ion. Ohtaki and Radnai also cited (their Table 2) values for the primary hydration number of Zn(II) from measurements with X-ray and neutron diffraction for a variety of different Zn(II) salts that yield $n_W = 5.3$ to 6.6, with the values clustering around $n_W = 6$ for the Zn(II) aquo ion in the absence of complex formation.

Kaatze *et al*. [60,61] reported complex permittivity measurements for ZnCl$_2$(aq) at 298.15 K over the concentration range $c(ZnCl_2) = 0.48$ to 7.4 mol·dm^{-3} using dielectric spectroscopy, along with the electrical conductivities required to separate the dielectric results into contributions from dielectric polarization processes and ionic drift. No contribution to the dielectric spectrum from dipolar ion complexes was observed at $c(ZnCl_2) = 0.48$ mol·dm^{-3}. At higher concentrations the results provided strong evidence for the presence of the dipolar complex ZnCl$^+$(aq) in addition to the fully dissociated ions. However, as noted by the authors, the neutral complex ZnCl$_2$(aq) and possibly the higher order complexes may not be dipolar and thus would not be detected. The fraction of ZnCl$^+$(aq) relative to the total concentration of Zn(II) derived from these measurements ranges between about 7% and 14% as estimated from Fig. 6 of reference [60], and shows an initial rapid increase followed by a gradual decrease with increrasing concentration (redissociation). Thermodynamic modeling

calculations using two selected sets of stability constants for the four monomeric $ZnCl_n^{2-n}$ complexes, deliberately chosen to have very different values for the stability constants, yielded the same qualitative trend with fairly good numerical agreement with the experimental results.

Salmon [57] listed published values of the stepwise stability constants for formation of various $ZnCl_n^{2-n}$ according to the general reaction:

$$ZnCl_{n-1}^{3-n}(aq) + Cl^-(aq) \underset{\leftarrow}{\overset{\rightarrow}{}} ZnCl_n^{2-n}(aq) \tag{5}$$

where n = 1 to 4 and with the corresponding association constants (concentration products) denoted by K_n. These reported values range from K_1 = 0.32 to 5.25, K_2 = 0.32 to 4.79, K_3 = 0.03 to 10, and K_4 = 0.01 to 2.34. Not only is there a wide range of K_n values, but the ratios of a pair of the K_i from an individual study generally differ considerably from those reported in different studies. For example, the ratios of stability constants for an individual study show variations of K_2/K_1 = 0.11 to 11 and K_4/K_1 = 5 × 10^{-3} to 2.9 among these studies. Hsie and Selman [62] similarly reported values of $\log_{10} K_n$ that include many of the K_n values listed by Salmon [57] along with those from several additional studies. Hsie and Selman also listed the "inert" electrolyte used to control the ionic strength during the stability constant measurements, which was generally $HClO_4$, $LiClO_4$, or $NaClO_4$.

These large variations in the reported value of K_n makes it impossible to determine which set is the most reliable. Obvious contributing factors to these inconsistent sets of stability constants are the difficulties in simultaneously extracting four different stability constants from a series of measurements along with differences in the ionic strength among the various studies. However, Hsie and Selman [62] also listed values of the stability constants for formation of complexes of the type $MZnCl_3^0$ where M^+ = H^+, Na^+, K^+, Rb^+, or Cs^+; $HZnCl_4^-$; $M_2ZnCl_3^+$ where M^+ = K^+, Rb^+, or Cs^+; and mixed complexes involving H^+ and Li^+. Not all of the studies reporting stability constants for the $ZnCl_n^{2-n}$ complexes corrected

their results for the presence of the protonated or alkali metal complexes, and this neglect adds to the uncertainties and inconsistencies.

For the analysis of the isopiestic data for the $ZnCl_2$(aq) and $\{xZnCl_2 + (1 - x)ZnSO_4\}$(aq) systems we accepted the value of $K_1^o = 4.5$ at 298.15 K from the study of Lutfullah *et al.* [18] as being the most reliable estimate because it was determined in the absence of other cations that would have produced additional types of complexes in the solutions and thereby increased uncertainties in the derived value of K_1^o. Although the $ZnCl^+$(aq) complex should be the predominant one in the molality range pertinent to the present study, some smaller amounts of higher-order $ZnCl_n^{2-n}$(aq) complexes are probably also present. As described in this section, the available experimental data are not sufficiently consistent to evaluate the concentrations of these higher-order complexes. However, in the $\{xZnCl_2 + (1 - x)ZnSO_4\}$(aq) mixtures studied here the Cl^-:Zn(II) ratio is < 2 (0.61 to 1.59) and thus the higher-order complexes will be less important, and it should be adequate to analyze our isopiestic results by including only the $ZnCl^+$(aq) complex.

4. Results and discussion

4.1. Relations between osmotic coefficients, mean and ionic activity coefficients, and composition scales when the solutions are treated as being fully dissociated electrolytes and when the $ZnCl^+$(aq) complex is explicitly considered

The thermodynamic properties of the $ZnCl_2$(aq), $ZnSO_4$(aq), and $\{xZnCl_2 + (1 - x)ZnSO_4\}$(aq) systems may be analyzed in terms of the stoichiometric molalities yielding, for example, the mean molal activity of the individual electrolytes, by formally assuming that they are completely dissociated. This is a traditional approach. As an alternative, the thermodynamic properties of these systems may instead be analyzed by assuming the

presence of complex formation. As described above, within the framework of Pitzer's ion-interaction model, $ZnSO_4$ will be formally treated as if it were a completely dissociated electrolyte, whereas the presence of the $ZnCl^+(aq)$ complex will be explicitly considered when analyzing the thermodynamic properties of $ZnCl_2(aq)$ and $\{xZnCl_2 + (1 − x)ZnSO_4\}(aq)$. In this section we give the relations between the different composition scales and the osmotic and activity coefficients based on these two different assumptions about speciation.

Let m_1 denote the stoichiometric or "as added" molality of $ZnCl_2$ and m_2 denote the stoichiometric or "as added" molality of $ZnSO_4$, not only in their single salt solutions but also in their mixtures. Then, the total molality of the solution, m_T, is given by

$$m_T = m_1 + m_2 \tag{6}$$

where both m_1 and $m_2 > 0$ mol·kg^{-1} when both electrolytes are present, and either $m_1 = 0$ or $m_2 = 0$ for a single electrolyte solution. If a portion of the Zn(II) is assumed to undergo association to form the $ZnCl^+$ complex, then the fraction associated, $\alpha(ZnCl^+)$, is given by

$$\alpha = m\left(ZnCl^+\right)\big/m_T \tag{7}$$

where $m(ZnCl^+)$ is the equilibrium molality of this complex. The corresponding equilibrium molalities of the other the ionic species are then given by:

$$m\left(Zn^{2+}\right) = \left(1-\alpha\right)m_T \tag{8}$$

$$m\left(SO_4^{2-}\right) = \left(1-x\right)m_T = m_2 \tag{9}$$

$$m\left(Cl^-\right) = \left(2x-\alpha\right)m_T \tag{10}$$

The ionic strength of the solutions based on assumed complete dissociation is given by

$$I = \left(1/2\right)\sum_i m_i \left\{z(i)\right\}^2$$
$$= 3m_1 + 4m_2 \tag{11}$$
$$= (4 − x)m_T$$

whereas the ionic strength calculated with the assumed equilibrium speciation (denoted with a subscript e for equilibrium) is given by:

$$I_e = (1/2) \sum_i \{m(i)\}_e \{z(i)\}^2$$
$$= (1/2)\{4m(Zn^{2+}) + m(ZnCl^+) + m(Cl^-) + 4m(SO_4^{2-})\} \tag{12}$$
$$= (4 - 2\alpha - x)m_T$$

Thus,

$$I_e = I - 2\alpha m_T \tag{13}$$

The osmotic coefficient is usually defined in terms of assumed complete dissociation, ϕ, but an alternative osmotic, ϕ_e, can be defined in terms of the equilibrium speciation. These two types of osmotic coefficients are related by their definitions:

$$\ln a_w = -\left(\sum_i \nu(i)m_i\right) M_w \phi$$
$$= -\left(\sum_i \{m(i)\}_e\right) M_w \phi_e \tag{14}$$

where a_w is the thermodynamic activity of water and $M_w = 0.0180153$ kg·mol^{-1} is the molar mass of water. For the assumption of complete dissociation,

$$\sum_i \nu(i)m_i = 3m_1 + 2m_2 = (2 + x)m_T \tag{15}$$

and for the assumption of equilibrium speciation with formation of the $ZnCl^+(aq)$ complex:

$$\sum_i \{m(i)\}_e = m(Zn^{2+}) + m(ZnCl^+) + m(Cl^-) + m(SO_4^{2-})$$
$$= (2 + x - \alpha)m_T \tag{16}$$

Therefore,

$$\phi_e = (2 + x)m_T \phi \Big/ \{m(Zn^{2+}) + m(ZnCl^+) + m(Cl^-) + m(SO_4^{2-})\}$$
$$= \{(2 + x)/(2 + x - \alpha)\}\phi \tag{17}$$

The corresponding relation between the mean molal activity coefficient, $\gamma_\pm$, of $ZnCl_2$ in $ZnCl_2$(aq) and the ionic activity coefficients is:

$$\gamma_\pm^3 = \gamma_e(Zn^{2+})\{\gamma_e(Cl^-)\}^2\left[m(Zn^{2+})\{m(Cl^-)\}^2/4(m_1)^3\right]$$
$$= \frac{(1-\alpha)(2-\alpha)^2}{4}\gamma_e(Zn^{2+})\{\gamma_e(Cl^-)\}^2 \tag{18}$$

The equations for the thermodynamic activities of the hypothetical pure binary electrolytes based on the equilibrium speciation $\{(Zn^{2+},2Cl^-), (Zn^{2+}, SO_4^{2-}), (ZnCl^+,Cl^-),$ and $(2ZnCl^+, SO_4^{2-})\}$ are:

$$a(Zn^{2+},2Cl^-) = m(Zn^{2+})\{m(Cl^-)\}^2\gamma_e(Zn^{2+})\{\gamma_e(Cl^-)\}^2/(m^o)^3$$
$$= (1-\alpha)(2x-\alpha)^2(\frac{m_T}{m^o})^3\gamma_e(Zn^{2+})\{\gamma_e(Cl^-)\}^2 \tag{19}$$

$$a(Zn^{2+},SO_4^{2-}) = m(Zn^{2+})m(SO_4^{2-})\gamma_e(Zn^{2+})\gamma_e(SO_4^{2-})/(m^o)^2$$
$$= (1-\alpha)(1-x)(\frac{m_T}{m^o})^2\gamma_e(Zn^{2+})\gamma_e(SO_4^{2-}) \tag{20}$$

$$a(ZnCl^+,Cl^-) = m(ZnCl^+)m(Cl^-)\gamma_e(ZnCl^+)\gamma_e(Cl^-)/(m^o)^2$$
$$= \alpha(2x-\alpha)(\frac{m_T}{m^o})^2\gamma_e(ZnCl^+)\gamma_e(Cl^-) \tag{21}$$

$$a(2ZnCl^+,SO_4^{2-}) = \{m(ZnCl^+)\}^2 m(SO_4^{2-})\{\gamma_e(ZnCl^+)\}^2\gamma_e(SO_4^{2-})/(m^o)^3$$
$$= \alpha^2(1-x)(\frac{m_T}{m^o})^3\{\gamma_e(Zn^{2+})\}^2\gamma_e(SO_4^{2-}) \tag{22}$$

where m^o = 1 mol·kg^{-1}.

4.2. Extended ion-interaction (Pitzer) model equations for $ZnSO_4$(aq)

Archer and Rard [63] described an extension of the equations of Pitzer and Mayorga [48] that represented available thermodynamic data for $MgSO_4$(aq) essentially to within experimental accuracy over wide ranges of molality and temperature. This extended form includes an ionic

strength third virial coefficient of the form described by Archer [28]. Albright *et al.* [21] and subsequently Miladinović *et al.* [27] included an additional $D^{(0)}(Zn,SO_4)$ term that was needed to represent the available osmotic and activity coefficients of $ZnSO_4(aq)$ at 298.15 K accurately. For the osmotic coefficient of $ZnSO_4(aq)$ their equation has the form:

$$\phi - 1 = -|z(Zn^{2+})z(SO_4^{2-})|A_\phi I^{1/2}/(1 + bI^{1/2}) + 2m_2\{\nu(Zn^{2+})\nu(SO_4^{2-})/\nu\}B^\phi(Zn,SO_4)$$
$$+ 4\,m_2^2\{\nu(Zn^{2+})^2\nu(SO_4^{2-})z(Zn^{2+})/\nu\}C^{T\phi}(Zn,SO_4)$$
$$+ 6\,m_2^3[\{\nu(Zn^{2+})\nu(SO_4^{2-})\}^2/\nu]\,D^{(0)}(Zn,SO_4) \tag{23}$$

where $\nu(i)$ has already been defined, $z(i)$ is the valence of an ion of type i, m_2 is the stoichiometric molality, and $I = 4m_2$. For this system, $\nu(Zn^{2+}) = \nu(SO_4^{2-}) = 1$, $\nu = \nu(Zn^{2+}) + \nu(SO_4^{2-}) = 2$, $z(Zn^{2+}) = +2$, $z(SO_4^{2-}) = -2$, and b = 1.2 $kg^{1/2} \cdot mol^{-1/2}$. At $T = 298.15$ K, $A_\phi = 0.391475$ $kg^{1/2} \cdot mol^{-1/2}$ [64]. The ionic-strength dependent quantities $B^\phi(Zn,SO_4)$ and $C^{T\phi}(Zn,SO_4)$ are defined as:

$$B^\phi(Zn,SO_4) = \beta^{(0)}(Zn,SO_4) + \beta^{(1)}(Zn,SO_4)\cdot\exp(-\alpha_1 I^{1/2}) +$$
$$\beta^{(2)}(Zn,SO_4)\cdot\exp(-\alpha_2 I^{1/2}) \tag{24}$$

and

$$C^{T\phi}(Zn,SO_4) = C^{(0)}(Zn,SO_4) + C^{(1)}(Zn,SO_4)\cdot\exp(-\omega I^{1/2}) \tag{25}$$

The values of the exponential coefficients are generally fixed at $\alpha_1 = 1.4$ $kg^{1/2} \cdot mol^{-1/2}$ and $\alpha_2 = 12$ $kg^{1/2} \cdot mol^{-1/2}$ for divalent metal sulfates [48]. The corresponding expression for the natural logarithm of the mean activity coefficient $\gamma_\pm$ of $ZnSO_4(aq)$ is:

$$\ln \gamma_\pm = -|z(Zn^{2+})z(SO_4^{2-})|A_\phi\{I^{1/2}/(1 + bI^{1/2}) + (2/b)\ln(1 + bI^{1/2})\} +$$
$$2m_2\{\nu(Zn^{2+})\nu(SO_4^{2-})/\nu\}[2\beta^{(0)}(Zn,SO_4) + 2\{\beta^{(1)}(Zn,SO_4)/\alpha_1^2 I\}\{1 -$$
$$(1 + \alpha_1 I^{1/2} - \alpha_1^2 I/2)\exp(-\alpha_1 I^{1/2})\} + 2\{\beta^{(2)}(Zn,SO_4)/\alpha_2^2 I\}\{1 - (1 + \alpha_2 I^{1/2} -$$
$$\alpha_2^2 I/2)\exp(-\alpha_2 I^{1/2})\}] + 2m_2^2\{\nu(Zn^{2+})^2\nu(SO_4^{2-})z(Zn^{2+})/\nu\}[3C^{(0)}(Zn,SO_4) +$$
$$4C^{(1)}(Zn,SO_4)\{6 - (6 + 6\omega I^{1/2} + 3\omega^2 I + \omega^3 I^{3/2} -$$
$$\omega^4 I^2/2)\exp(-\omega I^{1/2})\}/(\omega^4 I^2)] + 8m_2^3[\{\nu(Zn^{2+})\nu(SO_4^{2-})\}^2/\nu]D^{(0)}(Zn,SO_4) \tag{26}$$

Albright *et al.* [21] reported that the equation of Pitzer and Mayorga [48] was able to represent the experimental $ZnSO_4$(aq) ϕ values moderately well but some systematic cyclic deviations were present. Archer and Rard's extension [63] of the equation of Pitzer and Mayorga, equivalent to our Eq. (23) with $D^{(0)}(Zn,SO_4) = 0$, largely eliminated these systematic deviations and was able to represent the same results with near experimental accuracy up to about 3.3 $mol \cdot kg^{-1}$, but there were small systematic deviations at higher (supersaturated) molalities. However, including the $D^{(0)}(Zn,SO_4)$ term in Eq. (23) essentially removed these high-molality deviations and gave an accurate representation including in the supersaturated region.

Clegg *et al.* [65] have generalized the extended ion-interaction (Pitzer) model equations of Archer [28] for single electrolytes to represent multicomponent mixtures, including those undergoing self-association. Although their generalized extended Pitzer model equations could be further extended to include the $D^{(0)}(Zn,SO_4)$ term when analyzing the present results for $\{xZnCl_2 + (1 - x)ZnSO_4\}$(aq), this would add an unnecessary complication because the isopiestic measurements for the mixtures do not extend to the supersaturated region for $ZnSO_4$ where the $D^{(0)}(Zn,SO_4)$ term is needed. Consequently, we will analyze our isopiestic results without including the $D^{(0)}(Zn,SO_4)$ term.

Both Albright *et al.* [21] and Miladinović *et al.* [27] represented the available thermodynamic activity data for $ZnSO_4$(aq) with Eqs. (23) through (26) that include $D^{(0)}(Zn,SO_4)$ terms. Rard and Wijesinghe [66] described a method whereby the parameters of extended forms of Pitzer's ion-interaction model can be transformed directly into those for other ion-interaction models containing fewer parameters, with analytical solutions for the conversion equations. The extended Pitzer model of Miladinović *et al.* [27] was used as the

souce for the parameter transformations because their model was based on a larger data base that included their isopiestic data in addition to the earlier results of Albright et al. [21].

A slight modification of the approach of Rard and Wijesinghe [66] was used to convert the parameters for the ZnSO$_4$(aq) system. The $\beta^{(2)}$(Zn,SO$_4$)·exp($-\alpha_2 I^{1/2}$) term was introduced by Pitzer and Mayorga [48] to account for the negative deviations of the activity coefficients from the Debye-Hückel limiting law encountered for ZnSO$_4$(aq) and other electrolytes of this charge type. However, the large value $\alpha_2 = 12$ kg$^{1/2}$·mol$^{-1/2}$ was chosen to localize the effect of this term at low ionic strengths where the negative deviations are observed. For example, the contribution of this term to the osmotic coefficient, $m_2\beta^{(2)}$(Zn,SO$_4$)·exp($-\alpha_2 I^{1/2}$), is completely insignificant when $m_2 \geq 0.3$ mol·kg^{-1} and nearly insignificant ($\Delta\phi \approx 0.003$) at $m_2 = 0.1$ mol·kg^{-1} (the parameter transformation equations of Rard and Wijesinghe [66] are based on the osmotic coefficient).

The parametric transformation was performed in two stages. First, the $\beta^{(0)}$(Zn,SO$_4$), $\beta^{(1)}$(Zn,SO$_4$), $C^{(0)}$(Zn,SO$_4$), $C^{(1)}$(Zn,SO$_4$), and $D^{(0)}$(Zn, SO$_4$) of Miladinović et al. [27] were transformed into the $\beta^{(0)}$(Zn,SO$_4$), $\beta^{(1)}$(Zn,SO$_4$), $C^{(0)}$(Zn,SO$_4$), and $C^{(1)}$(Zn,SO$_4$) parameters of the new model while keeping the $\beta^{(2)}$(Zn,SO$_4$) parameter fixed. In this calculation the integrals of the transformation equations [66] were evaluated from $m_2 = 0$ to 3.56 mol·kg^{-1} where the upper molality is close to that of the saturated solution. Second, the $\beta^{(2)}$(Zn,SO$_4$) parameter of the new model was subsequently evaluated from the $\gamma_\pm$ values of Miladinović et al. by a least-squares calculation while keeping the other parameters fixed at their already transformed values. The resulting parameter values are reported in Table 2. The standard deviation $\sigma(\phi) = 0.0027$ for the present five-parameter model is based on comparison with the experimental ϕ values used by Miladinović et al. to constrain their original six-parameter source model, and it is only very slightly larger than $\sigma(\phi) = 0.0026$ for the six-parameter

model, indicating that these two models are nearly equivalent in accuracy for $m_2 \leq 3.56$ mol·kg^{-1}. Using the relation $K_1^\circ = -2\beta^{(2)}$ [48] yields $K_1^\circ = 137.4$, which is well within the range of published values: $111 \leq K_1^\circ \leq 309$ [47]. However, this agreement could be accidental because earlier analyses [21,48] yield values of $\beta^{(2)}$ that are smaller by about a factor of 2.

4.3. Extended ion-interaction (Pitzer) model equations for ZnCl$_2$(aq) and {xZnCl$_2$ + (1 − x)ZnSO$_4$}(aq)

Clegg et al. [65], in their Appendix I, have generalized the extended Pitzer single-electrolyte model of Archer [28] to represent electrolyte solution mixtures of arbitrary complexity. These equations have been applied successfully to complex mixtures including those undergoing self-association such as {xH$_2$SO$_4$ + (1 − x)MgSO$_4$}(aq) [67]. For the {xZnCl$_2$ + (1 − x)ZnSO$_4$}(aq) system, assuming that ZnCl$^+$ in present in equilibrium amounts, the Clegg et al. equations yield for the osmotic coefficient:

$$
\begin{aligned}
\phi_e = 1 + \Bigg\{ 2 \Big/ \sum_i m(i) \Bigg\} & \Bigg[-A_\phi (I_e)^{3/2} \Big/ \Big\{ 1 + b(I_e)^{1/2} \Big\} + \\
& m(\text{ZnCl}^+) m(\text{Cl}^-) \Big\{ B^\phi(\text{ZnCl},\text{Cl}) + ZC^{T\phi}(\text{ZnCl},\text{Cl}) \Big\} + \\
& m(\text{ZnCl}^+) m(\text{SO}_4^{2-}) \Big\{ B^\phi(\text{ZnCl},\text{SO}_4) + ZC^{T\phi}(\text{ZnCl},\text{SO}_4) \Big\} + \\
& m(\text{Zn}^{2+}) m(\text{Cl}^-) \Big\{ B^\phi(\text{Zn},\text{Cl}) + ZC^{T\phi}(\text{Zn},\text{Cl}) \Big\} + \\
& m(\text{Zn}^{2+}) m(\text{SO}_4^{2-}) \Big\{ B^\phi(\text{Zn},\text{SO}_4) + ZC^{T\phi}(\text{Zn},\text{SO}_4) \Big\} + \\
& m(\text{ZnCl}^+) m(\text{Zn}^{2+}) \Big\{ \theta(\text{ZnCl},\text{Zn}) + m(\text{Cl}^-)\psi(\text{ZnCl},\text{Zn},\text{Cl}) + m(\text{SO}_4^{2-})\psi(\text{ZnCl},\text{Zn},\text{SO}_4) \Big\} + \\
& m(\text{Cl}^-) m(\text{SO}_4^{2-}) \Big\{ \theta(\text{Cl},\text{SO}_4) + m(\text{ZnCl}^+)\psi(\text{ZnCl},\text{Cl},\text{SO}_4) + m(\text{Zn}^{2+})\psi(\text{Zn},\text{Cl},\text{SO}_4) \Big\} \Bigg]
\end{aligned}
\tag{27}
$$

and for the ionic activity coefficients:

$$\ln\gamma_e\left(\text{Zn}^{2+}\right) = 4F + m\left(\text{Cl}^-\right)\left\{2B(\text{Zn},\text{Cl}) + ZC^T(\text{Zn},\text{Cl})\right\} + m\left(\text{SO}_4^{2-}\right)\left\{2B(\text{Zn},\text{SO}_4) + ZC^T(\text{Zn},\text{SO}_4)\right\} +$$
$$2m\left(\text{ZnCl}^+\right)m\left(\text{Cl}^-\right)C^T(\text{ZnCl},\text{Cl}) + 2m\left(\text{ZnCl}^+\right)m\left(\text{SO}_4^{2-}\right)C^T(\text{ZnCl},\text{SO}_4) +$$
$$2m\left(\text{Zn}^{2+}\right)m\left(\text{Cl}^-\right)C^T(\text{Zn},\text{Cl}) + 2m\left(\text{Zn}^{2+}\right)m\left(\text{SO}_4^{2-}\right)C^T(\text{Zn},\text{SO}_4) +$$
$$m\left(\text{ZnCl}^+\right)\left\{2\theta(\text{ZnCl},\text{Zn}) + m\left(\text{Cl}^-\right)\psi(\text{ZnCl},\text{Zn},\text{Cl}) + m\left(\text{SO}_4^{2-}\right)\psi(\text{ZnCl},\text{Zn},\text{SO}_4)\right\} +$$
$$m\left(\text{Cl}^-\right)m\left(\text{SO}_4^{2-}\right)\psi(\text{Zn},\text{Cl},\text{SO}_4)$$

$$(28)$$

$$\ln\gamma_e\left(\text{ZnCl}^+\right) = F + m\left(\text{Cl}^-\right)\left\{2B(\text{ZnCl},\text{Cl}) + ZC^T(\text{ZnCl},\text{Cl})\right\} + m\left(\text{SO}_4^{2-}\right)\left\{2B(\text{ZnCl},\text{SO}_4) + ZC^T(\text{ZnCl},\text{SO}_4)\right\} +$$
$$m\left(\text{ZnCl}^+\right)m\left(\text{Cl}^-\right)C^T(\text{ZnCl},\text{Cl}) + m\left(\text{ZnCl}^+\right)m\left(\text{SO}_4^{2-}\right)C^T(\text{ZnCl},\text{SO}_4) +$$
$$m\left(\text{Zn}^{2+}\right)m\left(\text{Cl}^-\right)C^T(\text{Zn},\text{Cl}) + m\left(\text{Zn}^{2+}\right)m\left(\text{SO}_4^{2-}\right)C^T(\text{Zn},\text{SO}_4) +$$
$$m\left(\text{Zn}^{2+}\right)\left\{2\theta(\text{ZnCl},\text{Zn}) + m\left(\text{Cl}^-\right)\psi(\text{ZnCl},\text{Zn},\text{Cl}) + m\left(\text{SO}_4^{2-}\right)\psi(\text{ZnCl},\text{Zn},\text{SO}_4)\right\} +$$
$$m\left(\text{Cl}^-\right)m\left(\text{SO}_4^{2-}\right)\psi(\text{ZnCl},\text{Cl},\text{SO}_4)$$

$$(29)$$

$$\ln\gamma_e\left(\text{Cl}^-\right) = F + m\left(\text{ZnCl}^+\right)\left\{2B(\text{ZnCl},\text{Cl}) + ZC^T(\text{ZnCl},\text{Cl})\right\} + m\left(\text{Zn}^{2+}\right)\left\{2B(\text{Zn},\text{Cl}) + ZC^T(\text{Zn},\text{Cl})\right\} +$$
$$m\left(\text{ZnCl}^+\right)m\left(\text{Cl}^-\right)C^T(\text{ZnCl},\text{Cl}) + m\left(\text{ZnCl}^+\right)m\left(\text{SO}_4^{2-}\right)C^T(\text{ZnCl},\text{SO}_4) +$$
$$m\left(\text{Zn}^{2+}\right)m\left(\text{Cl}^-\right)C^T(\text{Zn},\text{Cl}) + m\left(\text{Zn}^{2+}\right)m\left(\text{SO}_4^{2-}\right)C^T(\text{Zn},\text{SO}_4) +$$
$$m\left(\text{SO}_4^{2-}\right)\left\{2\theta(\text{Cl},\text{SO}_4) + m\left(\text{ZnCl}^+\right)\psi(\text{ZnCl},\text{Cl},\text{SO}_4) + m\left(\text{Zn}^{2+}\right)\psi(\text{Zn},\text{Cl},\text{SO}_4)\right\} +$$
$$m\left(\text{ZnCl}^+\right)m\left(\text{Zn}^{2+}\right)\psi(\text{ZnCl},\text{Zn},\text{Cl})$$

$$(30)$$

$$\ln\gamma_e\left(\text{SO}_4^{2-}\right) = 4F + m\left(\text{ZnCl}^+\right)\left\{2B(\text{ZnCl},\text{SO}_4) + ZC^T(\text{ZnCl},\text{SO}_4)\right\} + m\left(\text{Zn}^{2+}\right)\left\{2B(\text{Zn},\text{SO}_4) + ZC^T(\text{Zn},\text{SO}_4)\right\} +$$
$$2m\left(\text{ZnCl}^+\right)m\left(\text{Cl}^-\right)C^T(\text{ZnCl},\text{Cl}) + 2m\left(\text{ZnCl}^+\right)m\left(\text{SO}_4^{2-}\right)C^T(\text{ZnCl},\text{SO}_4) +$$
$$2m\left(\text{Zn}^{2+}\right)m\left(\text{Cl}^-\right)C^T(\text{Zn},\text{Cl}) + 2m\left(\text{Zn}^{2+}\right)m\left(\text{SO}_4^{2-}\right)C^T(\text{Zn},\text{SO}_4) +$$
$$m\left(\text{Cl}^-\right)\left\{2\theta(\text{Cl},\text{SO}_4) + m\left(\text{ZnCl}^+\right)\psi(\text{ZnCl},\text{Cl},\text{SO}_4) + m\left(\text{Zn}^{2+}\right)\psi(\text{Zn},\text{Cl},\text{SO}_4)\right\} +$$
$$m\left(\text{ZnCl}^+\right)m\left(\text{Zn}^{2+}\right)\psi(\text{ZnCl},\text{Zn},\text{SO}_4)$$

$$(31)$$

where

$$Z = \sum_i \left\{m(i)\right\}_e \left|z(i)\right| = m\left(\text{ZnCl}^+\right) + 2m\left(\text{Zn}^{2+}\right) + m\left(\text{Cl}^-\right) + 2m\left(\text{SO}_4^{2-}\right) \qquad (32)$$

The ionic molalities are defined with Eqs. (7) to (10), I_e by Eq. (12), and

$$F = -A_\phi \left[\frac{(I_e)^{1/2}}{\{1 + b(I_e)^{1/2}\}} + (2/b)\ln\{1 + b(I_e)^{1/2}\} \right] +$$

$$m(\text{ZnCl}^+)m(\text{Cl}^-)\{B'(\text{ZnCl,Cl}) + ZC^{T'}(\text{ZnCl,Cl})/2\} +$$

$$m(\text{ZnCl}^+)m(\text{SO}_4^{2-})\{B'(\text{ZnCl,SO}_4) + ZC^{T'}(\text{ZnCl,SO}_4)/2\} + \qquad (33)$$

$$m(\text{Zn}^{2+})m(\text{Cl}^-)\{B'(\text{Zn,Cl}) + ZC^{T'}(\text{Zn,Cl})/2\} +$$

$$m(\text{Zn}^{2+})m(\text{SO}_4^{2-})\{B'(\text{Zn,SO}_4) + ZC^{T'}(\text{Zn,SO}_4)/2\}$$

The second-virial coefficients and their derivatives, for an arbitrary cation c and an arbitrary anion a, are given by:

$$B(c,a) = \beta^{(0)}(c,a) + \beta^{(1)}(c,a)g\{\alpha_1(c,a)(I_e)^{1/2}\} + \beta^{(2)}(c,a)g\{\alpha_2(c,a)(I_e)^{1/2}\} \qquad (34)$$

$$B'(c,a) = \left[\beta^{(1)}(c,a)g'\{\alpha_1(c,a)(I_e)^{1/2}\} + \beta^{(2)}(c,a)g'\{\alpha_2(c,a)(I_e)^{1/2}\} \right]/I_e \qquad (35)$$

$$B^\phi(c,a) = \beta^{(0)}(c,a) + \beta^{(1)}(c,a)\exp\{-\alpha_1(c,a)(I_e)^{1/2}\} + \beta^{(2)}(c,a)\exp\{-\alpha_2(c,a)(I_e)^{1/2}\} \qquad (36)$$

Analogously, for the third-virial coefficients:

$$C^T(c,a) = C^{(0)}(c,a) + 4C^{(1)}(c,a)h\{\omega(c,a)(I_e)^{1/2}\}, \qquad (37)$$

$$C^{T'}(c,a) = 4C^{(1)}(c,a)h'\{\omega(c,a)(I_e)^{1/2}\}\Big/I_e \qquad (38)$$

$$C^{T\phi}(c,a) = C^{(0)}(c,a) + C^{(1)}(c,a)\exp\{-\omega(c,a)(I_e)^{1/2}\} \qquad (39)$$

These equations contain the additional functions:

$$g(x) = 2\{1 - (1 + x)\exp(-x)\}\big/x^2 \qquad (40)$$

$$g'(x) = I_e\{\partial g(x)/\partial I_e\} = \exp(-x) - g(x) \qquad (41)$$

$$h(x) = \left[6 - \{6 + x(6 + 3x + x^2)\}\exp(-x) \right]\big/x^4 \qquad (42)$$

$$h'(x) = I_e\{\partial h(x)/\partial I_e\} = \{\exp(-x)/2\} - 2h(x) \qquad (43)$$

where $x = \alpha_i(c,a)(I_e)^{1/2}$ or $\omega(c,a)(I_e)^{1/2}$.

The $\beta^{(0)}$(Zn,SO$_4$), $\beta^{(1)}$(Zn,SO$_4$), $\beta^{(2)}$(Zn,SO$_4$), $C^{(0)}$(Zn,SO$_4$), and $C^{(1)}$(Zn,SO$_4$)

parameters have already been evaluated from the ZnSO$_4$(aq) thermodynamic activity data as

described in the preceeding section. In addition, the $\beta^{(2)}$ parameter is normally only used for

higher charge type electrolytes, and thus for our system $\beta^{(2)}$(Zn,Cl) = 0, $\beta^{(2)}$(ZnCl,Cl) = 0, and

$\beta^{(2)}$(ZnCl,SO$_4$) = 0. However, there are still 18 unknown parameters (12 for "binary"

electrolytes and 6 mixing parameters) that need to be evaluated from the ZnCl$_2$(aq) and

$\{x\text{ZnCl}_2 + (1 - x)\text{ZnSO}_4\}$(aq) activity data: $\beta^{(0)}$(Zn,Cl), $\beta^{(1)}$(Zn,Cl), $C^{(0)}$(Zn,Cl), $C^{(1)}$(Zn,Cl),

$\beta^{(0)}$(ZnCl,Cl), $\beta^{(1)}$(ZnCl,Cl), $C^{(0)}$(ZnCl,Cl), $C^{(1)}$(ZnCl,Cl), $\beta^{(0)}$(ZnCl,SO$_4$), $\beta^{(1)}$(ZnCl,SO$_4$),

$C^{(0)}$(ZnCl,SO$_4$), $C^{(1)}$(ZnCl,SO$_4$), θ(ZnCl,Zn), θ(Cl,SO$_4$), ψ(Zn,Cl,SO$_4$), ψ(ZnCl,Cl,SO$_4$),

ψ(ZnCl,Zn,Cl), and ψ(ZnCl,Zn,SO$_4$). The simultaneous evaluation of all 18 parameters would

be a formidable task, especially because the Zn^{2+}, ZnCl$^+$ and Cl$^-$ molalities must be evaluated

by iterative speciation calculations, and some of the resulting parameter values would be

highly correlated and some redundant to other parameters.

Including the presence of the species ZnCl$^+$ is essential to accurately model the

thermodynamic properties of ZnCl$_2$(aq) solutions. However, from ionic size considerations

we expect the (ZnCl$^+$,Cl$^-$) interactions to be much stronger than (ZnCl$^+$, SO$_4^{2-}$) interactions,

and thus largely determine the activity coefficients of the ZnCl$^+$ ion. Consequently, we made

the following simplification: $\beta^{(0)}$(ZnCl,SO$_4$) = 0, $\beta^{(1)}$(ZnCl,SO$_4$) = 0, $C^{(0)}$(ZnCl,SO$_4$) = 0, and

$C^{(1)}$(ZnCl,SO$_4$) = 0 and let the (ZnCl$^+$, SO$_4^{2-}$) interactions be represented by the

ψ(ZnCl,Cl,SO$_4$) and ψ(ZnCl,Zn,SO$_4$) mixing parameters. This reduced the number of model

parameters from 18 to 14.

The evaluation of model parameters was split into two parts. The parameters for

$\beta^{(0)}$(Zn,Cl), $\beta^{(1)}$(Zn,Cl), $C^{(0)}$(Zn,Cl), $C^{(1)}$(Zn,Cl), $\beta^{(0)}$(ZnCl,Cl), $\beta^{(1)}$(ZnCl,Cl), $C^{(0)}$(ZnCl,Cl),

$C^{(1)}$(ZnCl,Cl), θ(ZnCl,Zn) and ψ(ZnCl,Zn,Cl) at 298.15 K were evaluated first using the

critically assessed isopiestic results for $ZnCl_2$(aq) tabulated in Table 1 of Miladinović *et al.* [13], which include isopiestic data from references [7,10], together with mean activity coefficients from the Emf studies of Robinson and Stokes [10] and Lutfullah *et al.* [18]. The correct forms of the model equations for representing the thermodynamic activities of $ZnCl_2$(aq), Eqs. (27) through (33), are obtained by setting $m(SO_4^{2-}) = 0$.

It was necessary to calculate the molalities of the Zn^{2+}, $ZnCl^+$ and Cl^- ions for $ZnCl_2$(aq) solutions at 298.15 K by iterative speciation calculations. The total molalities of zinc and chloride must satisfy the following two mole balance equations (assuming that the concentration of free hydrogen and hydroxide ions are negligible):

$$m_1 = m(Zn^{2+}) + m(ZnCl^+) = m(Zn^{2+})\left\{1 + K_1^o m(Cl^-)\left[\gamma_e(Zn^{2+})\gamma_e(Cl^-)/\gamma_e(ZnCl^+)\right]\right\} \qquad (44)$$

$$2m_1 = m(Cl^-) + m(ZnCl^+) = m(Cl^-)\left\{1 + K_1^o m(Zn^{2+})\left[\gamma_e(Zn^{2+})\gamma_e(Cl^-)/\gamma_e(ZnCl^+)\right]\right\} \qquad (45)$$

where m_1 is the stoichiometric molality of the $ZnCl_2$(aq) solution and K_1^o is the corresponding thermodynamic association constant for the formation of $ZnCl^+$:

$$K_1^o = a_e(ZnCl^+)/[a_e(Zn^{2+})a_e(Cl^-)]$$
$$= m(ZnCl^+)\gamma_e(ZnCl^+)/[m(Zn^{2+})\gamma_e(Zn^{2+})m(Cl^-)\gamma_e(Cl^-)] \qquad (46)$$

As discussed above, $K_1^o = 4.5$ at 298.15 K was selected.

Initially, the mixing parameters and $m(ZnCl^+)$ were set equal to zero, values of $\gamma(Zn^{2+})$ and $\gamma(Cl^-)$ were approximated from the stoichiometric molalities using the extended Pitzer model and parameters for $ZnCl_2$(aq) reported by Miladinović *et al.* [13] that do not include complex formation, and the ion-interaction model parameters for the binary electrolyte

($ZnCl^+, SO_4^{2-} $) were set equal to zero. The resulting preliminary ionic activity coefficients were then used in Eqs. (44) and (45) to calculate an initial set of approximate ionic molalities of Zn^{2+}, $ZnCl^+$ and Cl^-; and these ionic molalities were then used with Eqs. (27) through (43) to generate a new set of ionic activity coefficients that were in turn used to generate an improved set of ionic molalities, *etc*. The iteration of the species molality and ionic activity coefficients calculations was continued until the calculated ionic strength I_e at each experimental molality differed by less than 0.01 % from the value obtained during the last cycle. For the least-squares evaluation of the model parameters, the quantities being used are ϕ and $\gamma_\pm$ (rather than ϕ_e and ionic activity coefficients) because their values do not change as the ionic molality calculations are refined. The resulting values of $\beta^{(0)}$(Zn,Cl), $\beta^{(1)}$(Zn,Cl), $C^{(0)}$(Zn,Cl), $C^{(1)}$(Zn,Cl), $\beta^{(0)}$(ZnCl,Cl), $\beta^{(1)}$(ZnCl,Cl), $C^{(0)}$(ZnCl,Cl), $C^{(1)}$(ZnCl,Cl), θ(ZnCl,Zn), and ψ(ZnCl,Zn,Cl) are reported in Table 2. Once these parameter values were established, values of θ(Cl,SO$_4$), ψ(Zn,Cl,SO$_4$), ψ(ZnCl,Cl,SO$_4$), and ψ(ZnCl,Zn,SO$_4$) were evaluated by a similar procedure using the isopiestic results for mixtures reported in Table 1, and their values are also reported in Table 2. Figure 2 shows the deviations, experimental minus model, for the osmotic coefficients of mixtures reported in Table 1.

Table 3 reports calculated values of α, ϕ, ϕ_e, γ_e(Zn^{2+}), γ_e(ZnCl$^+$), γ_e(Cl$^-$), and γ_e(SO$_4^{2-}$) as a function of the solution composition.

We note that Pitzer [68] described higher-order unsymmetrical mixing terms for pairs of ions of like sign but unequal change, θ^E, which are functions only of the charges of the pair of ions and of I_e. These terms were not included in the model equations because they are nearly insignificant at the ionic strengths of our isopiestic measurements.

4.3. Discussion

Figure 1, given earlier, is a plot of the experimental (stochiometric) osmotic coefficients ϕ of $\{x\mathrm{ZnCl_2} + (1-x)\mathrm{ZnSO_4}\}$(aq) from Table 1 along with those of the limiting binary solutions $\mathrm{ZnCl_2}$(aq) and $\mathrm{ZnSO_4}$(aq). The values of ϕ for the mixtures fall closer to the curve for $\mathrm{ZnCl_2}$(aq) rather than $\mathrm{ZnSO_4}$(aq), and also fall above the curves for both limiting binary solutions at higher molalities. This behavior is more complicated than observed for most mixtures of strong electrolytes, where the curves for the mixtures typically fall between those of the limiting binary solutions over most of the molality range. Similar complex behavior is also observed for the $x\mathrm{ZnCl_2} + (1-x)\mathrm{BaCl_2}\}$(aq) system at 298.15 K where the osmotic coefficients of the mixtures are shifted towards those of $\mathrm{ZnCl_2}$(aq), especially when $x > 0.6$ [14], and for the $\{x\mathrm{H_2SO_4} + (1-x)\mathrm{Na_2SO_4}\}$(aq) system at 298.15 K when $x > 0.5$ and where some of the mixture ϕ curves fall below the ϕ curve of $\mathrm{Na_2SO_4}$(aq) [69]. Sulfuric acid, like zinc chloride, is a partially associated electrolyte, and the complicated composition dependence of ϕ observed for these three mixed-electrolyte systems are obviously largely the result of changes in speciation due to complex formation.

Rard [69] used a simplified speciation calculation and found that a plot of ϕ_e versus I_e for $\{x\mathrm{H_2SO_4} + (1-x)\mathrm{Na_2SO_4}\}$(aq) showed more regular behavior as a function of x with no crossovers. Values of ϕ_e for $\{x\mathrm{ZnCl_2} + (1-x)\mathrm{ZnSO_4}\}$(aq) are reported in Table 3 and are plotted in Fig. 3 as functions of both m_T and I_e. The plot of ϕ_e versus I_e (bottom plot) also shows less complicated behavior than the plot using stoichiometric quantities, Fig. 1. The minor crossovers observed when $x > 0.6$ are possibly an artifact resulting from neglecting the presence of small amounts of higher-order zinc chloride complexes in our model equations.

Table 3 also reports ionic activity coefficients that can be combined to yield the activity coefficients of the hypothetical pure binary aqueous electrolytes $(\mathrm{Zn^{2+}}, 2\mathrm{Cl^-})$, $(\mathrm{Zn^{2+}}, \mathrm{SO_4^{2-}})$ and $(\mathrm{ZnCl^+}, \mathrm{Cl^-})$. Figures 4 and 5 show plots of $\gamma_e(\mathrm{Zn^{2+}})\{\gamma_e(\mathrm{Cl^-})\}^2$ and $\gamma_e(\mathrm{Zn^{2+}})\gamma_e(\mathrm{SO_4^{2-}})$, respectively, as functions of both m_T and I_e. On both plots, the activity

coefficient products fall in regular orders with the composition fraction x, which suggests that our model (even with its simplifications) describes the essential speciation and thermodynamic behavior of the $\{xZnCl_2 + (1 - x)ZnSO_4\}$(aq) system fairly well. Figure 6 gives the analogous plots for $\gamma_e(ZnCl^+)\gamma_e(Cl^-)$. These plots show more complicated behavior because of subtle changes in the extent of formation of $ZnCl^+$ as functions of x and m_T, and it is possible that some of the crossovers are artifacts of the simplifications made in deriving our extended ion-interaction model.

In summary, our extended ion-interaction model for $\{xZnCl_2 + (1 - x)ZnSO_4\}$(aq) gives an accurate representation of our experimental osmotic coefficients while incorporation the presence of the predominant complex $ZnCl^+$. However, it was necessary to ignore the presence of higher-order zinc chloride complexes when deriving the model parameters. In order to improve upon the present model, accurate spectroscopic determinations of the concentrations of all of the complexes present in $ZnCl_2$(aq) and $\{xZnCl_2 + (1 - x)ZnSO_4\}$(aq) solutions would be required but are not available.

References

1. Zinc and zinc alloys, in Kirk-Othmer Encyclopedia of Chemical Technology, third edition, Vol. 24, M. Grayson Executive Ed. and D. Eckroth Associate Ed., Wiley Interscience, New York, (1984), pp. 807–851.

2. Zinc, Office of Dietary Supplements, National Institutes of Health web site http://ods.od.nih.gov (accessed March 6, 2006).

3. Beck, F., Rüetschi, P.: Rechargeable batteries with aqueous electrolytes. Electrochim. Acta **45**, 2467–2482 (2000).

4. Douglas, D.L.: Status review of zinc/chlorine batteries, in Proceedings of the EPRI/LBL Workshop on the Electrochemistry of Zinc/Halogen Batteries, Electrochemical Engineering Consultants Inc., Northville, Michigan (March 1984), pp. 2.3–2.14.

5. Pozin, M.E.: Tehnologiii Mineralnih Solii, second ed., Gosudarstvennoe Nauchno-Technickeskoe Izdatelstvo Khimicheskoe Literaturi, Leningrad (1961).

6. Goldberg, R.N.: Evaluated activity and osmotic coefficients for aqueous solutions: bi-univalent compounds of zinc, cadmium, and ethylene bis(trimethylammonium) chloride and iodide. J. Phys. Chem. Ref. Data **10**, 1–55 (1981).

7. Rard, J.A., Miller, D.G.: Isopiestic determination of the osmotic and activity coefficients of $ZnCl_2$(aq) at 298.15 K. J. Chem. Thermodyn. **21**, 463–482 (1989).

8. Fricke, R., Havestadt, L.: Verdünnungsarbeiten und Verdünnungswärmen im Gebiet Konzentrierter Lösungen. Z. Electrochem. **33**, 441–455 (1927).

9. Foxton, F., Shutt, W.J.: The activity of zinc chloride in concentrated solution. Trans. Faraday Soc. **23**, 480–488 (1927).

10. Robinson, R.A., Stokes, R.H.: Part IV. The thermodynamics of zinc chloride solutions. Trans. Faraday Soc. **36**, 740–748 (1940).

11. Farrelly, R.O.: Complex ion formation in zinc salts, M. Sci. Thesis, University of New Zealand, Auckland, New Zealand (1945).

12. Stokes, R.H.: A thermodynamic study of bivalent metal halides in aqueous solution. Part XVII—Revision of data for all 2:1 and 1:2 electrolytes at 25°, and discussion of results. Trans. Faraday Soc. **44**, 295–307 (1948).

13. Miladinović, J., Ninković, R., Todorović, M., Jovanović, V.: Osmotic coefficient of the $ZnCl_2$(aq) at $T = 298.15$ K. J. Chem. Thermodyn. **35**, 1073–1082 (2003).

14. Pan, C.-F., Argersinger, Jr., W.J.: Isopiestic determination of the osmotic and relative activity coefficients in $BaCl_2$–$ZnCl_2$–H_2O at 25 °C. J. Chem. Eng. Data **32**, 205–210 (1987).

15. Horsch, W.G.: Potentials of the zinc and cadmium electrodes. J. Am. Chem. Soc. **41**, 1787–1800 (1919).

16. Ishikawa, F. Takai, T.: Free energies of solution of zinc chloride and cadmium halides (in Japanese). Rikagaku Kenkyusho Iho **16**, 1251–1261 (1937).

17. Harris, A.C., Parton, H.N.: The transport numbers of zinc chloride from e.m.f. measurements. Trans. Faraday Soc. **36**, 1139–1141 (1940).

18. Lutfullah, Dunsmore, H.S., Paterson, R.: Re-determination of the standard electrode potential of zinc and mean molal activity coefficients for aqueous zinc chloride at 298.15 K. J. Chem. Soc. Faraday Trans. 1 **72**, 495–503 (1976).

19. Agnew, A., Paterson, R., Transport in aqueous solutions of group IIB metal salts at 298.15 K. Part 6.–Irreversible thermodynamic parameters for zinc chloride and verification of Onsager's reciprocal relationships. J. Chem. Soc. Faraday Trans. 1 **74**, 2896–2906 (1978).

20. Rard, J.A., Clegg, S.L.: Critical evaluation of the thermodynamic properties of aqueous calcium chloride. 1. Osmotic and activity coefficients of 0–10.77 mol·kg^{-1} aqueous calcium chloride solutions at 298.15 K and correlation with extended Pitzer ion-interaction models. J. Chem. Eng. Data **42**, 819–849 (1997).

21. Albright, J.G., Rard, J.A., Serna, S., Summers, E.E., Yang, M.C.: Isopiestic determination of the osmotic and activity coefficients of $ZnSO_4$(aq) at T = 298.15 K, and the standard potential of the electrochemical cell $ZnHg_x$(two phase)|$ZnSO_4$(aq)|$PbSO_4$(s)| $PbHg_x$(two phase). J. Chem. Thermodyn. **32**, 1447–1487 (2000).

22. Robinson, R.A., Jones, R.S.: The activity coefficients of some bivalent metal sulfates in aqueous solution from vapor pressure measurements. J. Am. Chem. Soc. **58**, 959–961 (1936).

23. Ojkova, T., Makarow, L., Balarew, C., Miloschova, M.: Thermodynamische Untersuchung des Systems Zinksulfat–Nickelsulfat–Wasser bei 25 °C. Z. Phys. Chem. (Leipzig) **255**, 453–463 (1974).

24. Libus, W., Sadowska, T., Libus, Z.: Correlation between thermodynamic properties and coordination states of aqueous bivalent transition metal sulfates. J. Solution Chem. **9**, 341–354 (1980).

25. Filippov, V.K., Nokhrin, V.I., Muzalevskaya, A.P.: A thermodynamic study of the Na_2SO_4-$ZnSO_4$-H_2O and Na_2SO_4-$CdSO_4$-H_2O systems at 25 °C. Russ. J. Inorg. Chem. **30**, 1372–1374 (1985).

26. Miladinović, J., Todorović, M., Ninković, R.: Osmotic coefficient of the $ZnSO_4$(aq) at T = 298.15 K. J. Chem. Thermodyn. **34**, 1769–1776 (2002).

27. Miladinović, J., Ninković, R., Todorović, M., Jovanović, V.: Correlation of osmotic coefficient data for $ZnSO_4$(aq) at 25°C by various thermodynamic models. J. Solution Chem. **32**, 371–383 (2003).

28. Archer, D.G.: Thermodynamic properties of the NaCl + H_2O System. II. Thermodynamic properties of NaCl(aq), NaCl·$2H_2O$(cr), and phase equilibria. J. Phys. Chem. Ref. Data **21**, 793–829 (1992).

29. Archer, D.G.: Thermodynamic properties of the KCl + H_2O system. J. Phys. Chem. Ref. Data **28**, 1–17 (1999).

30. El Guendouzi, M., Mounir, A., Dinane, A.: Water activity, osmotic and activity coefficients of aqueous solutions of Li_2SO_4, Na_2SO_4, K_2SO_4, $(NH_4)_2SO_4$, $MgSO_4$, $MnSO_4$, $NiSO_4$, $CuSO_4$, and $ZnSO_4$ at T = 298.15 K. J. Chem. Thermodyn. **35**, 209–220 (2003).

31. Malatesta, F., Zamboni, R.: Activity and osmotic coefficients from the Emf of liquid membrane cells. VI-$ZnSO_4$, $MgSO_4$, $CaSO_4$, and $SrSO_4$ in Water at 25°C. J. Solution Chem. **26**, 791–815 (1997).

32. Kolár, P., Nakata, H., Tsuboi, A., Wang, P., Anderko, A.: Measurement and modeling of vapor–liquid equilibria at high salt concentrations. Fluid Phase Equil. **228–229**, 493–497 (2005).

33. Anstiss, R.G., Pitzer, K.S.: Thermodynamics of very concentrated aqueous electrolytes: LiCl, $ZnCl_2$, and $ZnCl_2$-NaCl at 25°C. J. Solution Chem. **20**, 849–858 (1991).

34. Bouchacourt, M., Saugier, M.-T., Cohen-Adad, R.: Système quarternaire réciproque Na^+, Zn^{2+}, SO_4^{2-}, Cl^-, H_2O. I. Les systèmes ternaires limites. Bull. Soc. Chim. France, Part 1 (**9–10**), 842–846 (1977).

35. Filippov, V.K., Rumyantsev, A.V., Popov, A.S.: unpublished solubility data cited in reference 33. Because of Prof. Filippov's death this data is not available.

36. Esparza, P., Yanes, C., Morales, J.: Activity coefficients of zinc sulfate solutions in aqueous-organic solvents and in electrolyte mixtures by Emf measurements. Bull. Electrochem. **9**, 135–137 (1993).

37. Weingärtner, H., Müller, K.J., Hertz, H.G., Edge, A.V.J., Mills, R.: Unusual behavior of transport coefficients in aqueous solutions of zinc chloride at 25 °C. J. Phys. Chem. **88**, 2173–2178 (1984).

38. Rard, J.A., Miller, D.G.: Mutual diffusion coefficients of $ZnCl_2$-H_2O at 298.15 K by Rayleigh interferometry. Z. Phys. Chem. (Neue Folge) **142**, 141–155 (1984).

39. Miller, D.G., Rard, J.A.: Generalized isothermal transport coefficients of $ZnCl_2$-H_2O at 25 °C. J. Mol. Liquids **52**, 145–179 (1992).

40. Bjerrum, N.: Dissociation of strong electrolytes. Z. Electrochem. **24**, 321–328 (1918).

41. Bjerrum, N.: The electric forces between ions and their activity (in Norwegian). Svensk. Kem. Tids. **38**, 2–18 (1926).

42. Bjerrum, N.: Ionic Asspociation. I. Influence of ionic association on the activity of ions at moderate degrees of association. Kgl. Danske Videnskab. Selskab. Math.-fys. Medd.[9] **7**, 1–48 (1926).

43. Mayer, J.E.: The theory of ionic solutions. J. Chem. Phys. **18**, 1426–1436 (1950).

44. Guggenheim, E.A.: Activity coefficients and osmotic coefficients of 2-2 electrolytes. Trans. Faraday Soc. **56**, 1152–1158 (1960).

45. Yokoyama, H. Yamatera, H.: Ion association of some 2:2 electrolytes in water at 25° C. II. Spectrophotometric studies of the ion association of magnesium, calcium, manganese, copper, and zinc sulfates. Bull. Chem. Soc. Japan **48**, 2719–2726 (1975).

46. Rudolph, W.W., Brooker, M.H., Tremaine, P.: Raman- and infrared spectroscopic investigation of aqueous $ZnSO_4$ solutions from 8 °C to 165 °C: inner- and outer-sphere complexes. Z. Phys. Chem. **209**, 181–207 (1999).

47. Wasylkiewicz, S.: Ion association in aqueous solutions of electrolytes. II. Mathematical model for sulphates of bivalent metals. Fluid Phase Equil. **57**, 277–296 (1990).

48. Pitzer, K.S., Mayorga, G.: Thermodynamics of electrolytes. III. Activity and osmotic coefficients for 2–2 electrolytes. J. Solution Chem. **3**, 539–546 (1974).

49. Pavićević, V., Ninković, R., Todorović, M., Miladinović, J.: Osmotic and activity coefficients of $\{y NaH_2PO_4 + (1 - y)Na_2SO_4\}$(aq) at the temperature 298.15 K. Fluid Phase Equil. **164**, 275–284 (1999).

50. Kolthoff, I.M., Sandell, E.B.: Textbook of Quantitative Inorganic Analysis, The Macmillan Company, New York (1945).

51. Owen, B.B., Gurry, R.W.: The electrolytic conductivity of zinc sulfate and copper sulfate in water at 25°. J. Am. Chem. Soc. **60**, 3074–3078 (1938).

52. Katayama, S.: Conductimetric determination of ion-association constants for calcium, cobalt, zinc, and cadmium sulfates in aqueous solutions at various temperatures between 0°C and 45°C. J. Solution Chem. **5**, 241–248 (1976).

53. Irish, D.E., McCarroll, B., Young, T.F.: Raman study of zinc chloride solutions. J. Chem. Phys. **39**, 3436–3444 (1963).

54. Maciel, G.E., Simeral, L., Ackerman, J.J.H.: Effect of complexation of zinc(II) on zinc-67 chemical shifts. J. Phys. Chem. **81**, 263–267 (1977).

55. Darbari, G.S., Richelson, M.R., Petrucci, S.: Ultrasonic study of aqueous solutions of $ZnCl_2$: from dilute solutions to hydrated melts. J. Chem. Phys. **53**, 859–866 (1970).

56. Dreier, P., Rabe, P.: EXAFS-study of the Zn^{2+} coordination in aqueous halide solutions. J. Physique **47 (supplement 12)**, C8-809–C8-812 (1986).

57. Salmon, P.S.: Hydration of complexed chloride ions in aqueous zinc(II) chloride solution. J. Phys. Chem. **93**, 1182–1184 (1989).

58. Matsubara, E., Waseda, Y.: An anomalous X-ray scattering study of an aqueous solution of $ZnCl_2$. J. Phys.: Condens. Matter **1**, 8575–8582 (1989).

59. Ohtaki, H., Radnai, T.: Structure and dynamics of hydrated ions. Chem. Rev. **93**, 1157–1204 (1993).

60. Kaatze, U., Lönnecke, V., Pottel, R.: Dielectric spectroscopy on aqueous solutions of zinc(II) chloride. Evidence of ion complexes. J. Phys. Chem. **91**, 2206–2211 (1987).

61. Kaatze, U., Lönnecke, V., Pottel, R.: Dielectric spectroscopy of aqueous $ZnCl_2$ solutions. Dependence upon solute concentration and comparison with other electrolytes. J. Mol. Liquids **34**, 241–255 (1987).

62. Hsie, W.C., Selman, J.R.: Mass transport in supported zinc halide solutions—II. Complexation and migration effects. Electrochem. Acta **30**, 1381–1392 (1985).

63. Archer, D.G., Rard, J.A.: Isopiestic investigation of the osmotic and activity coefficients of Aqueous $MgSO_4$ and the solubility of $MgSO_4 \cdot 7H_2O(cr)$ at 298.15 K: Thermodynamic properties of the $MgSO_4 + H_2O$ system to 440 K. J. Chem. Eng. Data **43**, 791–806 (1998); **45**, 716 (2000).

64. Archer, D.G., Wang, P.: The dielectric constant of water and Debye-Hückel limiting law slopes. J. Phys. Chem. Ref. Data **19**, 371–411 (1990).

65. Clegg, S.L., Rard, J.A., Pitzer, K.S.: Thermodynamic properties of 0–6 mol kg^{-1} aqueous sulfuric acid from 273.15 to 328.15 K. J. Chem. Soc., Faraday Trans. **90**, 1875–1894 (1994).

66. Rard, J.A., Wijesinghe, A.M.: Conversion of parameters between different variants of Pitzer's ion-interaction model, both with and without ionic strength dependent higher-order terms. J. Chem. Thermodyn. **35**, 439–473 (2003).

67. Rard, J.A., Clegg, S.L.: Isopiestic determination of the osmotic and activity coefficients of $\{zH_2SO_4 + (1-z)MgSO_4\}$(aq) at $T = 298.15$ K. II. Results for $z = (0.43040, 0.28758,$ and $0.14399)$ and analysis with Pitzer's Model. J. Chem. Thermodyn. **31**, 399–429 (1999).

68. Pitzer, K.S.: in Activity Coefficients in Electrolyte Solutions, 2nd ed., Pitzer, K.S.: editor, CRC Press, Boca Raton (1991), Chap. 3.

69. Rard, J.A.: Isopiestic determination of the osmotic and activity coefficients of $\{(1-y)H_2SO_4 + yNa_2SO_4\}$(aq) at the temperature 298.15 K. II. Results for $y = (0.12471, 0.24962,$ and $0.37439)$. J. Chem. Thermodyn. **24**, 45–66 (1992).

Table 3 Calculated values of the fraction α of the total solute molality present as $ZnCl^+$, stoichiometric osmotic coefficients ϕ, osmotic coefficients based on the calculated equilibrium speciation ϕ_e, and single ion activity coefficients γ_e, as a function of the $ZnCl_2$ solute molality fraction x at various rounded values of the total solute molality m_T for the $\{xZnCl_2 + (1-x)ZnSO_4\}$(aq) system at 298.15 K

| x	α	$\gamma_e(ZnCl^+)$	$\gamma_e(Zn^{2+})$	$\gamma_e(Cl^-)$	$\gamma_e(SO_4^{2-})$	ϕ	ϕ_e
$m_T = 1.0$ mol·kg^{-1}							
0.0	0	0.3689	0.0416	2.1991[a]	0.0416	0.4822	0.4822
0.2	0.1022	0.3973	0.0459	1.8766	0.0559	0.6365	0.6675
0.4	0.1990	0.4516	0.0516	1.6025	0.0730	0.7251	0.7906
0.6	0.2777	0.5423	0.0594	1.3628	0.0933	0.7736	0.8661
0.8	0.3249	0.6850	0.0694	1.1471	0.1177	0.7944	0.8987
1.0	0.3258	0.8983	0.0885	0.9452	0.1483[b]	0.8045	0.9025
$m_T = 1.2$ mol·kg^{-1}							
0.0	0	0.3819	0.0384	2.5859[a]	0.0384	0.4952	0.4952
0.2	0.1131	0.3938	0.0419	2.1422	0.0540	0.6550	0.6905
0.4	0.2148	0.4374	0.0464	1.7777	0.0735	0.7406	0.8134
0.6	0.2929	0.5233	0.0522	1.4688	0.0978	0.7827	0.8821
0.8	0.3348	0.6698	0.0596	1.1991	0.1291	0.7947	0.9026
1.0	0.3265	0.9026	0.0754	0.9540	0.1732[b]	0.7942	0.8912
$m_T = 1.4$ mol·kg^{-1}							
0.0	0	0.4094	0.0363	3.0270[a]	0.0363	0.5142	0.5142
0.2	0.1245	0.3988	0.0392	2.4327	0.0532	0.6787	0.7194
0.4	0.2304	0.4286	0.0427	1.9625	0.0753	0.7598	0.8405
0.6	0.3075	0.5074	0.0470	1.5774	0.1040	0.7944	0.9010
0.8	0.3453	0.6559	0.0523	1.2517	0.1436	0.7974	0.9096
1.0	0.3320	0.9080	0.0659	0.9646	0.2042[b]	0.7875	0.8855
$m_T = 1.6$ mol·kg^{-1}							
0.0	0	0.4535	0.0349	3.5334[a]	0.0349	0.5390	0.5390
0.2	0.1366	0.4117	0.0377	2.7511	0.0533	0.7075	0.7543
0.4	0.2460	0.4243	0.0403	2.1583	0.0781	0.7825	0.8719
0.6	0.3217	0.4943	0.0433	1.6897	0.1119	0.8087	0.9229
0.8	0.3563	0.6431	0.0469	1.3064	0.1610	0.8028	0.9198
1.0	0.3422	0.9156	0.0591	0.9785	0.2405[b]	0.7852	0.8863
$m_T = 1.8$ mol·kg^{-1}							
0.0	0	0.5184	0.0341	4.1183[a]	0.0341	0.5692	0.5692
0.2	0.1491	0.4328	0.0369	3.0994	0.0541	0.7416	0.7955
0.4	0.2615	0.4240	0.0388	2.3651	0.0818	0.8086	0.9075
0.6	0.3352	0.4834	0.0406	1.8062	0.1213	0.8256	0.9478
0.8	0.3678	0.6315	0.0428	1.3643	0.1811	0.8108	0.9334
1.0	0.3571	0.9259	0.0543	0.9970	0.2806[b]	0.7874	0.8937
$m_T = 2.0$ mol·kg^{-1}							
0.0	0	0.6110	0.0339	4.7971[a]	0.0339	0.6048	0.6048
0.2	0.1623	0.4626	0.0370	3.4785	0.0554	0.7808	0.8430
0.4	0.2770	0.4274	0.0382	2.5828	0.0864	0.8379	0.9473
0.6	0.3481	0.4743	0.0387	1.9274	0.1323	0.8448	0.9754
0.8	0.3798	0.6210	0.0398	1.4262	0.2040	0.8212	0.9500
1.0	0.3768	0.9392	0.0510	1.0202	0.3211[b]	0.7932	0.9072
$m_T = 2.2$ mol·kg^{-1}							
0.0	0	0.7419	0.0340	5.5879[a]	0.0340	0.6459	0.6459
0.2	0.1760	0.5024	0.0378	3.8879	0.0574	0.8253	0.8971
0.4	0.2923	0.4341	0.0383	2.8101	0.0918	0.8703	0.9910

0.6	0.3604	0.4669	0.0376	2.0534	0.1450	0.8662	1.0056
0.8	0.3922	0.6113	0.0376	1.4923	0.2293	0.8336	0.9694
1.0	0.4012	0.9557	0.0489	1.0482	0.3575 [b]	0.8018	0.9256
$m_T = 2.4$ mol·kg^{-1}							
0.0	0	0.9277	0.0346	6.5126 [a]	0.0346	0.6924	0.6924
0.2	0.1902	0.5537	0.0395	4.3256	0.0600	0.8753	0.9582
0.4	0.3076	0.4440	0.0391	3.0455	0.0982	0.9054	1.0385
0.6	0.3723	0.4609	0.0371	2.1840	0.1596	0.8895	1.0381
0.8	0.4053	0.6023	0.0362	1.5631	0.2566	0.8477	0.9911
1.0	0.4303	0.9753	0.0478	1.0803	0.3835 [b]	0.8118	0.9478

[a] Trace activity coefficient of the Cl$^-$ ion in a ZnSO$_4$(aq) solution of molality m_T. [b] Trace activity coefficient of the SO$_4^{2-}$ ion in a ZnCl$_2$(aq) solution of molality m_T.
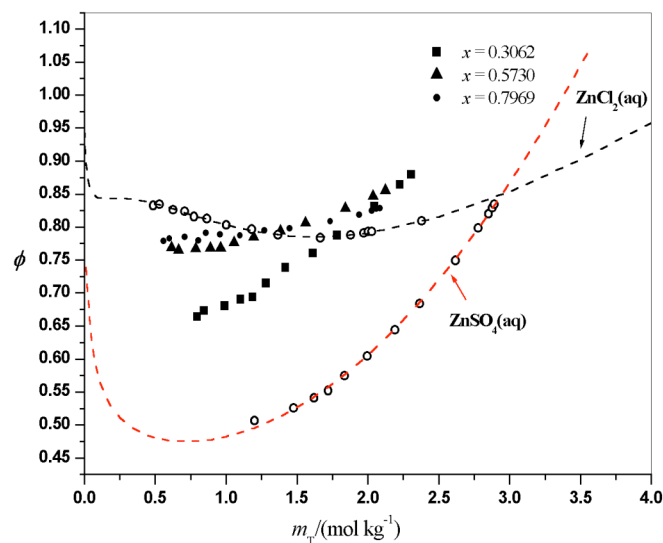
Fig. 1 Experimental osmotic coefficients ϕ of $\{x\text{ZnCl}_2 + (1 - x)\text{ZnSO}_4\}$(aq) at 298.15 K plotted against the total solute molality m_T at constant values of the ZnCl_2 molality fraction x. Dashed curves represent the smoothed osmotic coefficients of ZnCl_2(aq) and ZnSO_4(aq) that were calculated using the parameters evaluated here for the extended ion-interaction models. Open circles denote the present experimental results for the individual salts ZnCl_2(aq) and ZnSO_4(aq), and symbols for the mixtures are identified within the figure.
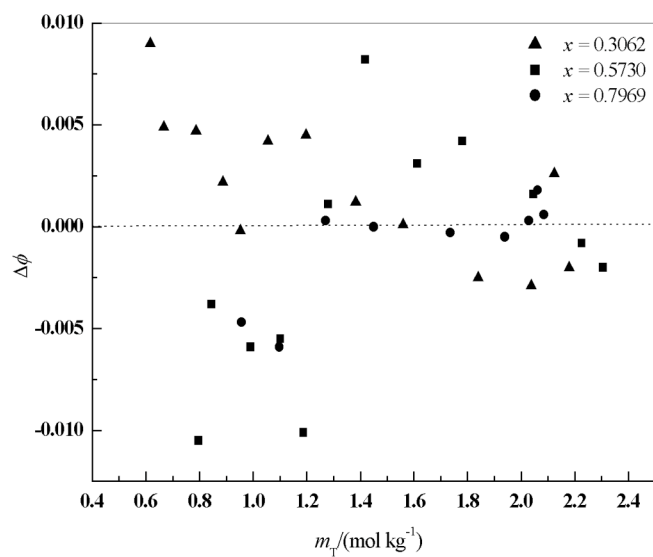
Fig. 2 Differences between experimental osmotic coefficients of $\{x\mathrm{ZnCl_2} + (1 - x)\mathrm{ZnSO_4}\}(\mathrm{aq})$ and least-squares fit values, $\Delta\phi$, for the molality range $m_\mathrm{T} \leq 2.3$ mol·kg^{-1}, using the parameters of Table II, for constant values of the $\mathrm{ZnCl_2}$ molality fraction x.
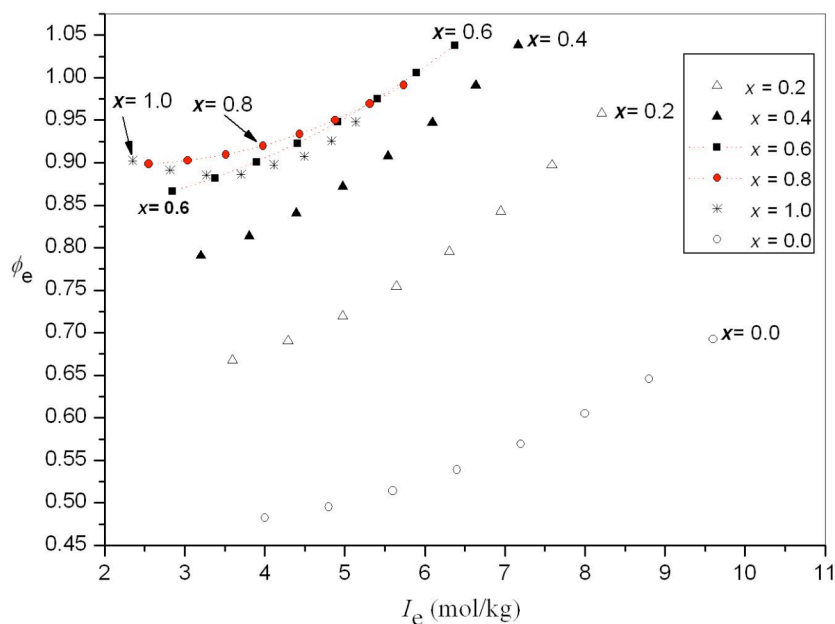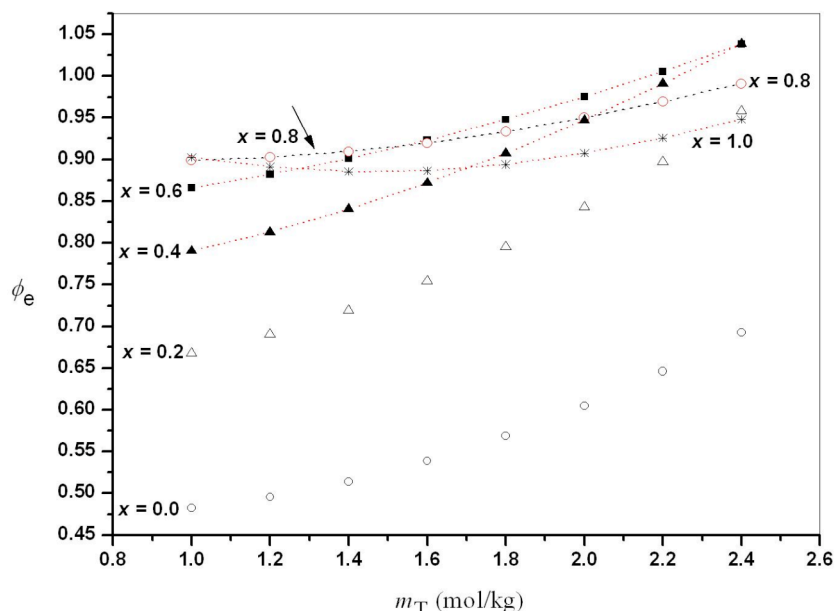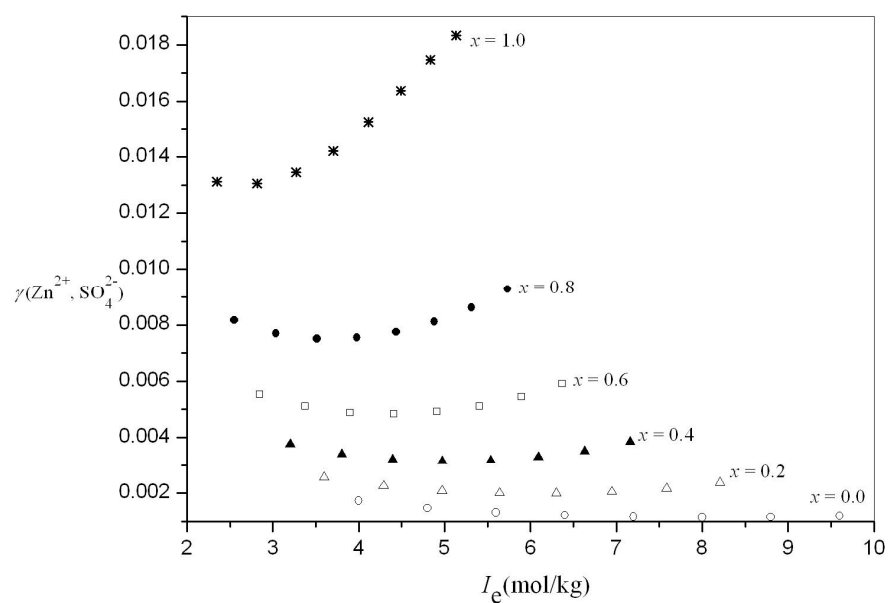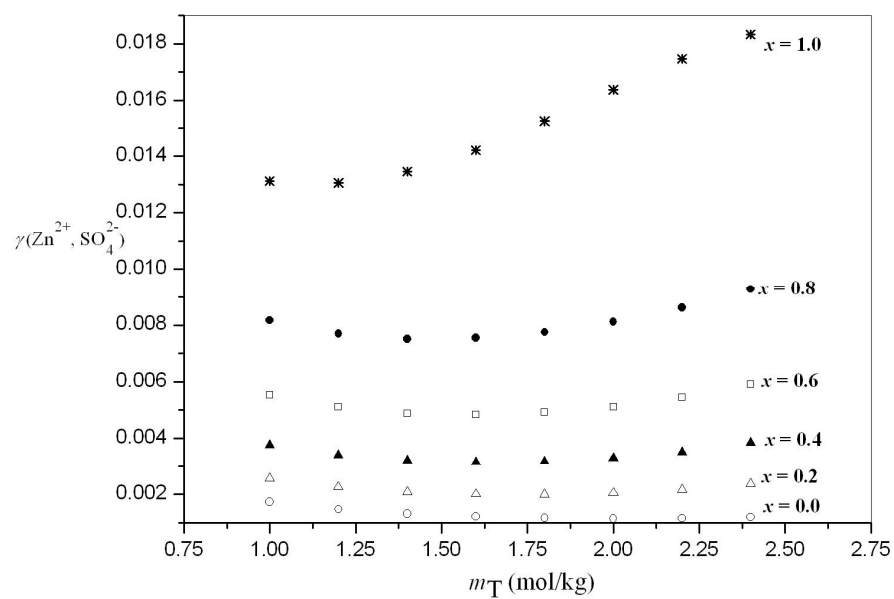
Fig. 3 Osmotic coefficients, ϕ_e, of $\{x\mathrm{ZnCl_2} + (1 - x)\mathrm{ZnSO_4}\}(aq)$ based on the equilibrium speciation, as a function of m_T (top plot) and I_e (bottom plot) at various $\mathrm{ZnCl_2}$ molality fractions, x, calculated with the model parameters of Table 2.
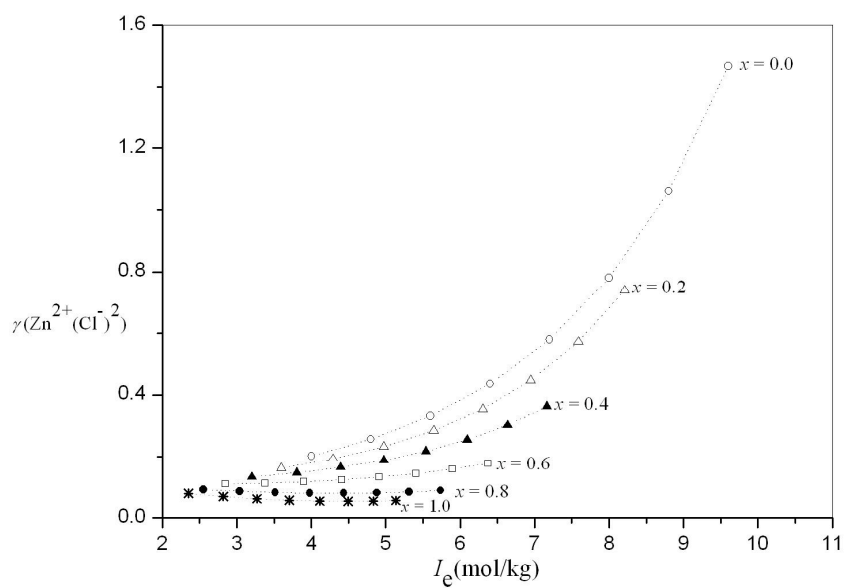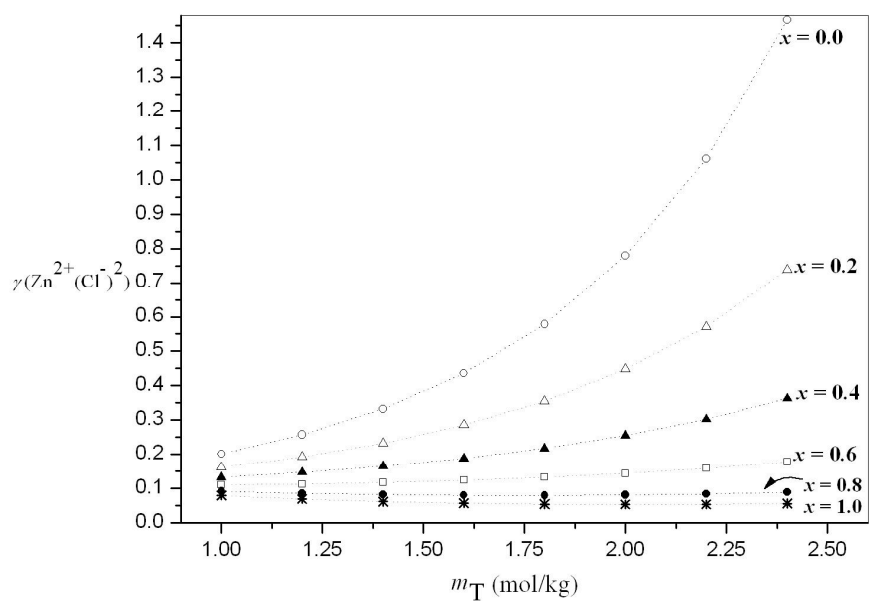
Fig. 4 Activity coefficients of the aqueous binary electrolyte $(Zn^{2+}, 2Cl^{-})$, $\gamma_e(Zn^{2+})\{\gamma_e(Cl^{-})\}^2$, based on equilibrium speciation as a function of m_T (top plot) and I_e (bottom plot) at various $ZnCl_2$ molality fractions, x, calculated with the model parameters of Table 2.

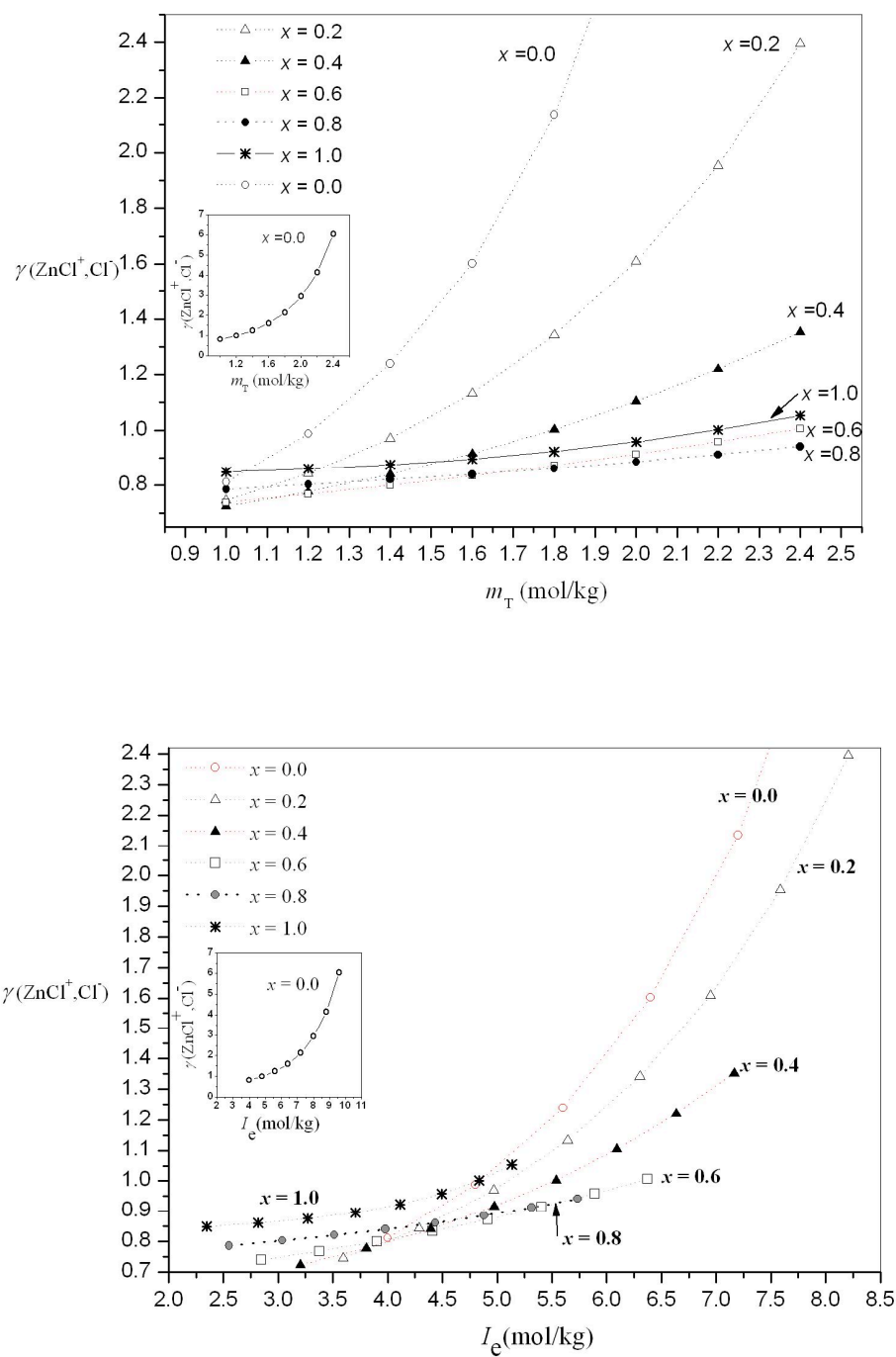**Fig. 5** Activity coefficients of the aqueous binary electrolyte (Zn^{2+}, SO_4^{2-}), $\gamma_e(Zn^{2+})\gamma_e(SO_4^{2-})$, based on equilibrium speciation as a function of m_T (top plot) and I_e (bottom plot) at various $ZnCl_2$ molality fractions, x, calculated with the model parameters of Table 2.

Fig. 6 Activity coefficients of the aqueous binary electrolyte (ZnCl$^+$,Cl$^-$), γ_e(ZnCl$^+$)γ_e(Cl$^-$), based on equilibrium speciation as a function of m_T (top plot) and I_e (bottom plot) at various ZnCl$_2$ molality fractions, x, calculated with the model parameters of Table 2.

Table 1. Isopiestic molalities m_R of the reference solution KCl(aq), isopiestic total molalities m_T and stoichiometric osmotic coefficients ϕ of $\{x\text{ZnCl}_2 + (1 - x)\text{ZnSO}_4\}$(aq) at 298.15 K, and the molality fraction x of ZnCl$_2$

$\dfrac{m_R}{\text{mol}\cdot\text{kg}^{-1}}$	$\dfrac{m_T}{\text{mol}\cdot\text{kg}^{-1}}$	ϕ	$\dfrac{m_T}{\text{mol}\cdot\text{kg}^{-1}}$	ϕ	$\dfrac{m_T}{\text{mol}\cdot\text{kg}^{-1}}$	ϕ	$\dfrac{m_T}{\text{mol}\cdot\text{kg}^{-1}}$	ϕ	$\dfrac{m_T}{\text{mol}\cdot\text{kg}^{-1}}$	ϕ
	$x = 0$		$x = 0.3062$		$x = 0.5730$		$x = 0.7969$		$x = 1.0$	
0.6783	1.2034	0.5063	0.7958	0.6640	0.6162	0.7686	(0.5599)[a]	(0.7788)[a]	0.4880	0.8324
0.7439	1.2535	0.5235	0.8452	0.6733	0.6667	0.7651	(0.5995)[a]	(0.7827)[a]	0.5340	0.8341
0.8649	1.4775	0.5259	0.9898	0.6808	0.7869	0.7675	(0.7076)[a]	(0.7853)[a]	0.6276	0.8256
0.9755	1.6223	0.5406	1.1014	0.6905	0.8875	0.7680	(0.8044)[a]	(0.7795)[a]	0.7098	0.8237
1.0561	1.7215	0.5519	1.1871	0.6941	0.9616	0.7680	(0.8586)[a]	(0.7913)[a]	0.7766	0.8156
1.1713	1.8382	0.5740	1.2794	0.7152	1.0557	0.7769	0.9566	0.7887	0.8656	0.8127
1.3375	1.9977	0.6046	1.4178	0.7388	1.1963	0.7848	1.0973	0.7871	1.0030	0.8028
1.5581	2.1949	0.6439	1.6113	0.7603	1.3833	0.7938	1.2709	0.7948	1.1828	0.7962
1.7763	2.3668	0.6835	1.7807	0.7878	1.5598	0.8063	1.4493	0.7982	1.3687	0.7880
2.1354	2.6184	0.7490	2.0451	0.8316	1.8403	0.8284	1.7350	0.8083	1.6687	0.7835
2.4000	2.7798	0.7983	2.2260	0.8645	2.0373	0.8467	1.9386	0.8185	1.8785	0.7876
2.5211	2.8530	0.8197	2.3055	0.8796	2.1240	0.8558	2.0281	0.8245	1.9719	0.7906
2.5692	2.8797	0.8286					2.0611	0.8279	2.0056	0.7932
2.5971	2.8950	0.8339			2.1787	0.8613	2.0843	0.8281	2.0298	0.7929
3.0689							2.3807	0.8093		

[a]These five values in parentheses were not used for the estimation of the extended ion-interaction model mixing parameters.

Table 2. Values for the extended ion-interaction (Pitzer) model parameters of $ZnCl_2$(aq) (treating the solutions as being mixtures of Zn^{2+}, $ZnCl^+$ and Cl^- ions), $ZnSO_4$(aq), and mixing parameters for $\{xZnCl_2 + (1 - x)ZnSO_4\}$(aq) at $T = 298.15$ K[a]

Parameter	Value	Parameter	Value	Parameter	Value	Parameter	Value
$\beta^{(0)}(Zn,Cl)$	−0.20828	$\beta^{(0)}(ZnCl,Cl)$	−0.0033975	$\beta^{(0)}(Zn,SO_4)$	−0.041883	$\theta(ZnCl,Zn)$	−0.15153
$\beta^{(1)}(Zn,Cl)$	2.3587	$\beta^{(1)}(ZnCl,Cl)$	1.1796	$\beta^{(1)}(Zn,SO_4)$	3.2024	$\theta(Cl,SO_4)$	0.54957
				$\beta^{(2)}(Zn,SO_4)$	−68.7143	$\psi(ZnCl,Zn,Cl)$	0.017331
$C^{(0)}(Zn,Cl)$	0.028386	$C^{(0)}(ZnCl,Cl)$	0.0010639	$C^{(0)}(Zn,SO_4)$	0.017943	$\psi(ZnCl,Zn,SO_4)$	0.32059
$C^{(1)}(Zn,Cl)$	0.10254	$C^{(1)}(ZnCl,Cl)$	−0.62841	$C^{(1)}(Zn,SO_4)$	0.40318	$\psi(ZnCl,Cl,SO_4)$	−0.20607
$\alpha_1(Zn,Cl)$	1.3	$\alpha_1(ZnCl,Cl)$	1.1	$\alpha_1(Zn,SO_4)$	1.4	$\psi(Zn,Cl,SO_4)$	−0.10534
				$\alpha_2(Zn,SO_4)$	12		
$\omega(Zn,Cl)$	2.5	$\omega(ZnCl,Cl)$	2.5	$\omega(Zn,SO_4)$	1.1		
m_T[b]	2.4	m_T[b]	2.4	m_T[b]	3.56	m_T[b]	2.3
$\sigma(\phi)$[c]	0.0019	$\sigma(\phi)$[c]	0.0019	$\sigma(\phi)$	0.0027	$\sigma(\phi)$	0.0044

[a]The accepted value of the thermodynamic constant for formation of the $ZnCl^+$ complex at 298.15 K is $K_1 = 4.5$ [18]. Units of $\beta^{(0)}$, $\beta^{(1)}$, and θ are kg·mol^{-1}; of $C^{(0)}$, $C^{(1)}$, and ψ are kg^2·mol^{-2}; and of α_1, α_2, and ω are kg$^{1/2}$·mol$^{-1/2}$. The reported parameters for $ZnSO_4$(aq) were derived from those for a different extended-ionic model reported by Miladinović *et al.* [27] by using a variant of the parameter conversion methodology of Rard and Wijesinghe [66] that is described in the text.

[b] The maximum stoichiometric molality of experimental results used for evaluation of these parameters, in mol·kg^{-1}.

[c]For the mean activity coefficients [10,18], $\sigma(\gamma_\pm) = 0.005$.