A Volumetric Pitzer Model for Aqueous Solutions of Zinc Sulfate up to Near-Saturation Concentrations at Temperatures from 293.15 to 393.15 K and Pressures up to 10 MPa

Tuomas Vielma[1*], Lubomir Hnedkovsky[2], Petri Uusi-Kyyny[3], Justin Salminen[4], Ville Alopaeus[3], Ulla Lassi[1], Glenn Hefter[2]

[1] Research Unit of Sustainable Chemistry, University of Oulu, FI-90014 Oulu, Finland

[2] Chemistry Department, Murdoch University, Murdoch, WA 6150, Australia

[3] Department of Chemical and Metallurgical Engineering, School of Chemical Engineering, Aalto University, FI-00076 Aalto, Finland

[4] Boliden Kokkola Oy, FI-67900 Kokkola, Finland

ABSTRACT: Literature data for the volumetric properties of aqueous solutions of zinc sulfate have been compiled and compared with extensive recently-available measurements. A semi-empirical Pitzer model has been derived from these data that reproduces the apparent molar volumes and compressibilities of zinc sulfate solutions with good accuracy to near-saturation concentrations ($m \lesssim$ 3.0 mol·kg^{-1}) over the temperature range $293.15 \leq T/\text{K} \leq 393.15$ and at pressures up to 10 MPa, using standard volumes, V^o, obtained by additivity of ionic values from the literature. By including the dependence of V^o on the compressibility of pure water, the model was able to predict apparent molar volumes with good accuracy even up 100 MPa at 298 K. Of potential use for engineering applications, imposition of the inequality $(\partial^2 V_\phi/\partial T^2)_{p,m} < 0$ to the Pitzer model has created the possibility of physically reasonable extrapolations to temperatures well beyond the parameterization range.

Keywords: density, molar volume, Pitzer, zinc sulfate

1. INTRODUCTION

Zinc sulfate is the main solute present in the process solutions of hydrometallurgical zinc plants and industrial galvanising operations; it also has a significant presence in acid mine drainage (AMD) waters of past and present zinc mines. Understanding the behaviour of these zinc bearing solutions requires detailed knowledge of their properties. Two reviews of the thermodynamic properties of ZnSO$_4$(aq) solutions, both of which included development of Pitzer models, have appeared recently.[1,2] However, neither of these publications considered volumetric properties, in part due to the lack of available data covering appropriate ranges of concentration, temperature and pressure. The only

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reported volumetric Pitzer model for $ZnSO_4$(aq) to date is that of Krumgalz et al.[3] but their model was restricted to 298.15 K and was parameterized exclusively on the results of Lo Surdo and Millero,[4] which extend only up to 0.9 mol·kg^{-1}.

Given the relevance of solution densities to engineering calculations, such as mass transfer and unit conversions, and their importance for deriving pressure dependencies of other thermodynamic properties, the limited volumetric database is somewhat surprising.[5] This situation has been addressed recently by the publication of two extensive, independently measured sets of density data by the present authors and colleagues (see the two papers preceding this article).[6,7] Both data sets (here labelled A[6] and B[7]) were measured with a vibrating tube densimeter (VTD). Set A covered the concentration and temperature ranges: $0.002 \leq m/\text{mol·kg}^{-1} \leq 2.5$ and $293.15 \leq T/\text{K} \leq 353.15$, respectively, at atmospheric pressure (AP, 0.1 MPa). Measurements were also reported at 323.15 K and 373.15 K at 0.3 MPa, using a custom-built high temperature densimeter (HTD). Set B covered the ranges $0.1 \leq m/\text{mol·kg}^{-1} \leq 3.0$ and $298.15 \leq T/\text{K} \leq 393.15$, at pressures $0.5 \leq p/\text{MPa} \leq 10$ (HP), with a few measurements in the range $293.15 \leq T/\text{K} \leq 363.15$ at AP with Hastelloy or glass VTDs. A review of the relevant literature data was included as a part of those two papers and so will not be repeated here but, for convenience, the available sources are listed in Table 1.

Table 1. Literature Sources for Densities of Aqueous Solutions of Zinc Sulfate

Authors	Year	Method	m / mol·kg^{-1}	T / K	p / MPa
Lamb and Lee[8]	1913	magnetic float	$5 \cdot 10^{-5}$–0.005	293.15	0.1^a
Gibson[9]	1934	pycnometer, piezometer	0.3–2.3	298.15	0.1,100
Purser and Stokes[10]	1951	pycnometer	0.01–2.0	298.15	0.1^b
Albright and Miller[11]	1975	pycnometer	0.09–3.6	298.15	0.1^b
Lo Surdo and Millero[4]	1980	vibrating tube	0.05–0.9	298.15	0.1^b
Söhnel and Novotný[12]	1985	compilation	0.13–4.1	273.15–373.15	0.1^b
Puchalska et al.[13]	1993	vibrating tube	0.01–1.5	288.15–328.15	0.1^b
Aseyev and Zaytsev[14]	1996	compilation	0.13–2.6	273.15–373.15	0.1^b

^{a}Stated to be 0.097 MPa. ^{b}Not stated but assumed to be 0.1 MPa.

2. DATA EVALUATION

Figure 1 compares the available literature data (including the most-recent results),[6,7] expressed as V_ϕ, at 298.15 K and 0.1 MPa. Sets A and B are in excellent agreement with each other although close inspection indicates the latter are rather more scattered. This is undoubtedly because the Hastelloy VTD (used for most of the Set B measurements)[7] is less sensitive than the glass-tube version used for most of Set A.[6] Other literature data fall evenly around the present results, with the pycnometric

values[9-11] lying slightly above (by ca. 0.5–1.0 cm^3·mol^{-1}) while the VTD results[4,13] lie a little below (ca. 0.5–1.5 cm^3·mol^{-1}). The overall spread in V_ϕ at 298.15 K is thus approximately ±1 cm^3·mol^{-1} over the whole concentration range. At higher temperatures the differences the between present results and those of Puchalska et al.[13] increase to 1–2 cm^3·mol^{-1}. Data from the compilations of Söhnel and Novotný[12] and Aseyev and Zaytsev[14] show rather different behaviour and so to preserve visual clarity are not shown in Figure 1. Values given by Söhnel and Novotný[12] in particular differ significantly from the experimental data.
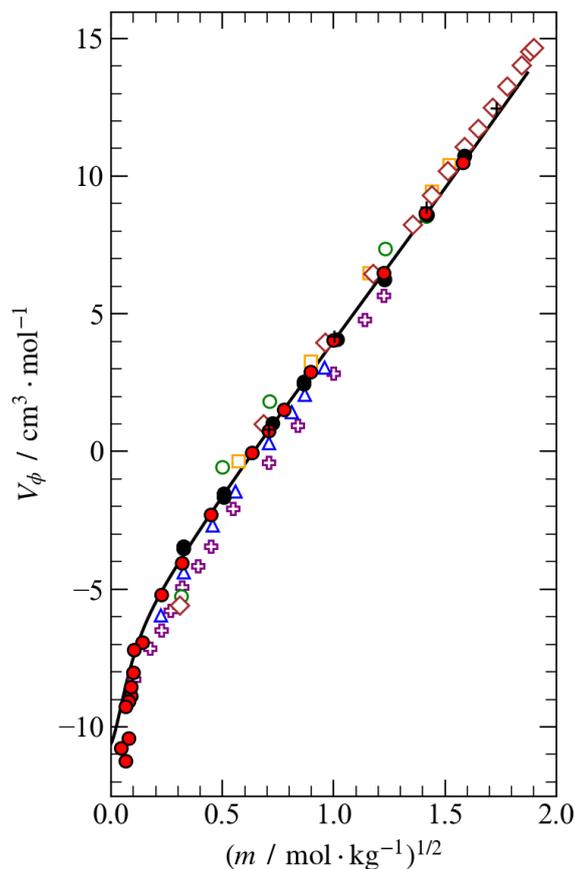
Figure 1. Apparent molar volumes V_ϕ of ZnSO$_4$(aq) solutions at 298.15 K and 0.1 MPa: red dots, Set A (AP);[6] black crosses, Set B (AP);[7] black dots, Set B (HP, 0.5 MPa);[7] orange squares, Gibson;[9] green circles, Purser and Stokes;[10] brown diamonds, Albright and Miller;[11] blue triangles, Lo Surdo and Millero;[4] purple crosses, Puchalska et al.[13] Solid line, present Pitzer model.

2.1. Behaviour at Low Concentrations. The early results of Lamb and Lee[8] are of great interest for understanding the volumetric behaviour of zinc sulfate solutions. These researchers developed an ultra-high-precision magnetic-float densimeter that could measure relative densities of electrolyte solutions down to concentrations of ~50 μmol·kg^{-1}. Very few reliable data have been reported for electrolytes of any charge type at such low concentrations.[5,15] We have adjusted their ZnSO$_4$(aq)

densities, reported at 293.15 K, to align with the IAPWS-95 equation-of-state for water[16] and converted them to apparent molar volumes V_ϕ for comparison with our data (Figure 2). Three important features of Lamb and Lee's data emerge. First, their results are, where comparison is possible, in excellent agreement with the low-concentration data of Set A.[6] Second, their V_ϕ values closely follow the Debye-Hückel limiting law (DHLL) but only at very low concentrations ($m \lesssim 1$ mmol·kg^{-1}); this is unusual because strong electrolytes typically show DHLL behaviour up to much
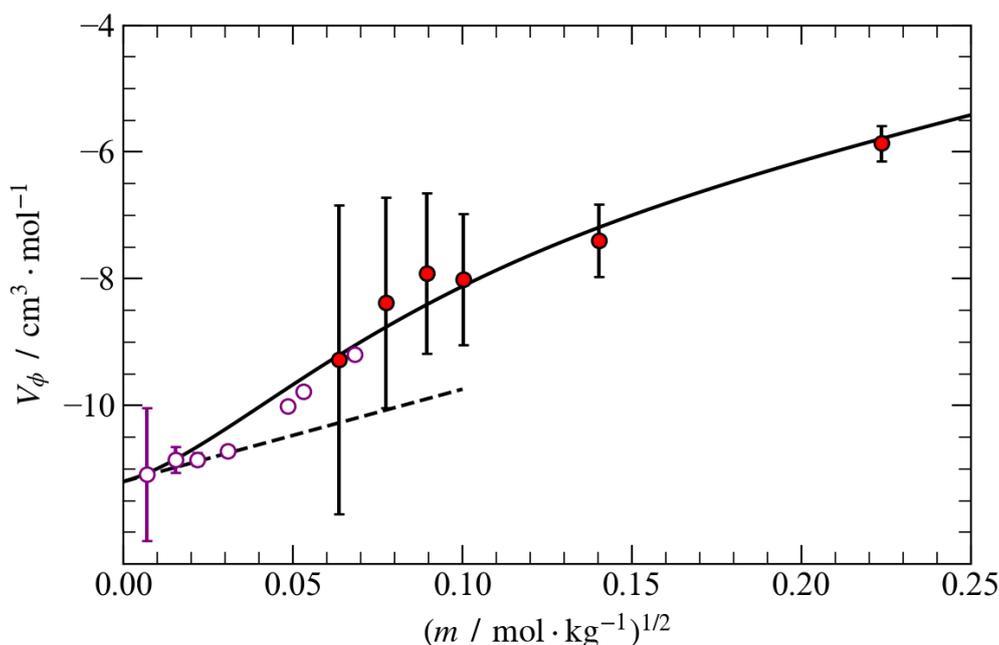
Figure 2. Apparent molar volumes V_ϕ of ZnSO$_4$(aq) solutions at low concentrations, 293.15 K and 0.1 MPa: purple circles, Lamb and Lee;[8] red dots, Set A.[6] Solid line, present model; dashed line, Debye-Hückel limiting law. Error bars correspond to combined standard uncertainty of each point.

higher concentrations ($m \lesssim 10$ mmol·kg^{-1}).[5] Finally, and most intriguingly, combination of Lamb and Lee's V_ϕ values with the low concentration data from Set A shows (Figure 2) a clear transition from one (approximately) linear region at $m \gtrsim 6$ mmol·kg^{-1} to another (the DHLL region) at $m \lesssim 1$ mmol·kg^{-1}.

While extraordinary, this pattern (Figure 2) is very similar to that discussed at length by Robinson and Stokes in their classic monograph[17] regarding the volumetric behaviour of dilute sulfuric acid solutions, H$_2$SO$_4$(aq), based on the work of Klotz and Eckert.[18] The behaviour of those solutions was interpreted as reflecting a change in speciation: in essence from a 1:1 electrolyte (H$^+$(aq) + HSO$_4^-$(aq)) to a 1:2 electrolyte (2H$^+$(aq) + SO$_4^{2-}$(aq)). It seems likely that a similar effect is operating for dilute solutions of ZnSO$_4$(aq), probably involving changes in the relative concentrations of the various types of ion pairs (solvent-separated and contact), which are known to occur in closely related

divalent metal sulfate solutions[19,20] and to have significant volumetric effects.[11] Indeed, it is possible to use data such as those in Figure 2, in combination with other relevant information, to estimate the molar volumes of the various ion pair types.[4] However, in view of the (mostly unknown) uncertainties in the available data, the absence of key auxiliary information, such as the stepwise ion pairing constants, and the assumptions that must be made to quantify the ion pair species, such an analysis of the current data is not justified at present.

No isothermal compressibilities, κ_T, appear to have been reported in the literature for ZnSO$_4$(aq) but Lo Surdo and Millero[4] have published isentropic (adiabatic) compressibilities, κ_S, obtained from speed-of-sound measurements. Conversion of these quantities to κ_T and their apparent molar values, $\kappa_{T\phi}$, can be made using a previously published Pitzer model,[2] and the isobaric expansivities α_p that can be estimated from the present results.[6,7] The variable-pressure data in Set B[7] can also be used to estimate $\kappa_{T\phi}$ directly from $V_\phi(p)$ plots, albeit with lower accuracy. At concentrations $m \geq 0.75$ mol·kg$^-$ ^{1} the $\kappa_{T\phi}$ values so derived are broadly consistent with Lo Surdo and Millero's results but are systematically higher. Below this concentration the calculated $\kappa_{T\phi}$ values *increase* (which is physically unrealistic) instead of decreasing. This is surprising, since V_ϕ(Set B) are in good agreement with the other data, including Set A, at near-atmospheric pressures and implies some (unsuspected) problems in the pressure measurements.

2.2. Modelling. Many more-or-less empirical models have been used to describe the volumetric properties of electrolyte solutions as functions of concentration, temperature and pressure.[5,21] To complement previous studies,[2] a comprehensive volumetric Pitzer model was developed to correlate all the available experimental data. While there are many variants of the Pitzer equations,[22] the most common for apparent molar volumes of a binary electrolyte solutions (containing one solute and the solvent) is:[3]

$$V_\phi = V^\circ + \nu|z_+z_-|\frac{A_V}{2b}\ln(1 + bI^{1/2}) + 2RT\nu_+\nu_-(mB^V + m^2\nu_+z_+C^V) \qquad (1)$$

where V° is the standard state (infinite dilution) partial molar volume of the electrolyte in the solvent, A_V is the Debye-Hückel limiting law constant for volumes (here calculated from the IAPWS-95 equation of state)[16,23], b is an empirical parameter fixed at 1.2 kg$^{1/2}$·mol$^{-1/2}$, R is the gas constant, and T the thermodynamic temperature in Kelvin. The quantities ν_+ and ν_- are, respectively, the stoichiometric numbers of cations and anions per formula unit, with $\nu = \nu_+ + \nu_-$, while z_+ and z_- are the (algebraic) charge numbers of the cation and anion. The empirical coefficients B^V and C^V describe the deviations of the volumetric properties from the DHLL. The value of C^V is assumed to be independent of ionic strength (I), whereas B^V is given by:

$$B^V(I) = \beta^{V(0)} + 2\beta^{V(1)} \frac{1 - (1 + \alpha_1 I^{1/2}) e^{-\alpha_1 I^{1/2}}}{\alpha_1^2 I} + 2\beta^{V(2)} \frac{1 - (1 + \alpha_2 I^{1/2}) e^{-\alpha_2 I^{1/2}}}{\alpha_2^2 I} \qquad (2)$$

where α_1 and α_2 are empirical parameters, which for a 2:2 electrolyte are fixed at 1.4 and 12 $kg^{1/2} \cdot mol^{-1/2}$, respectively.[3] The ionic strength was taken to be the stoichiometric quantity (i.e., ignoring ion pairing) and calculated as $I = 0.5 \, \Sigma m_i z_i^2$. The empirical parameters $\beta^{V(0)}$, $\beta^{V(1)}$, $\beta^{V(2)}$ and C^V were obtained by fitting the experimental data. As there are no theoretically-implied forms of temperature and pressure dependence for $V°$ or for the interaction parameters $\beta^{V(i)}$ and C^V, a purely empirical approach was adopted, in which the following general expression was used for the interaction coefficients:

$$Q(T, p) = q_1 + q_2 T + q_3 T^2 + q_4 T^3 + (p - p_r)(q_5 + q_6 T) \qquad (3)$$

where p_r is a reference pressure, taken to be 0.1 MPa for convenience, and q_i are adjustable parameters.

Equation 3 was chosen for its relatively simple mathematical form and satisfactory fit of the data. More complicated expressions containing extra fitting parameters were also tested but they did not yield significant improvements. Model parameters q_i were estimated using Bayesian statistics (PyMC3),[24] by fitting them to the present experimental data (Sets A and B)[6,7] and the compressibility data of Lo Surdo and Millero.[4] As such, the weight of each datum is determined by its estimated standard uncertainty. The modelling of $V°$ is discussed further below.

3. RESULTS AND DISCUSSION

3.1. Standard Molar Volumes. As has long been recognised,[5] it is probably not possible from density measurements alone to reliably determine $V°$ for 2:2 electrolytes in aqueous solution. This is likely due to the presence of noticeable concentrations of ion pairs that can significantly influence the derived V_ϕ values. Such effects can be seen in the present data in the form of the unusual shape of $V_\phi(m)$ at low m (Figure 2 and Section 2.1 above) and by the strong correlation between $V°$ and $\beta^{V(2)}$. Under these circumstances, and following the practice of previous investigators,[3] $V°$ values for fully dissociated $ZnSO_4(aq)$ were obtained by additivity using tabulated literature estimates for $V°(ion)$.

Here-in lies a problem: the volumes of doubly-charged ions are not particularly well established. This is because they have to be determined by measurements on appropriate 2:1 and 1:2 electrolytes[25] that also exhibit (albeit to a much lesser extent) some degree of ion pairing, e.g., $ZnCl_2(aq)$[26] and $Na_2SO_4(aq)$.[27,28] Despite its limitations, this approach is the best available at the present time.

Accordingly, values of $V°(SO_4^{2-})$ over the temperature range of interest were taken from the compilations of Marcus.[29,30] However, values for $V°(Zn^{2+})$ were available only from 293 K to 348 K

(at AP) and show a large scatter.[3,31-36] Extension of $V°(Zn^{2+})$ to higher temperatures and pressures is not straightforward. Thus, values of $V°(ZnSO_4)$ were obtained by combining $V°(Zn^{2+})$ and $V°(SO_4^{2-})$ at $T < 330$ K, where they are reasonably well characterized, and extrapolating them to 393 K. To ensure realistic behaviour of the modelled $V°$ values, the following functional equation, loosely based on the "density model" of aqueous solutions,[37] was adopted:

$$V°(T,p) = q_1 + q_2(p - p_r) + q_3 \kappa_{T,w} \tag{4}$$

where q_i are fitting parameters, p_r is again a reference pressure (0.1 MPa) and $\kappa_{T,w}$ is the isothermal compressibility of pure water. By including a dependence of $V°$ on the compressibility of pure water, the values of $V°$ are constrained to behave in a physically reasonable manner, i.e., to decrease at high T. As shown below, this approach also allowed successful extrapolation of V_ϕ up to 100 MPa at 298.15 K. To fit the parameter q_2, the value of $\kappa_S°(ZnSO_4)$ at 298.15 K, calculated from the data of Millero and Sharp,[38] was converted to $\kappa_T°$ and included in the parameter estimation as an experimental datum.
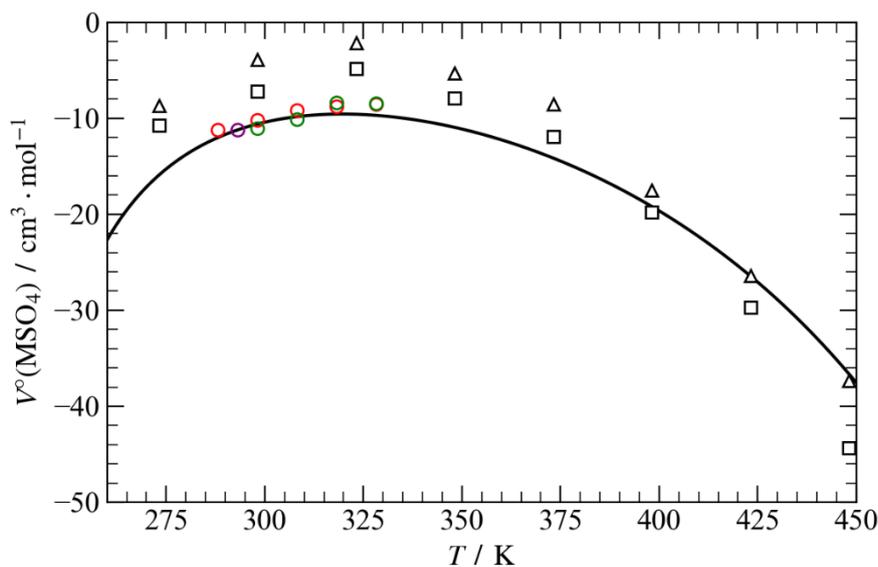
Figure 3. Standard volumes, $V°$, of selected $MSO_4(aq)$ solutions as a function of temperature at the saturation pressure of pure water. Solid line, current model (eq 4) for $ZnSO_4(aq)$; black squares, $MgSO_4(aq)$;[29,30] black triangles, $CaSO_4(aq)$.[29,30] Experimental values for $ZnSO_4(aq)$: red circles;[33] green circles;[13] purple circle, extrapolated from the data of Lamb and Lee[8] using the DHLL.

The estimated values for q_i are given in Table 2, while Figure 3 shows the $V°(ZnSO_4)$ values obtained via eq 4 as a function of temperature at the saturation vapour pressure of pure water, p_s. Also included in Figure 3 are the values of $V°(ZnSO_4)$ from the literature and, for comparison, the values of

$V°(CaSO_4)$ and $V°(MgSO_4)$ calculated from the ionic volumes, $V°(ion)$, given by Marcus.[29,30] The present model closely accounts for all the experimental data while the volumes of $CaSO_4(aq)$ and $MgSO_4(aq)$ suggest that the estimates of $V°(ZnSO_4)$ at $T > 330$ K are physically reasonable.

3.2. Pitzer Model of Apparent Molar Volumes. The optimised parameters for eq 3 are given in Table 2. As stated above, only three parameters in total were needed to describe the temperature and pressure dependences of $V°(ZnSO_4)$. For the interaction coefficients, reasonable agreement with the experimental data could be achieved with fourteen parameters. However, choosing this number of parameters leads, as often occurs with Pitzer models, to unphysical predictions outside the experimental range. For the present system this includes a sharp increase of V_ϕ, at high concentrations and temperatures. This behaviour arises from the rapid increase of A_V at high temperatures and the inability of the simple temperature dependencies of $\beta^{V(0)}$ and C^V to compensate for it. To circumvent this problem, and ensure smooth and physically reasonable extrapolation of the model beyond the studied range, which is of considerable interest for engineering calculations, the optimisation was constrained by enforcing the inequality $(\partial^2 V_\phi / \partial T^2)_{p,m} < 0$, based on Rowland's work.[39] This required an additional four adjustable parameters but ensured smooth and qualitatively correct extrapolations of the model to at least 470 K, which is well outside the studied range. However, as no data exist to validate the extrapolation, it should be treated only as a useful, physically reasonable estimate.

Table 2. Model Parameters q_i for Eq 3, Number in Parenthesis Correspond to Expanded Uncertainty in the Last Significant Digits at 0.95 Level of Confidence.[a]

	$V°$	$\beta^{V(0)}$	$\beta^{V(1)}$	$\beta^{V(2)}$	C^V
q_1	32.11(50)	3.15(18)e-02	3.73(90)e-02	9.28(93)e-01	-1.38(45)e-03
q_2	0.0388(20)	-2.65(13)e-04	-1.82(57)e-04	-4.86(15)e-03	1.24(42)e-05
q_3	-9.43(11)e+10	7.67(31)e-07	2.07(89)e-07	7.46(9)e-06	-3.74(13)e-08
q_4	-	-7.55(23)e-10	-	-	3.81(13)e-11
q_5	-	-7.18(35)e-06	-1.52(21)e-05	-	-
q_6	-	2.03(12)e-08	-	-2.697(50)e-06	-

[a]The units correspond to eqs 1 and 4 expressed in $cm^3 \cdot mol^{-1}$, $mol \cdot kg^{-1}$, K and MPa.

The variations of V_ϕ and $V°$ with temperature at the saturation vapour pressure of pure water are shown in Figure 4. Note that the solid lines correspond to the estimated soluble region for $ZnSO_4(aq)$, while the dashed lines are extrapolations into metastable (supersaturated) spaces.

Deviations of the present model from the experimental results of Sets A[6] and B[7] and literature data are shown in Figures 5, 6 and 7, respectively. The deviations are smallest for Set A, averaging about ± 0.1 $cm^3 \cdot mol^{-1}$ at high m (Figure 5) but, as is usual, increase rapidly at lower molalities ($m \lesssim 0.05$ $mol \cdot kg^{-1}$). This is due both to the limited resolution of the density measurements and the mathematical

form of the Pitzer equation. With regard to the latter, while the Pitzer model copes reasonably well with the unusual variation of V_ϕ at low m, the particular form of $\beta^{V(2)}$, eq 2, forces it to deviate from the DHLL at even smaller molalities, although the agreement is still fair (Figure 2).

In keeping with the lower sensitivity of the Hastelloy vibrating tube, the Set B data[7] show (Figure 6) considerably larger deviations than Set A,[6] of around $\pm(0.5$–1.5) cm^3·mol^{-1}, corresponding to relative deviations of (0.02–0.15) % in density. These deviations are also partly due to the larger weight given to the more precise and (presumably) more accurate data of Set A. It should, however, be mentioned that Set B is in good agreement with the high temperature data of Set A, measured with a custom-made HTD.[6]

Figure 7 shows the deviations of the literature data[4,8-11,13] from the present Pitzer model. Also included are the values calculated using the Pitzer model of Krumgalz et al.,[3] remembering that their model is limited to 298.15 K and was parameterized at $m \leq 0.9$ mol·kg^{-1}. Not surprisingly the deviations become extremely large at $m \gtrsim 1.5$ mol·kg^{-1}: a pertinent reminder of the typically poor extrapolative capabilities of Pitzer models.[22] Root mean square deviations (RMSD) and bias (calculated as average of the deviations $\Delta V_\phi = V_{\phi,\text{expt}} - V_{\phi,\text{calc}}$) of each dataset from the present model are given in Table 3.
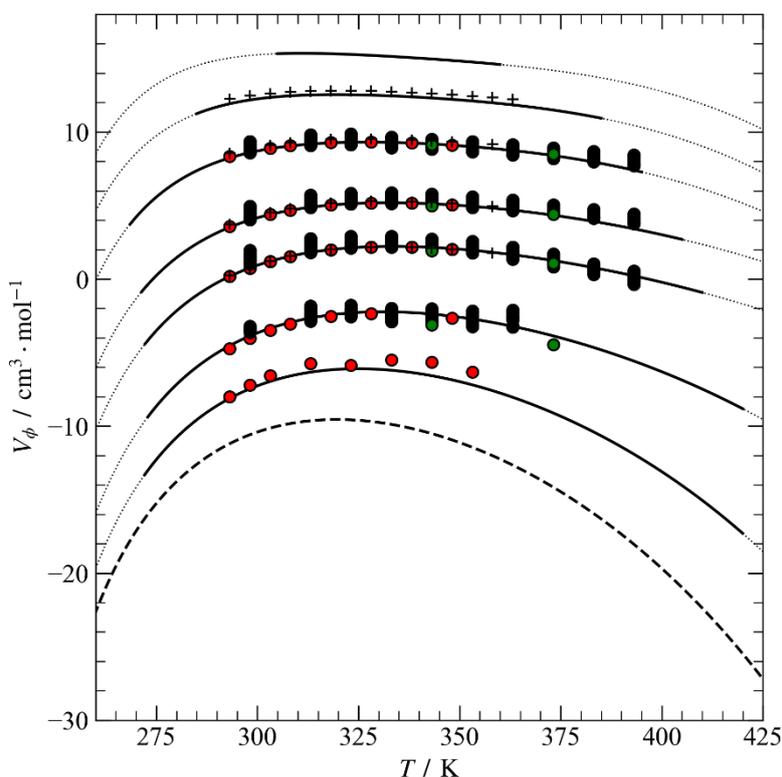
Figure 4. Temperature dependence of apparent molar volumes, $V_\phi(\text{ZnSO}_4(\text{aq}))$, at concentrations (bottom to top): $m/$ mol·kg^{-1} = 0, 0.01, 0.1, 0.5, 1, 2, 3, 4: red dots, Set A (AP);[6] green dots, Set A (HTD);[6] black dots, Set B (HP);[7] black crosses, Set B (AP).[7] Lines were calculated from the present

volumetric model (eqs 1 to 4) at the saturation pressure of pure water. The dashed line corresponds to $V°(ZnSO_4)$ (eq 4); solid lines correspond to the solubility range of $ZnSO_4$, calculated from a previous Pitzer model.[2] The dotted lines are extrapolations into the metastable (supersaturated) region.
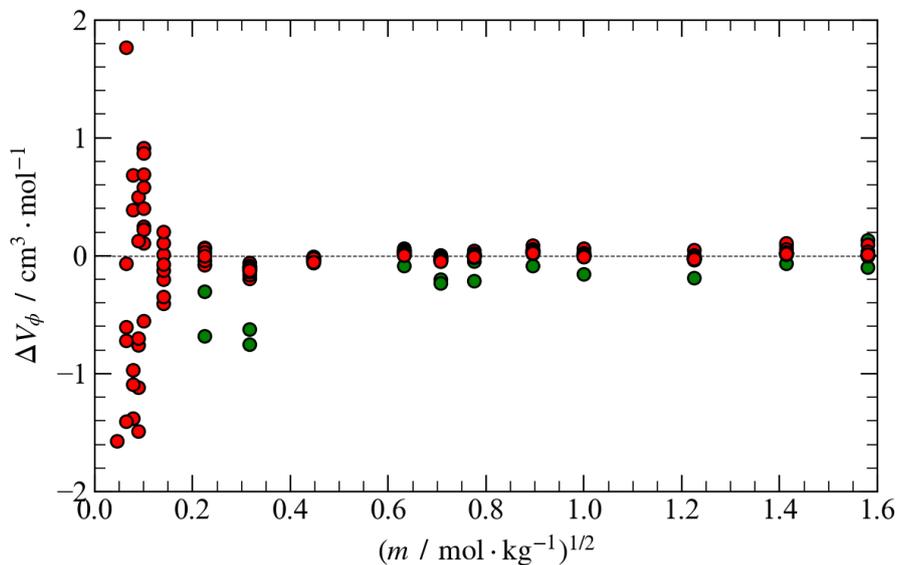
Figure 5. Deviations, $\Delta V_\phi = V_{\phi,\text{expt}} - V_{\phi,\text{calc}}$, of the experimental apparent molar volumes of Set A[6] from those calculated using the present Pitzer model. Red dots, AP; green dots, HTD.
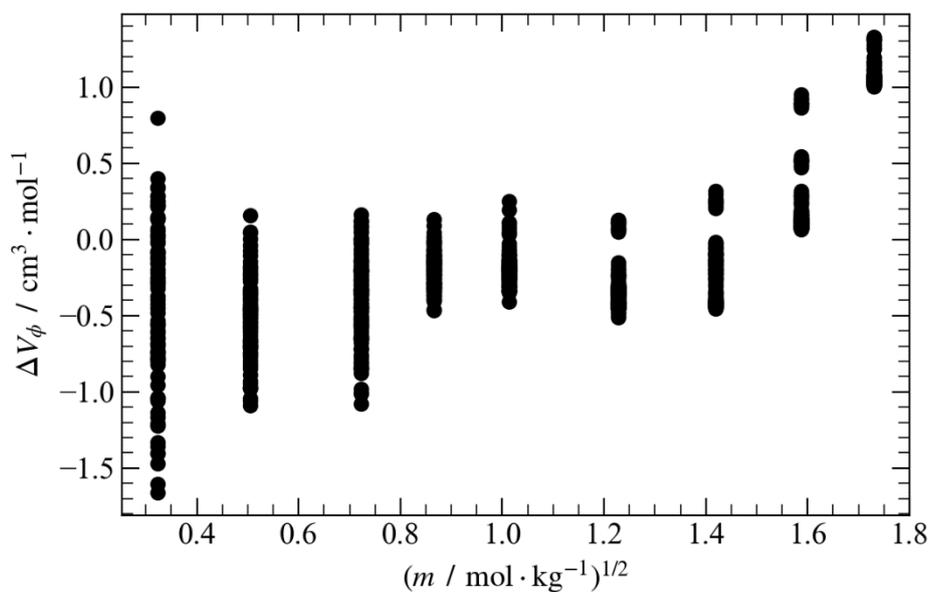
Figure 6. Deviations, $\Delta V_\phi = V_{\phi,\text{expt}} - V_{\phi,\text{calc}}$, of the experimental apparent molar volumes of Set B[7] from those calculated using the present Pitzer model.
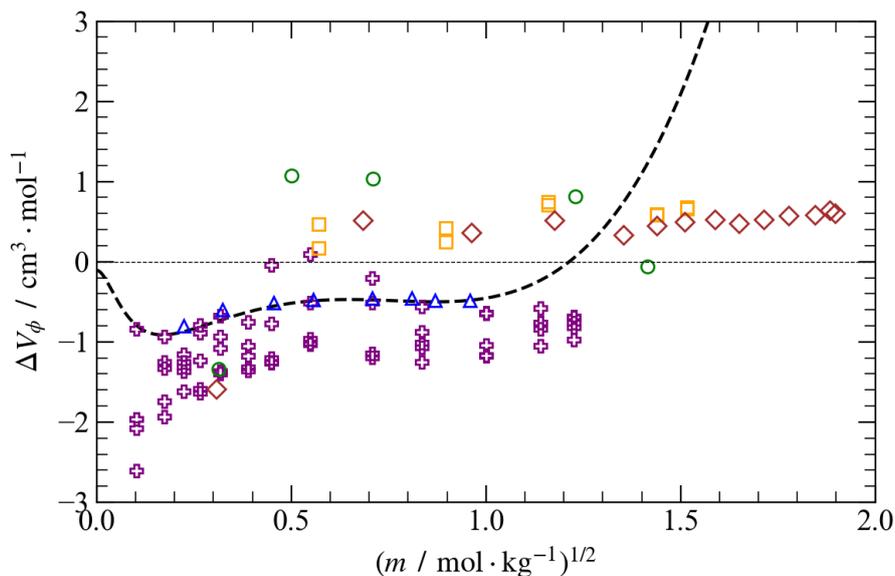
Figure 7. Deviations, $\Delta V_\phi = V_{\phi,\text{expt}} - V_{\phi,\text{calc}}$, of literature apparent molar volumes from those calculated using the present volumetric Pitzer model at 298.15 K: orange squares, Gibson;[9] green circles, Purser and Stokes;[10] brown diamonds, Albright and Miller;[11] blue triangles, Lo Surdo and Millero;[4] purple crosses, Puchalska et al. (at $288 \square T/\text{K} \square 328$).[13] The dashed line represents the Pitzer model of Krumgalz et al.[3]

Table 3. Root Mean Square Deviations (RMSD) and Biases (in V_ϕ) of the Various Datasets from the Present Model.

Reference	RMSD/cm³·mol⁻¹	Bias/cm³·mol⁻¹
Set A[6]	0.44	-0.07
Set B[7]	0.52	-0.10
Lamb and Lee[8]	0.21	-0.17
Gibson[9]	0.58	0.57
Purser and Stokes[10]	0.97	0.31
Albright and Miller[11]	0.65	0.36
Lo Surdo and Millero[4]	0.54	-0.53
Puchalska et al.[13]	1.17	-1.08

Figure 8 shows the isothermal compressibilities derived from the isentropic values of Lo Surdo and Millero[4] along with those calculated by linear approximation of the effects of pressure on the densities of Set B.[7] Despite its simple pressure dependency, the present model reproduces the experimental data with satisfying accuracy, given the relatively low precision of the Set B data (Figure 6).

3.3. Effects of Pressure. Volumetric properties of $ZnSO_4(aq)$ solutions outside of ambient pressures, have been reported rather sparingly (Table 1), so testing the performance of the model is difficult. Fortunately, Gibson[9] has reported solution densities at 0.1 MPa and the change in solution volume up to 100 MPa at 298.15 K. These results were converted to apparent molar volumes and are compared with the present model in Figure 9. Despite the significant extrapolation beyond the model's parameterization range, agreement with the experimental results is excellent: $\lesssim 1$ $cm^3 \cdot mol^{-1}$ in V_ϕ or $\lesssim 0.15$ % in densities, at both 0.1 and 100 MPa. This level of agreement between the model and the experimental data is more than adequate for most practical applications. It is important to note that the extrapolation to 100 MPa included the dependence of $V°$ on $\kappa_{T,w}$, with just a linear pressure dependence of the interaction parameters. This occurs because bulk properties of solutions largely reflect the properties of the solvent.
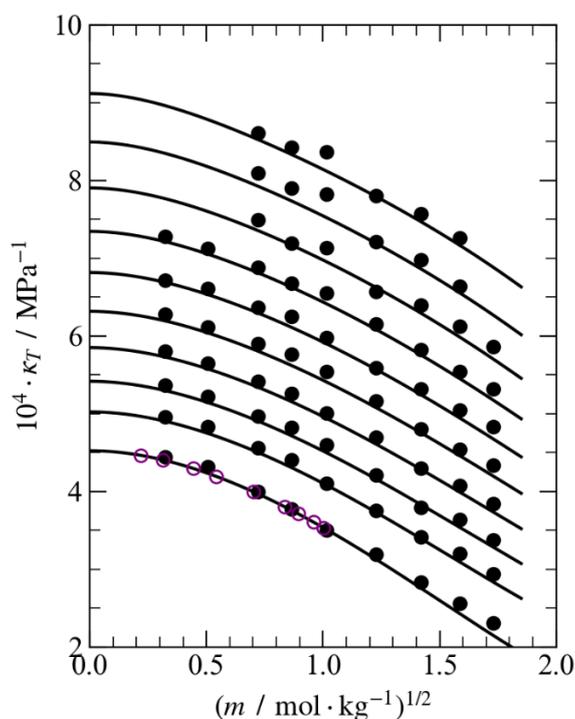
Figure 8. Isothermal compressibilities κ_T of $ZnSO_4(aq)$ as a function of concentration (as $m^{1/2}$) at temperatures (bottom to top), T/K = 298.15, 313.15, 323.15, 333.15, 343.15, 353.15, 363.15, 373.15, 383.15 and 393.15. Purple circles, Lo Surdo and Millero;[4] black dots, Set B.[7] Lines are calculated from the present model; for representational clarity the data have been offset by $4 \cdot 10^3$ $(MPa \cdot K)^{-1} \cdot (T - 298.15)$ K.
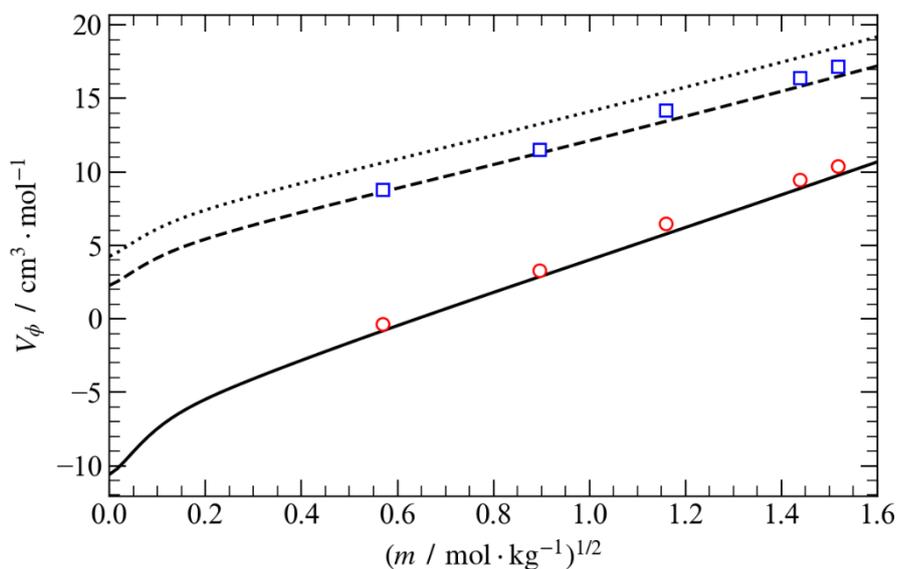
Figure 9. Apparent molar volumes V_ϕ of ZnSO$_4$(aq) predicted as a function of concentration (as $m^{1/2}$) by the present Pitzer model at 298.15 K and pressures 0.1 MPa (full line) and 100 MPa (dashed line). The dotted line corresponds to the V_ϕ values predicted without including the κ_T-dependence of V°. Experimental points are from Gibson.[9]

4. CONCLUSIONS

Recent independent measurements of the densities of ZnSO$_4$(aq) solutions are in excellent agreement with each other over wide ranges of concentration and temperature. Where comparisons are possible, they also lie within the spread of the literature values. Apparent molar volumes V_ϕ calculated from the present data vary smoothly with temperature and pressure up to near-saturation concentrations. A standard Pitzer model, parameterized on these data was adequate for describing the volumetric properties of ZnSO$_4$(aq) solutions over a wide range of conditions, including very low concentrations ($m \lesssim 0.01$ mol·kg^{-1}) where V_ϕ undergoes an unusual step-change, thought to be due to chemical speciation effects. By including a dependence of V° on κ_{Tw} (in addition to T and p) it was possible to predict V_ϕ with reasonable accuracy even up to 100 MPa at 298.15 K. It was also found that inclusion of the inequality $(\partial^2 V_\phi/\partial T^2)_{p,m} < 0$ in the model opened up the possibility of its physically reasonable extrapolation to temperatures well beyond its parameterization range, although there are at present no data available to test the accuracy of these predictions. The present model is therefore suitable for modelling the volumetric behaviour of ZnSO$_4$(aq) solutions in a wide range of industrial contexts.

AUTHOR INFORMATION
Corresponding Author
*E-mail: tuomas.vielma@oulu.fi
ORCID
Tuomas Vielma: 0000-0003-3598-9042
Lubomir Hnedkovsky: 0000-0002-3851-8070

Petri Uusi-Kyyny: 0000-0002-8339-4601
Justin Salminen: -
Ville Alopaeus: 0000-0001-9773-0998
Ulla Lassi: 0000-0001-5319-9525
Glenn Hefter: 0000-0001-9388-2783

Notes
The authors declare no competing financial interest.

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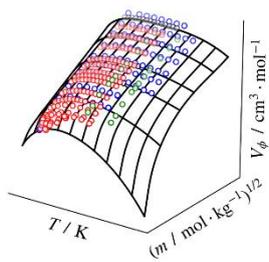
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