

A Pitzer-based Characterization of Aqueous Magnesium Chloride, Calcium Chloride and Potassium Iodide Solution Densities to High Temperature and Pressure

Darren Rowland^{a,*}, Peter M. May^a

^a*School of Chemical and Mathematical Sciences, Murdoch University, Murdoch, WA 6150*

Abstract

A comprehensive characterization of densities / apparent molar volumes for the aqueous solutions of magnesium chloride, calcium chloride and potassium iodide to high temperatures and pressures has been performed based on the Pitzer equations. The unusual availability of overlapping high quality independent sets of experimentally measured data for these systems allows the relevant thermodynamic quantities to be calculated with a high degree of confidence over wide ranges of conditions (< 8 mol/kg; 273–573 K; 0.1–100 MPa). A realistic assessment of experimental uncertainty indicates that an adequate description of volumetric behaviour is achieved by the standard Pitzer model without extensions. The experimental accuracy implied by differences between independent observers, however, is more than one order of magnitude worse than typically-claimed estimates of experimental precision.

Keywords: Electrolytes, Density, Apparent molar volume, Pitzer equations

1. Introduction

The recent publication of high quality density data for $\text{MgCl}_2(\text{aq})$, $\text{CaCl}_2(\text{aq})$ and $\text{KI}(\text{aq})$ under superambient conditions [1] provides an unusual opportunity to investigate the effectiveness of thermodynamic modelling capabilities

*Corresponding author. Tel: +61 8 9360 1393. Fax: +61 8 9360 6452

Email addresses: d.rowland@murdoch.edu.au (Darren Rowland),
p.may@murdoch.edu.au (Peter M. May)

at the current state-of-the-art. Taken together with previously described authoritative datasets, there is now a sufficient number of independent property values not only to test the goodness-of-fit of theoretical models but also to assess realistically the experimental uncertainty and thus to avoid more degrees of freedom than are warranted in the model-fitting process.

Since magnesium chloride and calcium chloride are particularly important in environmental and industrial contexts, a number of models for the density and other thermodynamic properties have been published previously (Table 1). However, many of these works are 1–2 decades old and are not consistent with the most up-to-date thermodynamic properties of water. Mao and Duan [2] have criticised the better-known models [3–5] for aqueous chloride solutions identifying some frequent flaws such as non-thermodynamically conforming trends at high concentration and failure to extrapolate to the density of pure water. Al Ghafri *et al.*'s [1] modelling approach also re-optimized the density of pure water, producing differences with convincing correlations. Above all, the primary problem with the models in Table 1, as with any critical review of thermodynamic data, is that they become superseded whenever new, high-quality measurements are performed. The JESS automated facility [6] for parameterization and modelling of physicochemical property data of aqueous solutions, which has been used in the present work, is designed to address this problem.

The present work extends the temperature range and provides a unified model of the volumetric properties of MgCl_2 , CaCl_2 and KI through a comprehensive characterization of published densities / apparent molar volumes to high temperatures and pressures based on the Pitzer equations.

2. Methods

The Pitzer equations describe the Gibbs energy of electrolyte solutions [10]. Differentiation of the Pitzer equations with respect to pressure yields the apparent molar volume [11]

$$\begin{aligned} \phi V = V^\circ + |z_M z_X| (A_V = 2b) \ln(1 + bI^{1/2}) \\ + m_X RT [2m B_{MX}^V + m^2 (m_X)^{1/2} C_{MX}^{\phi V}] \end{aligned} \quad (1)$$

$$B_{MX}^V = \frac{(0)V}{MX} + \frac{(1)V}{MX} g(I^{1/2})$$

Table 1: Literature models for solution density covering a range of temperature conditions

System	Ref	ρ /MPa	T /K	m_{\max} /(\text{mol.kg}^{-1})
MgCl ₂	[1]	<68.5	298–473	5.0
	[2]	0.1–30	273–543	3.0
	[3]	0.1–100	273–627	6.17
	[7]	0.1–2	273–473	1.0
	[8]	0.1	273–373	7.0
CaCl ₂	[1]	<68.5	298–473	6.0
	[2]	0.1–60	273–523	6.0
	[5]	0.1–60	298–398	6.0
	[4]	0.1–40	273–523	6.15
	[9]	0.1–40	270–526	4.6
	[7]	0.1–2	273–473	1.0
KI	[8]	0.1	273–373	8.0
	[1]	<68.5	298–473	1.06

$$g(x) = 2[1 - (1 + x) \exp(-x)] = x^2$$

where Z_M and Z_X are the charges on the cation and anion, ν_M and ν_X are the stoichiometric coefficients of the ions with $\nu = \nu_M + \nu_X$ and $I = 0.5 |Z_M Z_X| m$ is the stoichiometric ionic strength of the solution. The parameters $b = 1.2$ (kg.mol^{-1})^{1/2} and $\beta = 2.0$ (kg.mol^{-1})^{1/2} are the standard Pitzer values and are used in this work. The theoretical Debye-Hückel slope, A_V , is calculated using the formulation of Fernandez *et al.* [12] with the properties of water from the IAPWS 95 release [13]. The parameters which need to be optimised are V° , ${}^{(0)}V_{MX}$, ${}^{(1)}V_{MX}$ and $C_{MX}^{\phi V}$, all as functions of temperature and pressure.

The values of V° usually exhibit a complex dependence on temperature and pressure [14, 15]. As recommended by Archer [15], certain numerical difficulties associated with this parameter can be reduced [14] by re-writing equation (1) to make it relative to a non-zero reference concentration, m_r .

$$\begin{aligned} \phi V + \nu_w = n_r &= V(m_r) = n_r \\ &+ |Z_M Z_X| (A_V = 2b) \ln[(1 + bI^{1/2}) = (1 + bI_r^{1/2})] \\ &+ \nu_M \nu_X RT [2(m B_{MX}^V(I) - m_r B_{MX}^V(I_r))] \\ &+ (m^2 - m_r^2) (\nu_M \nu_X)^{1/2} C_{MX}^{\phi V} \end{aligned}$$

where ν_w is the volume of 1 kg of pure solvent at the temperature and pressure

of the solution and n_r is the number of moles of solute. In this way, $V(m_r)$ is taken as an adjustable parameter, having less extreme temperature and pressure variation than the infinite dilution property. The parameterization of $V(m_r)=n_r$ is

$$\begin{aligned}
V(m_r)=n_r = & 100v_1 + v_2 T=T^\circ + v_3 1 \times 10^{-2}(T=T^\circ)^2 \\
& + v_4 1 \times 10^{-5}(T=T^\circ)^3 \\
& + v_5(\rho=\rho^\circ) + v_6 1 \times 10^{-2}(\rho=\rho^\circ)(T=T^\circ) \\
& + v_7 1 \times 10^{-4}(\rho=\rho^\circ)(T=T^\circ)^2 \\
& + v_8 1 \times 10^{-2}(\rho=\rho^\circ)^2 \\
& + v_9 1 \times 10^{-4}(\rho=\rho^\circ)^2(T=T^\circ)
\end{aligned} \tag{2}$$

where T° is 1.0 K, ρ° is 1.0 MPa and the v_j are parameters to be determined. The remaining Pitzer parameters share a common form which is representative of those models used most often in the literature [14–18]:

$${}^{(0)}V_{\text{MX}} = f_1(\rho; T)=m^\circ \tag{3}$$

$${}^{(1)}V_{\text{MX}} = f_2(\rho; T)=m^\circ \tag{4}$$

$$C_{\text{MX}}^{\phi V} = f_3(\rho; T)=m^{\circ 2} \tag{5}$$

$$\begin{aligned}
f_i(\rho; T) = & 1 \times 10^{-2}\{b_{i,1} + b_{i,2} \ln(T=T_r)\} \\
& + b_{i,3} 1 \times 10^{-2}[(T - T_r)=T^\circ] \\
& + b_{i,4} 10[T^\circ=(620 \text{ K} - T) - T^\circ=(620 \text{ K} - T_r)] \\
& + b_{i,5} 1 \times 10^3[T^\circ=(T - 227 \text{ K}) - T^\circ=(T_r - 227 \text{ K})] \\
& + 2 \times 10^{-4}(\rho=\rho^\circ)\{b_{i,6} + b_{i,7} \ln(T=T_r)\} \\
& + b_{i,8} 1 \times 10^{-2}[(T - T_r)=T^\circ] \\
& + b_{i,9} 10[T^\circ=(620 \text{ K} - T) - T^\circ=(620 \text{ K} - T_r)] \\
& + b_{i,10} 1 \times 10^3[T^\circ=(T - 227 \text{ K}) - T^\circ=(T_r - 227 \text{ K})]
\end{aligned} \tag{6}$$

where m° is 1.0 mol.kg⁻¹, $T_r \equiv 298.15$ K and the $b_{i,j}$ are model parameters.

Since the equations are cast in terms of the apparent molar volume, experimental values of the density (or density difference relative to water) are converted using the relation

$$\phi V = M = + (1000=m)(1= - 1= w) \tag{7}$$

where M is the molar mass of the solute and ρ_w is the density of pure water calculated using the IAPWS formulation [13].

Given that the reliability of empirical models can be greatly influenced by the quality and quantity of available data, locations of the density data in the $(\rho; T; m)$ -space were plotted for MgCl_2 (Figure 1), CaCl_2 (Figure 2) and KI (Figure 3). Magnesium chloride data are available across most of the multidimensional range of conditions, including independently-measured density values at high pressure near $T = (298, 373 \text{ and } 448)$ K. However, data are more limited above 473 K and extend to only 3 mol.kg^{-1} in this region. The calcium chloride system has even fewer gaps in its data coverage, with multiple measurement sources at high temperatures and pressures. On the other hand data for potassium iodide are comparatively scarce. While the recent values of Al Ghafri *et al.* [1] extend the data to 473 K and high pressure, there are no measurements at concentrations above 1 mol.kg^{-1} at temperatures greater than 373 K. Since the data are lacking at non-ambient pressure, the ${}_{\text{KI}}^{(1)V}$ and $C_{\text{KI}}^{\phi V}$ parameters were taken as pressure independent during model-fitting. As equations (2)–(6) are linear with respect to all of the unknown parameters, best-fitting values can be determined using singular value decomposition [6, 19].

3. Results

3.1. MgCl_2

Most of the selected density data for aqueous magnesium chloride solutions were found to be mutually consistent. Overall, more than 78% of the apparent molar volume data have residuals within $\pm 0.5 \text{ cm}^3.\text{mol}^{-1}$ and more than 92% of the data have residuals less than $1.0 \text{ cm}^3.\text{mol}^{-1}$ in magnitude. Since independent observations of the apparent molar volumes under identical conditions differ by $0.5\text{--}2.0 \text{ cm}^3.\text{mol}^{-1}$, it can be concluded that the available data are very well represented by the present model. However, some data points received little or no weight in the final fit (details given in Supporting Information). Especially at low concentrations, the secondary data tables of Aseyev and Zaytsev [20] and Laliberté [21] show large deviations in the apparent molar volume, probably due to the method of conversion from density which is highly sensitive to the density used for pure water. Similarly, the two lowest-concentration data values of Miller *et al.* [22] were excluded.

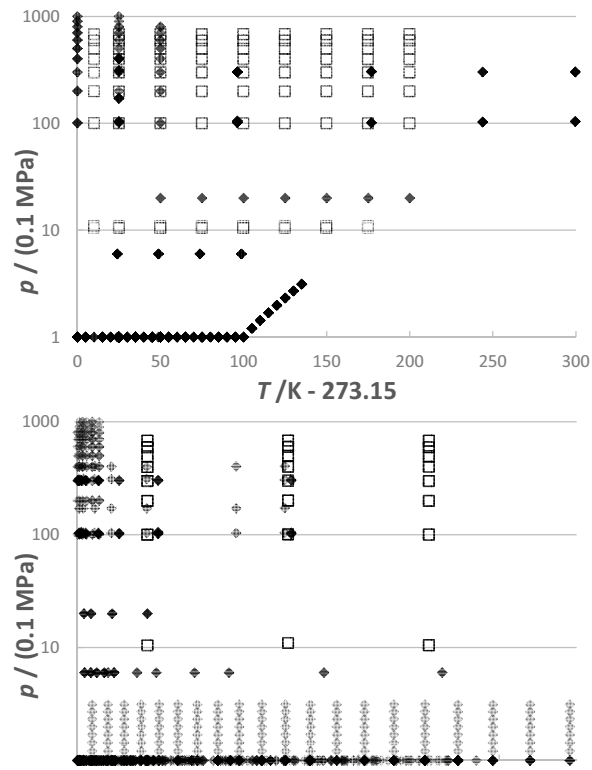


Figure 1: Location of MgCl_2 volumetric data in (p, T, m) space. Open squares indicate data of Al Ghafri *et al.*[1] Filled diamonds correspond to all other data. Darker colouring represents greater number density of data.

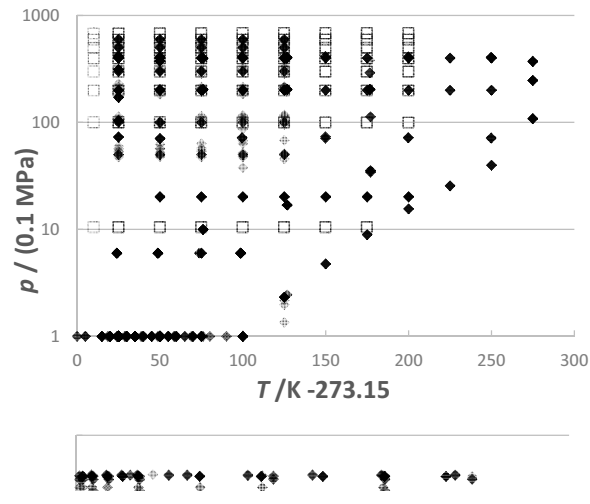


Figure 2: Locations of CaCl_2 volumetric data in (p, T, m) space. Symbols have the same meaning as in Figure 1.

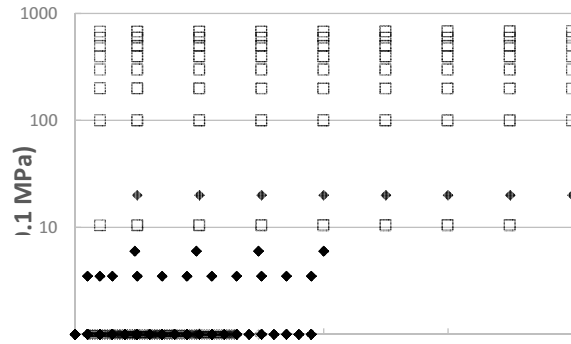


Figure 3: Locations of KI volumetric data in (p, T, m) space. Symbols have the same meaning as in Figure 1.

Table 2: Volumetric Pitzer parameters for MgCl_2 ($m_r = 5.0 \text{ mol.kg}^{-1}$)

j	$v_j(V(m_r))$	$b_{1,j}(\frac{{}^{(0)}V}{\text{MX}})$	$b_{2,j}(\frac{{}^{(1)}V}{\text{MX}})$	$b_{3,j}(C_{\text{MX}}^{\phi V})$
1	3.364	0.01518	-0.02678	-0.001302
2	-0.9652	0.05537	-13.95	-0.02667
3	0.2686	0.0000	4.194	0.009362
4	-0.2260	-0.1110	-47.28	-0.1934
5	0.1171	0.002587	-0.03718	-0.0002311
6	-0.07758	-0.006510	0.02344	0.001013
7	0.008894	0.0000	19.31	0.07072
8	-0.02613	-0.03468	-5.935	-0.01344
9	0.007794	0.6593	50.36	0.06166
10		-0.004040	0.04912	0.001138

The high-concentration data of Isono [23] are systematically high for $m > 3 \text{ mol.kg}^{-1}$ and were given no weight.

The best-fitting parameters in the general model for MgCl_2 are shown in Table 2. The reference concentration was chosen as 5 mol.kg^{-1} since this is the highest concentration at which there is a significant number of data over a wide range of conditions (see Figure 1). The deviations between the model and the data of Al Ghafri *et al.* [1] are minor (Figure 4), being mostly less than $\pm 0.5 \text{ cm}^3.\text{mol}^{-1}$. However, there is a small but noticeable cycling of the residuals with temperature at the highest solution concentration.

As noted above, there are some locations in the multidimensional space where data have been independently measured. The residuals of the experimental apparent molar volumes from the model near particular temperatures and pressures are shown in Figure 5. The agreement between different data sources at ambient temperature is evidently close to $0.5 \text{ cm}^3.\text{mol}^{-1}$. At higher temperatures, the two main data sources are Obšil *et al.* [24] and Al Ghafri *et al.* [1]. At concentrations near 1.0 mol.kg^{-1} the difference between the measured apparent molar volume is approximately $1.0 \text{ cm}^3.\text{mol}^{-1}$. At 3 mol.kg^{-1} , the difference approximately doubles to $2.0 \text{ cm}^3.\text{mol}^{-1}$, corresponding to a difference in the experimental density of 0.4–0.5% (see Supporting Information).

The experimental precision attributed by Al Ghafri *et al.* to their density results is 0.05% [1]. The data of Obšil *et al.* are claimed to be accurate to

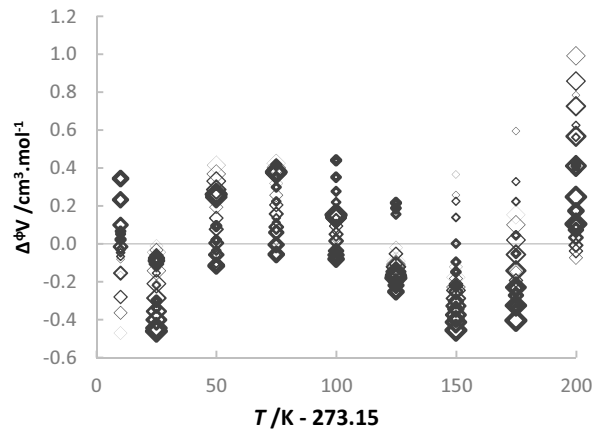


Figure 4: Apparent molar volume deviations between the MgCl_2 data of Al Ghafri *et al.* [1] and the present model. Larger symbols denote higher concentration, thicker symbols denote higher pressure.

better than 0.1% in density at high concentration [27]. It is apparent that the differences between the measurements from these sources are significantly larger than these uncertainty estimates.

3.2. CaCl_2

The available calcium chloride data are largely consistent and the present model achieves a high-quality fit. More than 77% of the data have residuals within $\pm 0.5 \text{ cm}^3 \cdot \text{mol}^{-1}$ and 91% are within $\pm 1.0 \text{ cm}^3 \cdot \text{mol}^{-1}$. As with MgCl_2 , some data from Isono [23] for CaCl_2 were of lower quality: the data at $m < 1 \text{ mol} \cdot \text{kg}^{-1}$ were given lesser weight than the higher concentration data. The secondary data from Laliberté [21] display systematic deviations at concentrations less than $1.5 \text{ mol} \cdot \text{kg}^{-1}$ and were excluded. Apart from this, only a few isolated points from other references were excluded (see Supporting Information). The optimised parameters of the final fit are given in Table 3.

The residuals to the Al Ghafri *et al.* [1] data exhibit a systematic positive bias of around $0.2\text{--}0.5 \text{ cm}^3 \cdot \text{mol}^{-1}$ (Figure 6). There are several other sources of density data for calcium chloride solutions at high pressure over a range of temperature. The differences between nearby data from independent observers generally increase with increasing temperature and pressure, but are

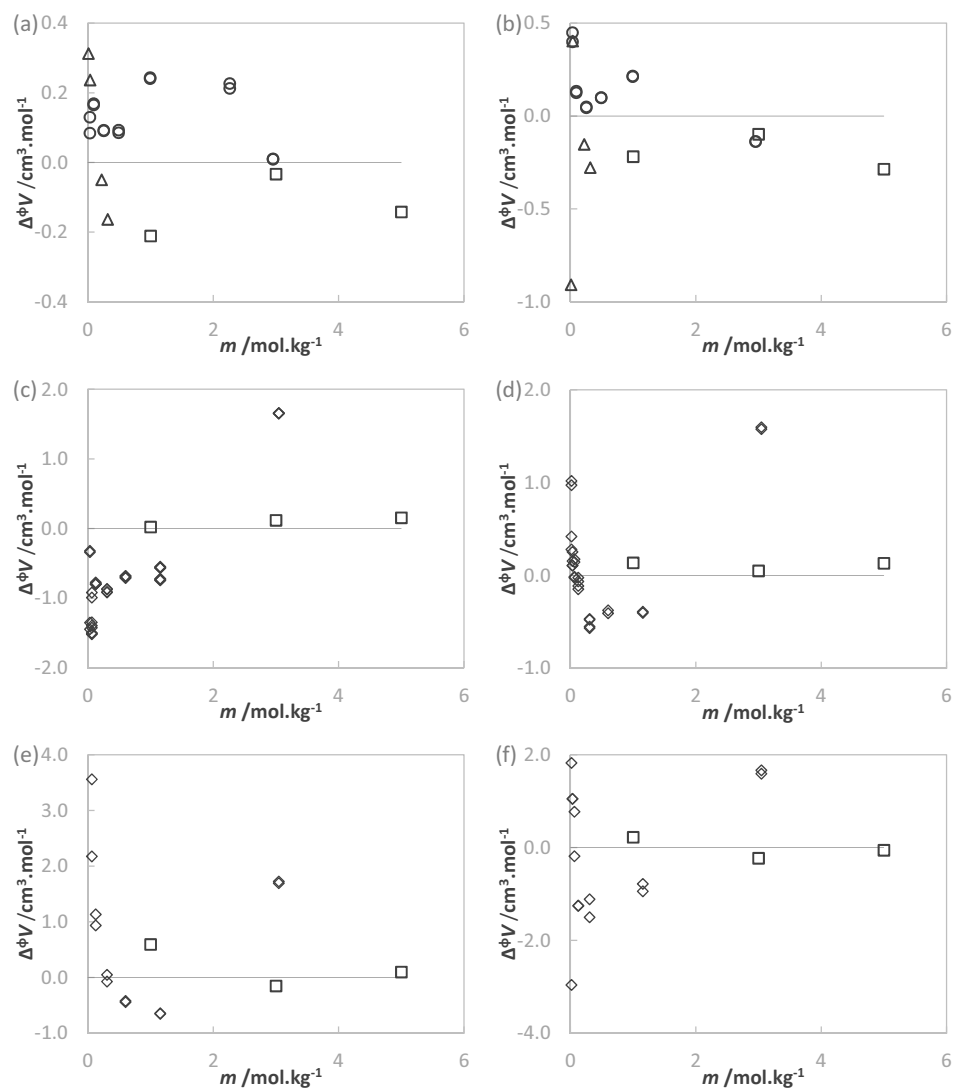


Figure 5: Apparent molar volume residuals for MgCl_2 from independent sources at high pressure: triangles [25], circles [26], squares [1], diamonds [24]. (a) 10 MPa, 298 K; (b) 30 MPa, 298 K; (c) 10 MPa, 373 K; (d) 30 MPa, 373 K; (e) 10 MPa, 448 K; (f) 30 MPa, 448 K.

Table 3: Volumetric Pitzer parameters for CaCl_2 ($m_r = 6.0 \text{ mol.kg}^{-1}$)

j	$v_j(V(m_r))$	$b_{1,j}(\frac{{}^{(0)}V}{\text{MX}})$	$b_{2,j}(\frac{{}^{(1)}V}{\text{MX}})$	$b_{3,j}(C_{\text{MX}}^{\phi V})$
1	1.726	0.01312	-0.02427	-0.0003884
2	0.1051	0.0000	-6.722	-0.04483
3	-0.009339	0.03474	1.898	0.008440
4	0.01570	-1.156	-19.06	0.04423
5	0.04837	0.002719	-0.01293	-0.0004847
6	-0.02993	-0.001595	0.02574	-0.0001673
7	0.0006138	0.0000	6.299	0.04312
8	-0.09847	-0.02593	-1.643	-0.009002
9	0.02940	0.9965	7.796	-0.03946
10		-0.001445	0.03149	0.0003265

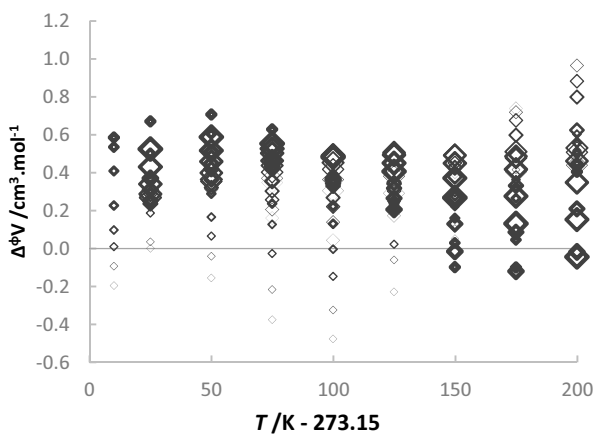


Figure 6: Apparent molar volume deviations between the CaCl_2 data of Al Ghafri *et al.* [1] and the present model. Larger symbols denote higher concentration, thicker symbols denote higher pressure.

typically $0.5\text{--}1.0\text{ cm}^3\cdot\text{mol}^{-1}$ (Figure 7).

The bias exhibited by the Al Ghafri *et al.* data is counter-balanced by those of the other high-pressure datasets (Figure 8). The present model represents the majority of the high-pressure data to within $\pm 0.6\text{ cm}^3\cdot\text{mol}^{-1}$, while the datasets of Gates and Wood [28], Oakes *et al.* [4] and Safarov *et al.* [5] are responsible for some of the larger outliers.

Safarov *et al.* report that their model reproduces their solution density data with an average deviation of 0.02% [5]. Al Ghafri *et al.* state their density uncertainty is less than 0.05% [1]. Oakes *et al.* [4] place maximum limits between 0.02–0.04% on the error in their density data. The stated standard errors of the Gates and Wood density datasets [26, 28] are less than 0.02%. Depending on the experimental conditions, differences in the apparent molar volume of $0.5\text{--}1.0\text{ cm}^3\cdot\text{mol}^{-1}$ correspond to differences in the solution density of 0.2–0.4% (see Supporting Information). Again, this is significantly greater than the stated uncertainty in each of the cited works.

The data of Kumar [29] exhibit the largest residuals (up to $\pm 5.5\text{ cm}^3\cdot\text{mol}^{-1}$) from the model. The data of Saluja and LeBlanc [30] have residuals which show systematically positive deviations of up to $2\text{ cm}^3\cdot\text{mol}^{-1}$ from the present model.

3.3. KI

The data for potassium iodide are represented quite satisfactorily by the model. Even some of the earliest datasets [31, 32] are in notably good accord with the present fits. Almost 90% of the residuals are between $\pm 0.5\text{ cm}^3\cdot\text{mol}^{-1}$. Swenson and Woolley’s [33] potassium iodide data at low concentration ($m < 0.2$) contain large standard errors and exhibit large systematic deviations from their model. Therefore, they were excluded from the present model-fitting. Data from the secondary sources of Aseyev and Zaytsev [20] and Laliberté [21] were also excluded (see Supporting Information for details).

During initial fitting it was apparent that some of the Al Ghafri *et al.* [1] data at $0.9\text{ mol}\cdot\text{kg}^{-1}$ were systematically low by approximately $2\text{ cm}^3\cdot\text{mol}^{-1}$ when converted to apparent molar volumes. These data were retained in the model-fitting but with reduced weight. Our model parameters for the best fit are given in Table 4.

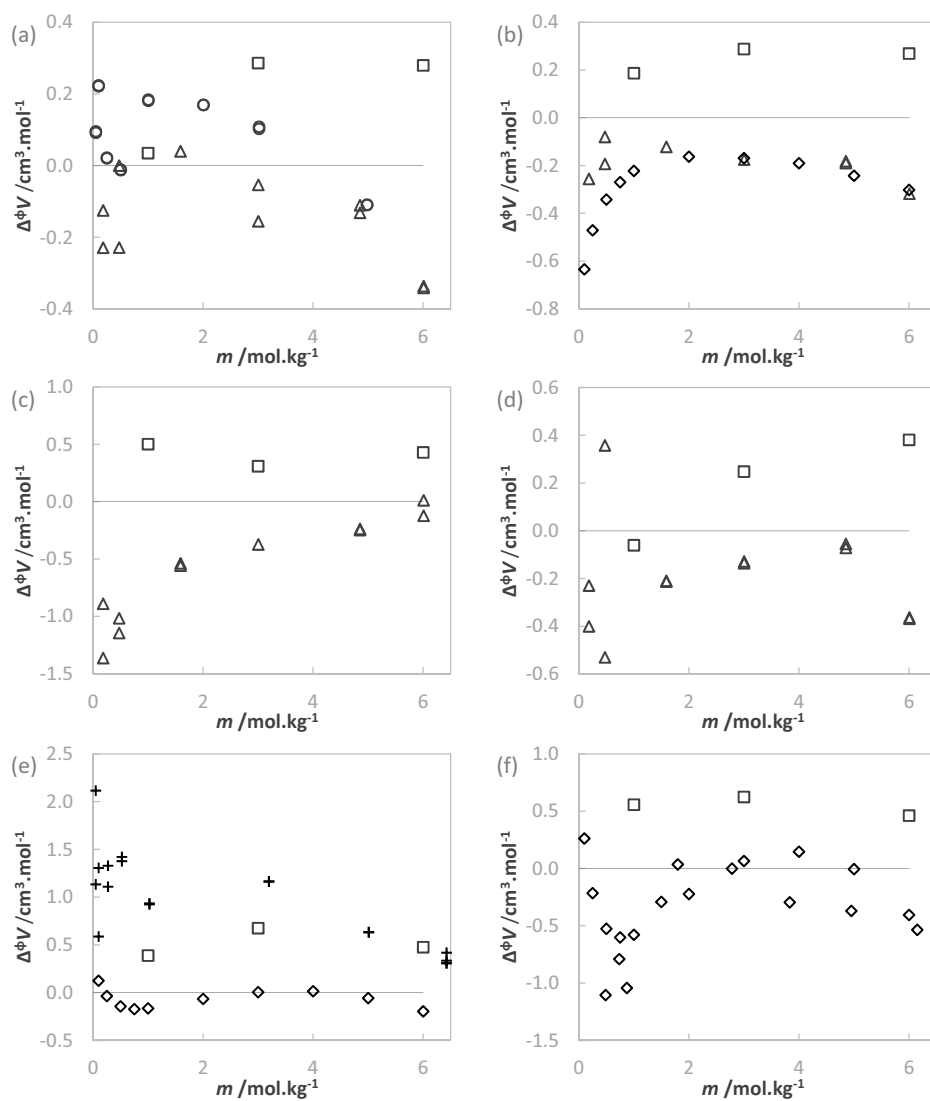


Figure 7: Apparent molar volume residuals for CaCl_2 from independent sources at high pressure: triangles [5], circles [26], squares [1], diamonds [4], pluses [28]. (a) 10 MPa, 298 K; (b) 20 MPa, 298 K; (c) 60 MPa, 298 K; (d) 10 MPa, 398 K; (e) 20 MPa, 448 K; (f) 40 MPa, 473 K.

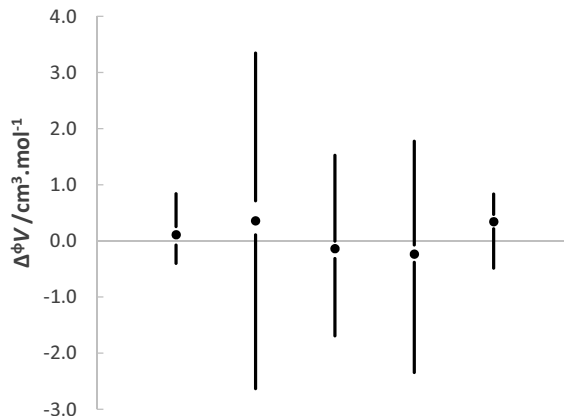


Figure 8: Quartile plot of the apparent molar volume residuals from the main CaCl_2 datasets at high pressure. From left to right: Gates and Wood (1985) [26], Gates and Wood (1989) [28], Oakes *et al.* [4], Safarov *et al.* [5], Al Ghafri *et al.* [1]

The residuals of the Al Ghafri *et al.* [1] data are uniformly small — within $\pm 0.4 \text{ cm}^3 \cdot \text{mol}^{-1}$ — except for the outlying data mentioned above (see Figure 9). Otherwise, there are no significant trends with temperature, pressure or concentration.

Since there are comparatively few data for potassium iodide, independently measured data at similar (non-ambient) conditions are rare. One of the only primary sources of high-concentration $\text{KI}(\text{aq})$ density data is Swenson and Woolley [33] at 0.35 MPa. The residuals between the model and the data of Swenson and Woolley [33] are shown in Figure 10. It is apparent that the data are correlated very well by the model over the full range of concentration, with only a few outlying data at the lower temperatures. However, this is to be expected given the flexibility of the Pitzer equations and the fact that there is only one source of high-temperature data.

The dataset of Saluja *et al.* [34] shows some of the largest residuals from the modelled apparent molar volumes. The data are scattered at low concentrations, probably because of the numerical sensitivities inherent in converting between density and apparent molar volume.

Table 4: Volumetric Pitzer parameters for KI ($m_r = 2.0 \text{ mol.kg}^{-1}$)

j	$v_j(V(m_r))$	$b_{1,j}(\frac{{}^{(0)}V}{\text{MX}})$	$b_{2,j}(\frac{{}^{(1)}V}{\text{MX}})$	$b_{3,j}(C_{\text{MX}}^{\phi V})$
1	5.600	-0.01006	-0.005340	-0.001359
2	-0.2315	-1.710	8.546	0.3322
3	0.04340	0.4607	-2.298	-0.08783
4	0.07336			
5	-0.9116	-0.003468	0.02594	0.0009192
6	0.4600	-0.01986		
7	-0.07624	0.2999		
8	-0.09949	-0.08603		
9	0.03893			
10		-0.0009463		

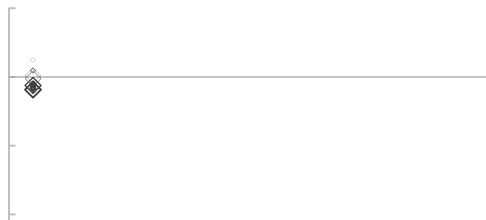


Figure 9: Apparent molar volume deviations between the KI data of Al Ghafri *et al.* [1] and the present model. Larger symbols denote higher concentration, thicker symbols denote higher pressure.

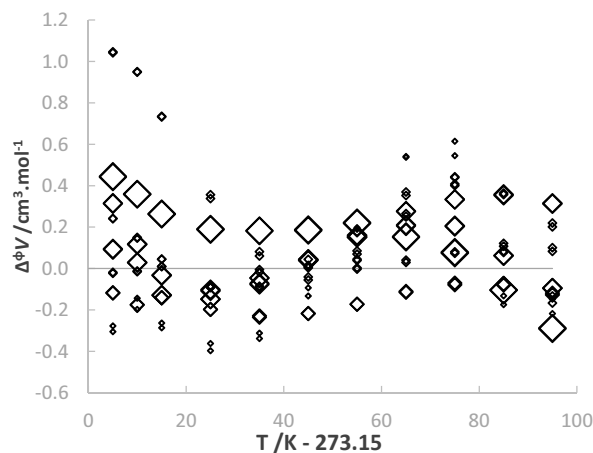


Figure 10: Apparent molar volume deviations between the KI data of Swenson and Woolley [33] and the present model. Larger symbols denote higher concentration.

3.4. Comparisons with literature models

An extensive analysis of aqueous electrolyte solution volumes at 298.15 K was described by Krumgalz *et al.* [35]. Apparent molar volumes calculated from their published parameters are compared to those of the present work (Table 5). The calculated values are in very good agreement. The largest differences in Table 5 occur at infinite dilution. This is to be expected since the uncertainty in the apparent molar volume data is greatest at low concentrations.

Wang *et al.* [3] and Mao and Duan [2] presented models of MgCl_2 apparent molar volumes valid over a range of temperatures and pressures. These models and the present model are compared at several temperatures and pressures (Figure 11). Mao and Duan have provided a computer program for calculating the density using their model. Since their program reports the density only to 5 decimal places, the conversion to apparent molar volume (equation (7)) at low concentration is subject to significant numerical error and the values below 0.01 mol.kg^{-1} are not shown. Both of the literature models are only valid to 3 mol.kg^{-1} and display worrying evidence of flexing (second derivative changes sign producing inflection points, most visible for Wang *et al.* at 373.15 K and for Mao and Duan at 473.15 K), which is potentially indicative of an inappropriate number of parameters in the models.

Table 5: Comparison of apparent molar volumes from Krumgalz *et al.* [35] and this work

Solute	$m / \text{mol.kg}^{-1}$	[35]	this work	Δ
MgCl_2	0.0	14.08	13.91	0.17
	1.0	20.24	20.28	-0.04
	3.0	24.50	24.40	0.10
	6.0	27.80	27.78	0.02
CaCl_2	0.0	17.61	17.59	0.02
	1.0	23.87	23.85	0.02
	3.0	28.13	28.09	0.04
	6.0	32.67	32.58	0.09
KI	0.0	45.22	45.20	0.02
	1.0	46.84	46.83	0.01
	3.0	47.92	48.05	-0.13
	8.0	49.18	49.23	-0.05

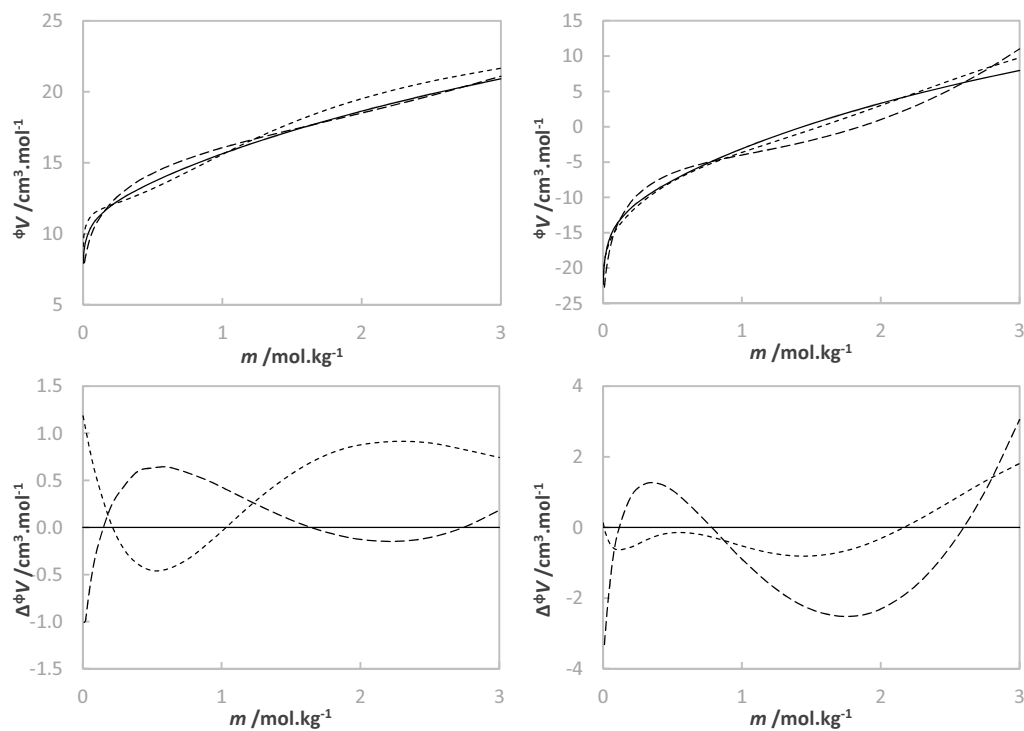


Figure 11: Comparison of apparent molar volumes for $\text{MgCl}_2(\text{aq})$ calculated from the present model (solid lines), Wang *et al.* [3] (short-dashed lines) and Mao and Duan [2] (long-dashed lines). Left: 373.15 K, 2 MPa; right: 473.15 K, 30 MPa.

4. Discussion

Direct comparison of experimental results from different literature sources is problematic because measurements taken at the exact same set of pressure, temperature and concentration conditions are rare. This makes it difficult to know whether two sets of data are in agreement. Indeed, in some instances investigators disagree even in their assessment. For example, Obšil *et al.* [24] describe Ellis' MgCl_2 density data [36] as incompatible with their own. However, Wang *et al.* [3] say that the “data of Obšil are in accordance with Ellis” and Mao and Duan [2] find that these datasets are consistent. This discrepancy may arise because the experimental error attributed by Obšil *et al.* to their dataset [24] is smaller than can be warranted from a comparison involving many different sources. Alternatively, it may reflect different analytical perspectives: Obšil *et al.* [24] were focussed on specific numerical characteristics of the datasets, while both Wang *et al.* [3] and Mao and Duan [2] gave greater consideration to broader data trends, since their primary aim was to develop models to smooth the data and achieve a coherent (thermodynamically consistent) representation of the solution density over a range of conditions. In this context, typically data are only considered unacceptable when they cause spurious artefacts in the form of the fitting function.

There are many similar examples in the literature where it is difficult to appraise data quality objectively. Holmes *et al.* [9] found that authors frequently claimed both higher accuracy and precision of aqueous calcium chloride densities than implied when the data were compared to other sources. In particular, as reported by Monnin [8], Kumar and Atkinson [37] stated an error of less than 5 ppm in their $\text{CaCl}_2(\text{aq})$ density measurements, whereas Monnin's fit of the data indicated it to be closer to 400 ppm.

The results of this work confirm that the claimed uncertainty of experimental datasets is much less (i.e. more optimistic) than can be seen when the results of independent investigators are compared. Similarly, it is clear that many physicochemical property models described in the literature utilize too many degrees of freedom in the parameter fitting process. Thermodynamic models having excessive numbers of empirical parameters are capable of representing experimental data with high precision. However, the accuracy of the model naturally becomes poorer.

Moreover, serious problems can arise when there are significant gaps in the available data. The Pitzer equations are particularly susceptible to this condition and the development of ‘extended’ Pitzer (or other) equations, which has become prevalent in the literature, makes the problem worse. These are issues which are currently under investigation in our laboratory and will be the subject of a future communication.

5. Conclusion

Notwithstanding the difficulties described above and the tendency for over-optimism regarding the size of experimental errors, both the $\text{MgCl}_2(\text{aq})$ and $\text{CaCl}_2(\text{aq})$ systems investigated are remarkable for their data coverage and the extent of agreement achieved between independent measurements of density over a wide range of pressure, temperature and concentration. Apart from $\text{NaCl}(\text{aq})$, which has been extensively characterized, there are few comparable electrolyte solution datasets. These data therefore offer an important opportunity to test objectively future theoretical models for electrolyte solutions under superambient conditions. They also engender confidence in the set of standard Pitzer equation parameters now available.

Acknowledgement

Professor Glenn Hefter is thanked for his usual constructive comments in the preparation of this paper. Some helpful comments by an anonymous reviewer are appreciated.

References

- [1] S. Al Ghafri, G. C. Maitland, J. P. M. Trusler, *J. Chem. Eng. Data* 57 (2012) 1288–1304.
- [2] S. Mao, Z. Duan, *J. Chem. Thermodyn.* 40 (2008) 1046–1063.
- [3] P. Wang, K. S. Pitzer, J. M. Simonson, *J. Phys. Chem. Ref. Data* 27 (1998) 971–991.
- [4] C. S. Oakes, J. M. Simonson, R. J. Bodnar, *J. Solution Chem.* 24 (1995) 897–916.

- [5] J. T. Safarov, G. N. Najafov, A. N. Shahverdiyev, E. Hassel, *J. Mol. Liq.* 116 (2005) 165–174.
- [6] P. M. May, D. Rowland, E. Königsberger, G. Hefter, *Talanta* 81 (2010) 142–148.
- [7] R. C. Phutela, K. S. Pitzer, P. P. S. Saluja, *J. Chem. Eng. Data* 32 (1987) 76–80.
- [8] C. Monnin, *J. Solution Chem.* 16 (1987) 1035–1048.
- [9] H. F. Holmes, R. H. Busey, J. M. Simonson, R. E. Mesmer, *J. Chem. Thermodyn.* 26 (1994) 271–298.
- [10] K. S. Pitzer, *J. Phys. Chem.* 77 (1973) 268–277.
- [11] K. S. Pitzer, *Ion Interaction Approach: Theory and Data Correlation*, CRC Press, Boca Raton, Florida, USA, pp. 75–153.
- [12] D. P. Fernandez, A. R. H. Goodwin, E. W. Lemmon, J. M. H. Levelt Sengers, R. C. Williams, *J. Phys. Chem. Ref. Data* 26 (1997) 1125–1166.
- [13] W. Wagner, A. Pruss, *J. Phys. Chem. Ref. Data* 31 (2002) 387–535.
- [14] P. S. Z. Rogers, K. S. Pitzer, *J. Phys. Chem. Ref. Data* 11 (1982) 15–81.
- [15] D. G. Archer, *J. Phys. Chem. Ref. Data* 21 (1992) 793–829.
- [16] K. S. Pitzer, J. C. Peiper, R. H. Busey, *J. Phys. Chem. Ref. Data* 13 (1984) 1–102.
- [17] D. G. Archer, *J. Phys. Chem. Ref. Data* 28 (1999) 1–17.
- [18] E. Königsberger, *Monatsh. Chem.* 132 (2001) 1363–1386.
- [19] W. H. Press, S. A. Teukolsky, W. T. Vetterling, B. P. Flannery, *Numerical Recipes in FORTRAN*, 2nd Edn., Cambridge Univ. Press, Cambridge, U.K., 1992.
- [20] G. G. Aseyev, I. D. Zaytsev, *Volumetric Properties of Electrolyte Solutions*, Begell House Inc., N.Y., U.S.A., 1996.
- [21] M. Laliberté, *J. Chem. Eng. Data* 54 (2009) 1725–1760.

- [22] D. G. Miller, J. A. Rard, L. B. Eppstein, J. G. Albright, *J. Phys. Chem.* 88 (1984) 5739–5748.
- [23] T. Isono, *J. Chem. Eng. Data* 29 (1984) 45–52.
- [24] M. Obšil, V. Majer, G. T. Heffer, V. Hynek, *J. Chem. Thermodyn.* 29 (1997) 575–593.
- [25] C. T. Chen, R. T. Emmet, F. J. Millero, *J. Chem. Eng. Data* 22 (1977) 201–207.
- [26] J. A. Gates, R. H. Wood, *J. Chem. Eng. Data* 30 (1985) 44–49.
- [27] V. Hynek, M. Obšil, V. Majer, J. Quint, J.-P. E. Grolier, *Int. J. Thermophys.* 18 (1997) 719–732.
- [28] J. A. Gates, R. H. Wood, *J. Chem. Eng. Data* 34 (1989) 53–56.
- [29] A. Kumar, *J. Solution Chem.* 15 (1986) 409–412.
- [30] P. P. S. Saluja, J. C. LeBlanc, *J. Chem. Eng. Data* 32 (1987) 72–76.
- [31] G. P. Baxter, C. C. Wallace *J. Am. Chem. Soc.* 38 (1916) 70–105.
- [32] A. F. Scott, V. M. Oberhaus, R. W. Wilson, *J. Phys. Chem.* 38 (1934) 931–940.
- [33] D. M. Swenson, E. M. Woolley, *J. Chem. Thermodyn.* 40 (2008) 54–66.
- [34] P. P. S. Saluja, R. J. Lemire, J. C. LeBlanc, *J. Chem. Thermodyn.* 24 (1992) 181–203.
- [35] B. S. Krungalz, R. Pogorelsky, K. S. Pitzer, *J. Phys. Chem. Ref. Data* 25 (1996) 663–689.
- [36] A. J. Ellis, *J. Chem. Soc. (A)* (1967) 660–664.
- [37] A. Kumar, G. Atkinson, *J. Phys. Chem.* 87 (1983) 5504–5507.

Glossary of symbols

Roman

A_V : Debye-Hückel parameter for volume

B : second virial coefficient

b : Pitzer equation constant

$b_{i,j}$: optimized model coefficients

C^ϕ : third virial coefficient

l : stoichiometric ionic strength

M : molar mass

m : concentration

n : number of moles of solute

p : pressure

R : universal gas constant

T : temperature

${}^\phi V$: apparent molar volume

V, v : volume

v_j : optimized model coefficients

Z : algebraic ionic charge

Greek

β : Pitzer equation constant

β^0 : second virial term

Δ : property difference

ρ : density

ν : stoichiometric coefficient

Subscript

M : cation

r : reference property

w : water

X : anion

Superscript

◦ : standard state

V : volume