

Aqueous electrolyte solution modelling: Limitations of the Pitzer equations

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Abstract

Despite intense efforts, general thermodynamic modelling of aqueous electrolyte solutions still presents a difficult challenge, with no obvious method of choice. Even though the Pitzer equations seemingly provide a well-established theoretical framework applicable to many chemical systems over a wide range of temperatures and pressures, they are not as widely adopted as their early promise might have suggested. This is strikingly illustrated by the simultaneous appearance in the literature of numerous, different (and potentially incompatible) Pitzer models alongside a proliferation of alternative theoretical approaches with inferior capabilities.

To better understand this problem, the ability of the Pitzer equations to represent the physicochemical properties of aqueous solutions has been systematically investigated for exemplar electrolyte systems. Pitzer ion-interaction parameters have been calculated for selected systems by least-squares regression analysis of published solution data for activity coefficients, osmotic coefficients, relative enthalpies, heat capacities, volumes and densities to high temperatures and pressures. Although satisfactory fits can be achieved when the ranges of conditions are carefully chosen and when sufficient data are available to constrain the regression, the fits obtained tend otherwise to be unsatisfactory. The Pitzer equations do not cope well with gaps and other deficiencies in the regressed data. Profound difficulties, poorly recognized hitherto, can also arise because of variation in the sensitivity of the Pitzer functions to values for different physicochemical properties when these are combined. Given the dimensionality of numerous related thermodynamic properties, all changing as functions of composition,

temperature and pressure, these problems are difficult to detect, let alone address, especially in multicomponent systems. The growing practice of improving fits simply by adding basis functions (thereby increasing the number of adjustable parameters) should be depreciated because it increases the likelihood of error propagation, introduces subjectivity, makes independent verification difficult and has deleterious implications for both automated data processing and for consistency between thermodynamic models.

1. INTRODUCTION

Numerous theoretical frameworks for aqueous electrolyte solution modelling have been described in the literature, including some recent examples appearing in Afanas'ev (2011), Fraenkel (2011), Haghtalab et al. (2011), Hsieh and Lin (2011), Hu et al. (2011), Lamperski and Pluciennik (2011), Li et al. (2011), Partanen (2012), Sun and Dubessy (2012), Tian et al. (2012) and Xiao and Song (2011). Of these various approaches none has been more widely adopted than that of Pitzer (1973). This is because the Pitzer equations enable convenient calculation of a comprehensive suite of aqueous solution thermodynamic properties (Pitzer, 1991) with unmatched precision over wide ranges of temperature and pressure (Grenthe et al., 1997) for strong electrolytes and their mixtures. Ever since Harvie and Weare (1980) and Harvie et al. (1984) showed that the successive precipitation of salts from evaporating seawater could be predicted using the Pitzer formalism, such equations have often been adopted for aqueous geochemical and other modeling, being included in a number of software packages such as PHREEQC (Parkhurst and Appelo, 1999), EQ3/6 (Wolery, 1996), OLI Analyser (Reddy and Lewis, 2006) and The Geochemist's Workbench (Bethke, 1998). Some very large Pitzer models

have been developed for multicomponent solutions, including one for seawater containing 16 major ionic components and a number of trace elements (Millero and Pierrot, 1998) and our 11-component model for industrial Bayer liquors (concentrated alkaline aluminate solutions used in alumina refining) (Königsberger et al., 2005; Königsberger et al., 2011). The Pitzer framework is even being used in the development of SI-traceable chemical activity determination (Berdat et al., 2009), including suggestions for improving the definition of pH (Buck et al., 2002; Waters and Millero, 2013), with significant implications for the major multinational effort to assess the long-term risks of radioactive waste disposal (Kim et al., 2010; Baechler et al., 2012). These developments might give the impression that modelling of the thermodynamic properties of electrolyte solutions using the Pitzer equations has become routine. However, such an impression would be mistaken.

Progress since the 1980s towards a comprehensive, integrated and predictive thermodynamic modelling capability has been limited. This reflects persistent deficiencies in theory. It has not yet been possible to couple in a satisfactory way 'specific ion interaction models' like those of Pitzer with chemical speciation calculations of chemically reactive systems, particularly in multicomponent mixtures with strong complex formation. New fundamental insights are needed to move forward: as Kunz and Neueder (2010) remarked, it has proved “easier to fly to the moon than to describe the free energy of even the simplest salt solutions beyond a concentration of 0.1 M or so”.

Some of the reasons why the thermodynamics of aqueous electrolyte solutions has remained intractable are well known: the strong departure of ionic solutions from ideality due to short- and

long-range electrostatic interactions (Grenthe et al., 1997, p. 327); the empirical nature of, and associated parameter correlation in, the extended Debye-Hückel modelling functions currently available (Marshall et al., 1995); and the need to rely on approximation methods for making temperature corrections to thermodynamic data (Puigdomenech et al., 1997). More subtle difficulties have also begun to receive attention. One is the combinatorial explosion of function parameters arising with multicomponent mixtures (Voigt, 2011), which is implicit in Brønsted's specific ion interaction theory (Brønsted, 1922a; Brønsted, 1922b; Guggenheim, 1935) and strongly manifest in the Pitzer formalism. Others are the ongoing paucity of reliable experimental data available for function parameter regression (Voigt, 2011) and the prohibitive burden of critical data assessment and fitting (Archer, 1990). It nevertheless remains puzzling why it is so difficult to describe aqueous electrolyte solutions that are in general well-behaved, since almost all thermodynamic properties at $T \lesssim 573$ K vary both smoothly and for the most part gradually (Pitzer, 1979).

This paper describes a systematic investigation of the use of the Pitzer equations for modelling aqueous electrolyte solutions over wide ranges of composition, concentration, temperature and pressure. An attempt is made to understand the strengths *and* weaknesses of the Pitzer approach, to establish its limitations and to explore ways by which it might be more effectively applied. Data fitted include binary salt solutions (those containing one electrolyte + water) and ternary solutions (containing two electrolytes + water). The approach employed was as general as possible, covering data sets from widespread sources. Perhaps most importantly the approach is free from the subjective assessments that arise inevitably when modelling functions are being proposed or being applied to newly-measured experimental results.

2. THEORY

The original Pitzer equations and their many subsequent variants have been described in detail elsewhere so only a very brief outline is presented here to provide the necessary background.

For multicomponent electrolyte solutions the Pitzer equations are conveniently defined (Pitzer, 1991) via an expression for the excess Gibbs energy (Eq. (1)):

$$\begin{aligned}
 G^E(w_w RT)^{-1} = & -A_\phi (4I b^{-1}) \ln(1 + bI^{1/2}) + 2 \sum_c \sum_a m_c m_a [B_{ca} + (\sum_c m_c z_c) C_{ca}] \\
 & + 2 \sum_c \sum_{c'} m_c m_{c'} [2 C_{cc'} + \sum_a m_a C_{cc'a}] \\
 & + 2 \sum_a \sum_{a'} m_a m_{a'} [2 C_{aa'} + \sum_c m_c C_{caa'}] \quad (1)
 \end{aligned}$$

where R and T have their usual meanings, w_w is the mass of the solvent (in kg), A_ϕ is the Debye-Hückel constant for osmotic coefficients (Fernández et al., 1997) (at $T = 298.15$ K, $A_\phi = 0.3915$ kg^{1/2} mol^{-1/2}), I is the stoichiometric molality-based ionic strength ($I = 0.5 \sum m_i z_i^2$), m_c and m_a are the molalities of cations and anions respectively, z_c is the algebraic charge of the cation, C_{ca} , $C_{cc'}$, $C_{aa'}$, $C_{cc'a}$ and $C_{caa'}$ are ion-interaction coefficients described below, and the summations span all cations $c < c'$ and anions $a < a'$. The constant b is temperature and pressure independent and is given the value 1.2 (kg mol⁻¹)^{1/2} for all solutes. In Eq. (1), terms describing interactions involving neutral solutes are omitted (see Pitzer (1991) for the full equations).

The second virial coefficient B_{ca} depends on ionic-strength (Eq. (2)), whereas the third virial coefficient C_{ca} is independent of ionic strength.

$$B_{ca} = \beta^{(0)}_{ca} + 2\beta^{(1)}_{ca}[1 - (1 + \alpha_1 I^{1/2}) \exp(-\alpha_1 I^{1/2})] (\alpha_1^2 I)^{-1} \\ + 2\beta^{(2)}_{ca}[1 - (1 + \alpha_2 I^{1/2}) \exp(-\alpha_2 I^{1/2})] (\alpha_2^2 I)^{-1} \quad (2)$$

In the original Pitzer equations, α_1 and α_2 are temperature- and pressure-independent theory-based coefficients; $\alpha_1 = 2.0 \text{ (kg mol}^{-1}\text{)}^{1/2}$ and $\alpha_2 = 0 \text{ (kg mol}^{-1}\text{)}^{1/2}$ (i.e., $\beta^{(2)}_{ca}$ is not needed) unless both ions are divalent (when $\alpha_1 = 1.4 \text{ (kg mol}^{-1}\text{)}^{1/2}$ and $\alpha_2 = 12 \text{ (kg mol}^{-1}\text{)}^{1/2}$) or more highly charged (e.g., $\alpha_1 = 2.0 \text{ (kg mol}^{-1}\text{)}^{1/2}$ and $\alpha_2 = 50 \text{ (kg mol}^{-1}\text{)}^{1/2}$ for 3:2 electrolytes (Pitzer, 1991)). Thus at fixed pressure and temperature, G^E is expressed in terms of up to four adjustable parameters $\beta^{(0)}_{ca}$, $\beta^{(1)}_{ca}$, $\beta^{(2)}_{ca}$ and C_{ca} per *binary* electrolyte.

Terms arising from interactions involving two (different) ions of the same charge are required for ternary mixtures of electrolyte solutions with either a common anion (c' , $c'a$) or a common cation (aa' , caa'). For unsymmetrical mixing, that is, when the charges on c and c' (or a and a') differ, the theory requires that an electrostatic mixing term, ${}^E_{ij}$, which is dependent only on the charges of the ions i and j , the ionic strength and on solvent properties (hence on temperature and pressure), appears in ${}_{ij}$, which is then given by ${}_{ij} = {}_{ij} + {}^E_{ij}$ (Pitzer, 1991). Thus, at fixed pressure and temperature, G^E is expressed in terms of (an extra) two adjustable parameters, ${}_{ij}$ and ${}_{ijk}$, per *ternary* electrolyte mixture. Interactions involving three ions of the same charge are neglected so, for multicomponent electrolyte mixtures, only adjustable Pitzer parameters for binary and ternary solutions need to be considered.

Expressions for other excess thermodynamic quantities can be derived from G^E in a thermodynamically consistent manner (Pitzer, 1991). For example, the osmotic coefficient of the solvent, ϕ , and the activity coefficients of the solutes, γ_i , are obtained by appropriate partial differentiation with respect to composition. Apparent molar enthalpies, heat capacities, volumes and compressibilities are related to the first and second partial derivatives with respect to temperature and pressure. Since these differentiations are carried out only on the Debye-Hückel coefficient and the Pitzer parameters (but not on the temperature- and pressure-independent molalities and constants α_1 , α_2 and b), the mathematical form of Eq. (1) is retained (Pitzer, 1991). Owing to the improved performance of computers and evaluation software, the determination of the empirical parameters in the above equations is now increasingly facile.

The pressure and temperature dependencies of Pitzer parameters are given by purely empirical functions such as Eq. (3).

$$X(P, T) = w_1(P/P^\circ) + w_2(P/P^\circ) T^\circ/T + w_3(P/P^\circ) \ln(T/T^\circ) + w_4(P/P^\circ) T/T^\circ + w_5(P/P^\circ) (T/T^\circ)^2 + w_6(P/P^\circ) T^\circ/(T_U - T) + w_7(P/P^\circ) T^\circ/(T - T_L) \quad (3)$$

where T° is 1.0 K and P° is 1.0 MPa. Values of $T_U = 680$ K and $T_L = 227$ K have been found appropriate to achieve a good fit for NaCl(aq) in the range $273 < T/\text{K} < 573$ (Pitzer et al., 1984). Depending on the data to be described by the model, the $w_i(P/P^\circ)$ in Eq. (3) may either be simple constant coefficients or functions of pressure. For NaCl(aq) up to $P = 100$ MPa, power series up to the third order in P have been used (Pitzer et al., 1984), resulting in a total of 53 coefficients for Eq. (3). Similar Pitzer models have been published for other binary electrolyte systems.

The standard state partial molar volume V^0 and heat capacity C_p^0 can have complex temperature dependences (Rogers and Pitzer, 1982; Archer, 1992; Archer and Carter, 2000). The numerical difficulties associated with these quantities can be reduced (Rogers and Pitzer, 1982) by re-writing the equation for the corresponding apparent molar quantity of a binary solute to be relative to a non-zero reference molality (Archer and Carter, 2000)

$$\begin{aligned} \phi V = & [V(m_r) - v_w]n_r^{-1} + v|z_M z_X|A_V(2b^{-1})[\ln(1 + bI^{1/2}) - \ln(1 + bI_r^{1/2})] \\ & + 2v_M v_X RT[mB_{MX}^V(I) - m_r B_{MX}^V(I_r) + v_M z_M(m^2 - m_r^2)C_{MX}^V] \end{aligned}$$

where v_w is the volume of 1 kg of water at the experimental pressure and temperature, $V(m_r)$ is the volume of a reference solution containing 1 kg of water and n_r moles of solute, m_r is the molality of that solution and B_{MX}^V and C_{MX}^V are the derivatives with respect to pressure of B_{MX} and C_{MX} . The temperature and pressure dependence of $V(m_r)$ is represented in this work by the function:

$$\begin{aligned} V(m_r)n_r^{-1} = & f_{v,1} + f_{v,2}(T/T^\circ) + f_{v,3}(T/T^\circ)^2 + f_{v,4}(T/T^\circ)^3 + (P/P^\circ)(f_{v,5} + f_{v,6}(T/T^\circ) \\ & + f_{v,7}(T/T^\circ)^2) + (P/P^\circ)^2(f_{v,8} + f_{v,9}(T/T^\circ)) \end{aligned}$$

As described by Archer (1992), the functional form of $C_p(m_r)/n_r$ can be made dependent on temperature only:

$$C_p(m_r)n_r^{-1} = f_{c,1} + f_{c,2}(T/T^\circ) + f_{c,3}(T/T^\circ)^2 + f_{c,4}T^\circ/(T_U - T) + f_{c,5}T^\circ/T + f_{c,6} \ln(T/T^\circ)$$

since its pressure dependence is contained within the expression for $V(m_r)n_r^{-1}$ where, here, $f_{v,n}$ and $f_{c,n}$ are the optimised coefficients.

3. METHODS

As summarised in Section 1, many limitations of the Pitzer equations are well known in the literature. This paper focuses on four ‘Case Studies’ that, taken together, provide insights into less well-recognised but critical difficulties with the Pitzer approach. The electrolytes NaCl(aq), MgCl₂(aq) and CaCl₂(aq) were selected for this purpose because: (a) they have been extensively quantified experimentally, particularly under non-ambient conditions; (b) they have relatively high solubilities; and (c) they feature prominently in natural brine solutions. Not surprisingly these systems have also been the subject of numerous previous Pitzer-based characterizations (Table 1).

Most of the present work was performed using the JESS (Joint Expert Speciation System) software package (May and Murray, 1991; May and Murray, 2001; May et al., 2010; Rowland and May, 2010; May et al., 2011; Rowland and May, 2012; Rowland and May, 2013). The JESS physicochemical property database (FIZ) (May et al., 2010) currently contains more than 400,000 data entries, mostly for electrolytes (ca. 300 binary and >200 ternary systems). This database provides sufficient coverage to explore the modelling of physicochemical properties in systematic ways (May et al., 2010; Rowland and May, 2013) not previously practicable. Most importantly for meaningful analysis of modelling functions, it is necessary to have systems, such as NaCl(aq), CaCl₂(aq) and MgCl₂(aq), that have been measured sufficiently often by independent investigators to permit a realistic assessment of experimental errors (Rowland and May, 2013).

Table 1 Literature sources of multidimensional Pitzer models for binary solutions NaCl(aq), MgCl₂(aq) and CaCl₂(aq)

Ref.	<i>T</i> (K)	<i>P</i> (MPa)	<i>m</i> _{max} (mol kg ⁻¹)
NaCl(aq)			
Rogers and Pitzer (1982)	273—573	0.1—100	5.5
Pitzer et al. (1984)	273—573	0.1—100	6
Archer (1992) ^a	250—600	0.1—100	6
Archer and Carter (2000) ^a	250—600	0.1—100	6
MgCl₂(aq)			
Phutela et al. (1987)	273—473	<i>P</i> _{sat} ^b	1
Holmes et al. (1997) ^a	273—523	0.1—40	5.9
Wang et al. (1998) ^a	240—627	0.1—100	25
CaCl₂(aq)			
Phutela and Pitzer (1983)	298—473	<i>P</i> _{sat}	4
Ananthaswamy and Atkinson (1985) ^a	273—373	0.1	9
Phutela et al. (1987)	273—473	<i>P</i> _{sat}	1
Holmes et al. (1997) ^a	270—526	0.1—40	4.6
Gruszkiewicz and Simonson (2005) ^a	273—573	<i>P</i> _{sat}	<i>m</i> _{sat}

^a Using various extended forms of the Pitzer equations; ^b Below 373.15 K *P*_{sat} = 0.1 MPa, else saturation pressure

In Case Studies A and B, the full range of relevant physicochemical property data for the three selected systems was extracted from the relevant JESS database and processed using the standard

JESS optimization and simulation facilities available for implementation of the Pitzer equations (May et al., 2010). The overall strategy adopted for critical data selection and processing was similar to that described in our analysis of aqueous binary electrolyte solutions at $P = 0.1$ MPa and $T = 298.15$ K (May et al., 2011). Singular value decomposition (May et al., 2010), a computational technique that avoids numerical ill-conditioning and minimizes the impacts of correlation (Press et al., 1992), has again been applied within the JESS calculations.

With Case Studies C and D, all thermodynamic properties were calculated using the Gibbs-energy minimizer incorporated into the ChemSage/FactSage/ChemApp software family (Eriksson and Hack, 1990; Petersen and Hack, 2007; Eriksson and Königsberger, 2008; Bale et al., 2009). ChemSage (Eriksson and Hack, 1990). ChemSage requires tailor-made data files containing, in the present case, coefficients for temperature functions of Pitzer parameters and standard Gibbs energies (Eriksson and Hack, 1990). These coefficients were either taken directly from the literature or optimised with respect to the relevant experimental data (Königsberger and Eriksson, 1995).

4. RESULTS

4.1. Case Study A: General regression of reliable literature data at non-ambient conditions

This Case Study confirms that the Pitzer equations in their standard form can accurately describe the physicochemical properties of the aqueous solutions of numerous binary electrolytes over wide ranges of conditions when the fitted data are reasonably consistent.

Optimizations based on the form of the Pitzer equations outlined in Section 2 were performed for NaCl(aq), MgCl₂(aq) and CaCl₂(aq). Suitable sets of conditions, given in Table 2, were determined following a preliminary survey. The upper temperature limit, $T \leq 523$ K, was imposed on MgCl₂(aq) and CaCl₂(aq) because of well-known difficulties at higher temperatures (Holmes et al., 1994; Holmes and Mesmer, 1996). Several factors were considered in choosing suitable upper concentration limits, including the number of data available and the best-fitting concentration limit at ambient temperature (May et al., 2011). However, since such choices are inherently subjective, a concentration of 6 mol kg⁻¹ was adopted for uniformity.

Table 2 Chosen ranges for JESS-derived multidimensional Pitzer models^a

System	T (K)	P (MPa)	m_{\max} (mol kg ⁻¹)	N_d	N_P
NaCl(aq)	273—573	0.1—100	6	70283	63
MgCl ₂ (aq)	273—523	0.1—100	6	4748	59
CaCl ₂ (aq)	273—523	0.1—68	6	6033	57

^a N_d = number of data points; N_P = number of optimized coefficients.

The standard deviations between the experimental data and the models are given in Table 3. Standard deviations for each property are given separately for data up to and including $T \leq 373.15$ K and for data at $T > 373.15$ K.

Table 3 Standard deviations of FIZ data from the JESS Pitzer models

System	Conditions	$\ln \gamma$	ϕ	ϕ_L ^a	ΔH_{dil} ^{a,b}	ϕC_p ^c	ϕV ^d
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NaCl(aq)	$T \leq 373.15$ K	0.0019	0.0025	0.053	0.032	4.1	0.21
	$T > 373.15$ K	0.005	0.0027	1.2	0.25	7.8	1.3
MgCl ₂ (aq)	$T \leq 373.15$ K	0.013	0.009	0.58	0.17	9.5	0.52
	$T > 373.15$ K	0.026	0.014	0.66	0.27	15	0.97
CaCl ₂ (aq)	$T \leq 373.15$ K	0.015	0.015	0.34	0.094	12	0.49
	$T > 373.15$ K	0.027	0.013	0.99	0.55	33	0.79

^a Units: kJ mol⁻¹; ^b Apparent molar enthalpy of dilution; ^c Units: J K⁻¹ mol⁻¹; ^d Units: cm³ mol⁻¹

The representation of the thermodynamic properties of NaCl(aq) by the Pitzer equations over the given conditions was highly satisfactory. In particular, the activity and osmotic coefficients were well-correlated over the entire temperature range (Fig. 1). The apparent molar relative enthalpy and enthalpy of dilution were also accurately characterised by the model, although the standard deviation of the apparent molar relative enthalpy data was anomalously large. This was primarily due to inclusion of the *simulated* results of Busey et al. (1984) at $T = 573.15$ K which differ from the present model by 6 kJ mol⁻¹ at $m = 5$ mol kg⁻¹. Accordingly, these data were assigned minimal weight in the optimization. The volumetric properties were also described with good accuracy, with standard deviations of 0.22 cm³ mol⁻¹ in ϕV for $T \leq 373.15$ K and 1.3 cm³ mol⁻¹ at $T > 373.15$ K. The standard deviation of ϕV at higher temperatures is perhaps larger than expected but is attributable to the inclusion of data from numerous sources that differ by up to 8 cm³ mol⁻¹ or more (Table 4).

Table 4 Comparison between different literature studies for apparent molar volumes of NaCl(aq) at $m = 0.5$ mol kg⁻¹, $P = 20$ MPa at $T \approx 573$ K

Ref.	ϕV (cm ³ mol ⁻¹)
Grant-Taylor (1981)	-41.6
Rogers and Pitzer (1982)	-34.4
Pitzer et al. (1984)	-34.4
Majer et al. (1988)	-40.8
Archer (1992)	-39.9

Some systematic deviations in the apparent molar heat capacity are also evident (Fig. 2), but only at high pressures where there are no supporting experimental (as opposed to simulated) data.

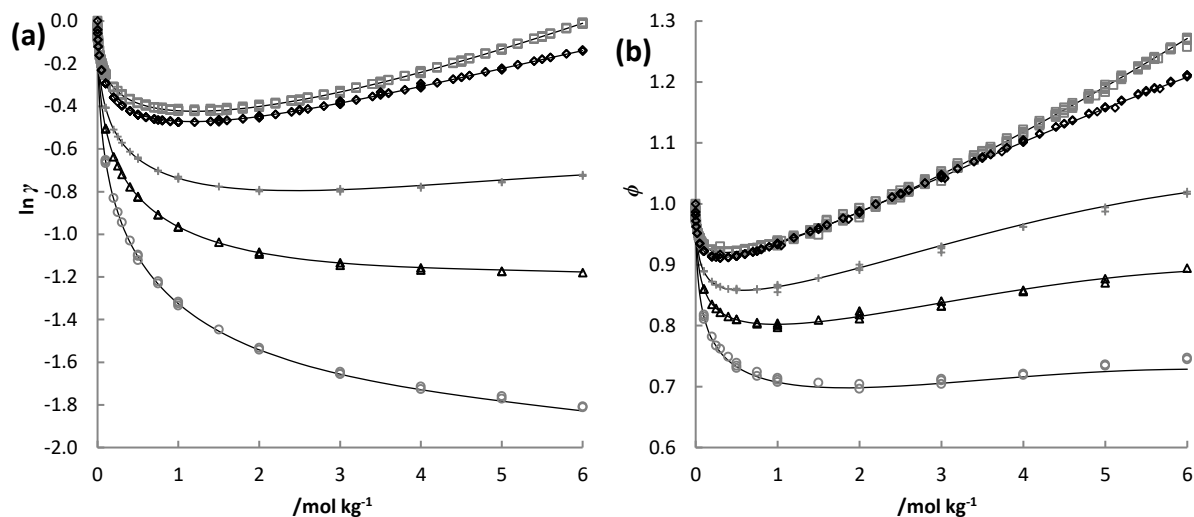


Fig. 1. (a) Activity coefficients and (b) osmotic coefficients of NaCl(aq) as a function of concentration at: $T/K \approx 298$ (squares), 373 (diamonds), 473 (pluses), 523 (triangles) and 573 (circles). Pressure is the greater of saturation vapour pressure or 0.1 MPa. Main data sources: Pitzer et al. (1984), Busey et al. (1984) and Archer (1992). Lines from the JESS Pitzer model.

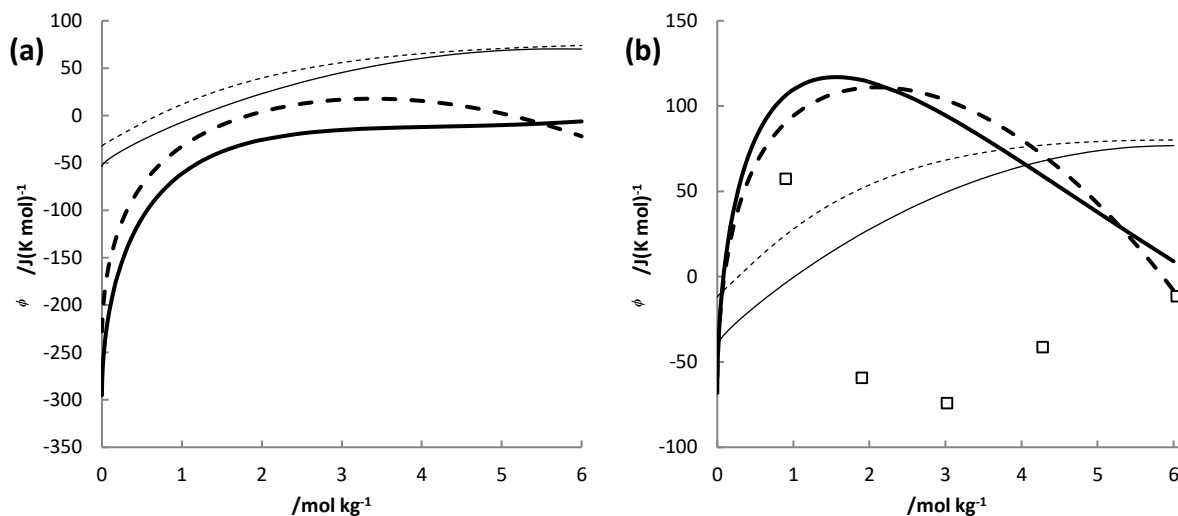


Fig. 2 Apparent molar heat capacity of NaCl(aq) as a function of concentration at pressures of: (a) 80 MPa and (b) 100 MPa, with $T/\text{K} = 273.15$ (thin lines) and 573.15 (thick lines). Dashed lines are from the correlation of Archer (1992). Solid lines are from the JESS Pitzer model. Points are from Puchkov et al. (1976) for $T = 573.15$ K (extrapolated from saturation pressure to approximately 100 MPa) and were not included in Archer's optimization, nor that of this work.

The $\text{MgCl}_2(\text{aq})$ activity and osmotic coefficients are described with impressive accuracy (Figs. 3 and 4). The standard deviations of the fit to ϕV were $0.52 \text{ cm}^3 \text{ mol}^{-1}$ for $T \leq 373.15 \text{ K}$, and $0.97 \text{ cm}^3 \text{ mol}^{-1}$ for $T > 373.15 \text{ K}$, while those for ϕC_p were $9.5 \text{ J}(\text{K mol})^{-1}$ and $15 \text{ J}(\text{K mol})^{-1}$, respectively. Examples of the ϕC_p fits are shown in Fig. 5.

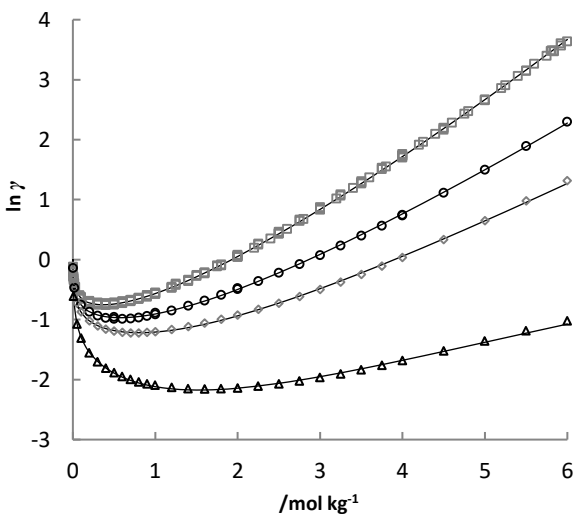


Fig. 3 Activity coefficients of $\text{MgCl}_2(\text{aq})$ as a function of concentration at $T/\text{K} \approx 298$ (squares), 373 (circles), 423 (diamonds) and 523 (triangles). Main data sources: Goldberg and Nuttall (1978), Wang et al. (1998) and Christov (2009b). Lines from the JESS Pitzer model.

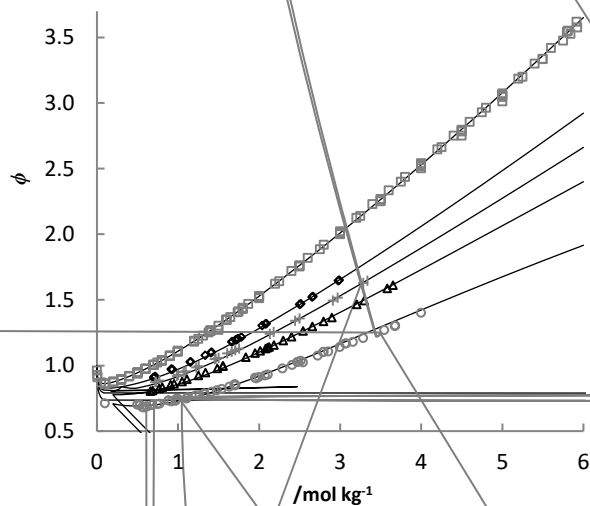


Fig. 4 Osmotic coefficients of $\text{MgCl}_2(\text{aq})$ as a function of concentration at $T/\text{K} \approx 298$ (squares), 383 (diamonds), 413 (pluses), 443 (triangles) and 498 (circles). Main data sources: Goldberg and Nuttall (1978), Rard and Miller (1981), Holmes and Mesmer (1996) and Holmes et al. (1997). Lines from the JESS Pitzer model.

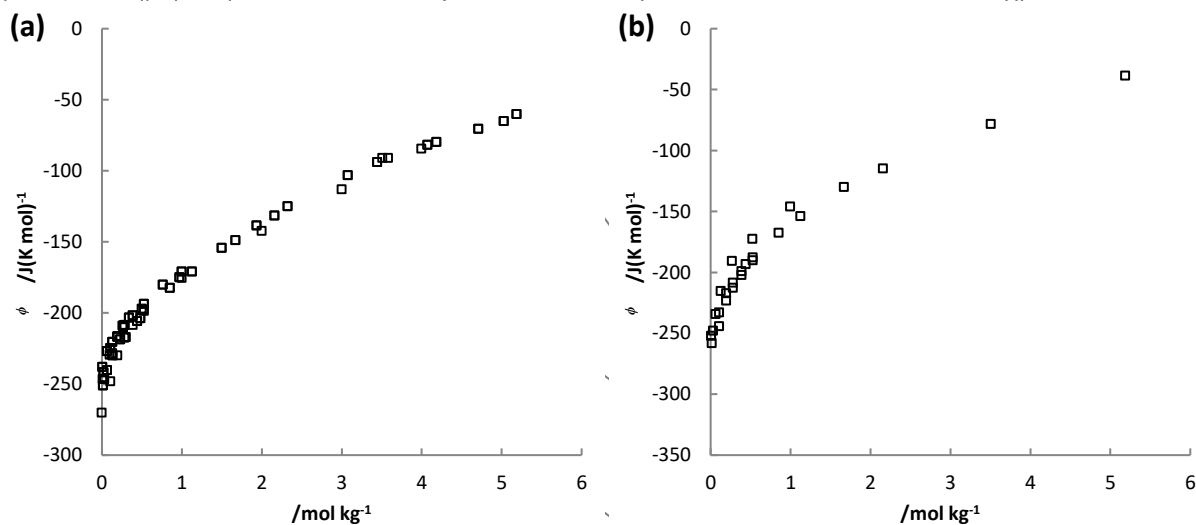


Fig. 5 Apparent molar heat capacities of $\text{MgCl}_2(\text{aq})$ as a function of concentration at: (a) $T = 298.15 \text{ K}$; (b) $T = 373.15 \text{ K}$. Main data sources: Perron et al. (1974, 1981), Saluja and LeBlanc (1987), Saluja et al. (1995), Holmes et al. (1997) and Call et al. (2000). Lines from the JESS Pitzer model.

For $\text{CaCl}_2(\text{aq})$ the activity and osmotic coefficients were also well-correlated by the standard Pitzer equations at $m \leq 6 \text{ mol kg}^{-1}$, albeit with some deviations in ϕ at the highest concentrations (Fig. 6). While these differences exceed the likely experimental uncertainties, they are small and it is difficult to know their true significance. The standard deviations of the fit to ϕV are $0.5 \text{ cm}^3 \text{ mol}^{-1}$ for $T \leq 373.15 \text{ K}$ and $0.8 \text{ cm}^3 \text{ mol}^{-1}$ for $T > 373.15 \text{ K}$, which is satisfactory. Those for ϕC_p are also reasonable, being $12 \text{ J (K mol)}^{-1}$ for $T \leq 373.15 \text{ K}$ and $33 \text{ J (K mol)}^{-1}$ for $T > 373.15 \text{ K}$.

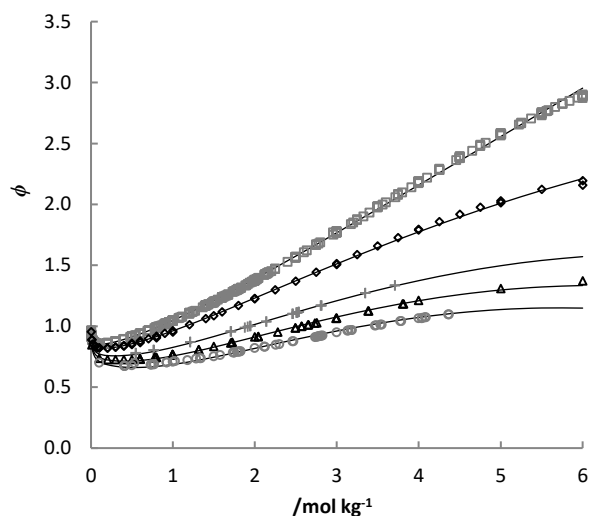


Fig. 6. Osmotic coefficients of $\text{CaCl}_2(\text{aq})$ as a function of concentration at: $T/\text{K} \approx 298$ (squares), 373 (diamonds), 443 (pluses), 473 (triangles) and 498 (circles). Main data sources: Rard and Spedding (1977), Goldberg and Nuttall (1978), Ananthaswamy and Atkinson (1985), Holmes et al. (1994) and Gruskiewicz and Simonson (2005).

4.2. Case Study B: General regression of inconsistent literature data at non-ambient conditions

This Case Study demonstrates that various severe problems can arise when Pitzer-fitted data sets are incomplete and/or thermodynamically inconsistent. The resulting numerical pathologies are not always easily detectable and, in particular, will not necessarily show up in the fitted objective function and/or the residuals.

The MgCl₂(aq) system was selected for this Case Study as it is known to be reliably represented at $T \leq 523$ K using the standard Pitzer equations (Case Study A above). However, additional data are available at $524 \leq T/\text{K} \leq 573.5$ (Table 5).

Table 5 Data sources for modelling the properties of MgCl₂(aq) at $T > 523$ K

Reference	Property	T (K)	P (MPa)	m (mol kg ⁻¹)	# data
White et al. (1988)	C_p	549.0	10.1—17.9	0.03—2.26	46
	C_p	573.5	17.9	0.03—2.26	23
Holmes and Mesmer (1996)		524	P_{sat}	0.42—3.95	21
Obšil et al. (1997)	– w	572.6	10.4—30.3	0.03—3.04	28
Wang et al. (1998)	γ	573	P_{sat}	0.001—6	32
		573	P_{sat}	0.001—6	32
	V	573	10—30	0.001—3	72

Pitzer parameters were thus determined for MgCl₂(aq) over a range of conditions spanning $P =$ (0.1 to 100) MPa, $T =$ (273 to 573) K and $m =$ (0 to 6) mol kg⁻¹. The set of basis functions was the same as that used above for the optimization to $T = 523$ K. As a result, an increase in the value of the objective function relative to Case Study A was observed. The standard deviations for the different physicochemical properties are given in Table 6.

Table 6 Standard deviations of FIZ data for $\text{MgCl}_2(\text{aq})$ from the Pitzer model optimised to $T = 573 \text{ K}$. Numbers in bold are significantly greater than corresponding values in Table 3.

Conditions	$\ln \gamma$	ϕ	ϕ_L^a	ΔH_{dil}^a	ϕC_p^b	ϕV^c
$T \leq 373.15 \text{ K}$	0.013	0.009	0.77	0.26	19	0.63
$T > 373.15 \text{ K}$	0.026	0.016	0.92	0.26	57	1.7

^a Units: kJ mol^{-1} ; ^b Units: $\text{J K}^{-1} \text{ mol}^{-1}$; ^c Units: $\text{cm}^3 \text{ mol}^{-1}$

Although the high-temperature data were poorly represented (Table 6), for example with spurious minimum in $\phi C_p(T)$ (Fig. 7), more striking were the large deviations in $\phi C_p(m)$ arising at low temperatures (Fig. 8, dashed lines). The effect in Fig. 7 illustrates the critical dependence of the fit on the weights given to data for a particular property and for different ranges of conditions, neither of which can be established objectively.

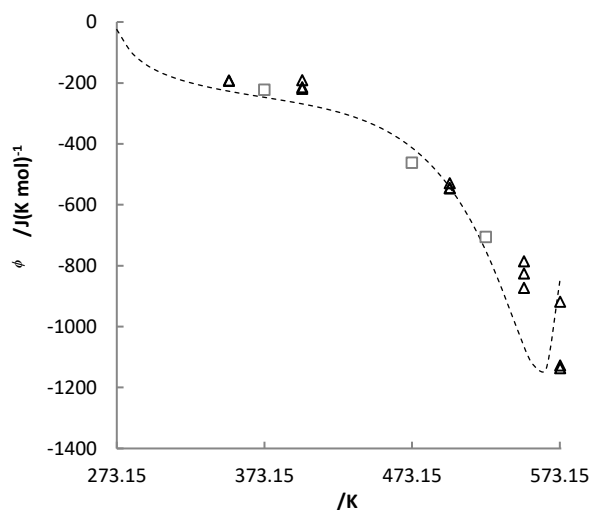


Fig. 7. Apparent molar heat capacity of $\text{MgCl}_2(\text{aq})$ as a function of temperature at $P \approx 17.9 \text{ MPa}$ and $m = 0.03 \text{ mol kg}^{-1}$. Data sources: White et al. (1988) (triangles) and Wang et al. (1998) (squares).

Moreover, under certain conditions of temperature and pressure, the slope of $\phi C_p(m)$ is negative in dilute solutions but reverses sign to approach the theoretical Debye-Hückel limiting slope. This non-physical behaviour results directly from attempting to constrain a large number of empirical parameters using incoherent (high-temperature) data. Detecting these kinds of non-physical trends requires close human inspection since they might occur in regions of the multidimensional space where no data are available, in which case there would be no significant adverse effect on the weighted sum of squared residuals.

A noticeable improvement in the correlation of $\phi C_p(m)$ at near-ambient temperatures (Fig. 8, solid lines) was achieved by changing the weights of the high-temperature data. However, weighting inevitably involves some degree of subjectivity and the difference between the two models was insignificant over the whole multidimensional space.

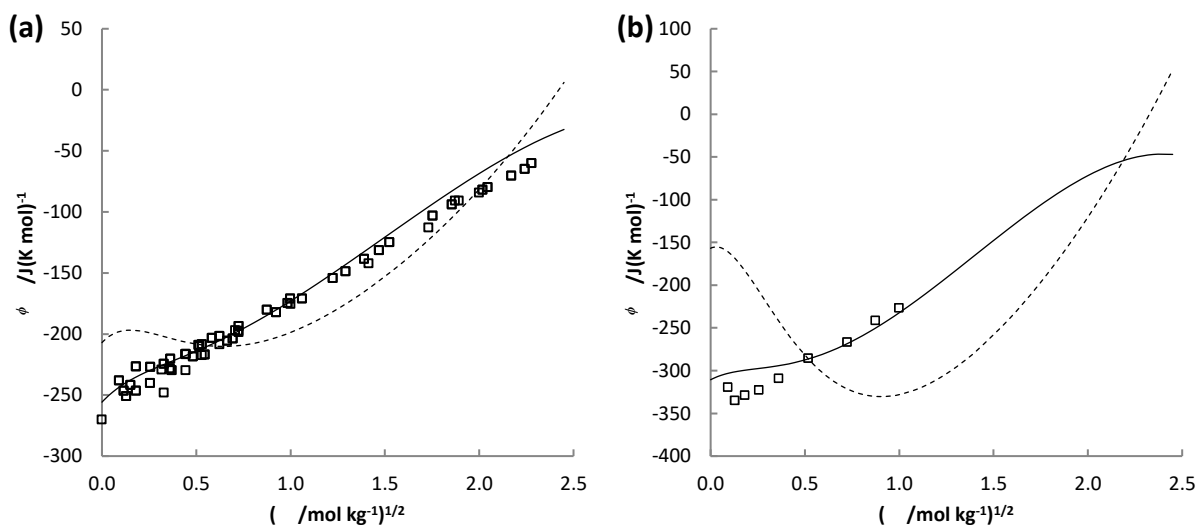


Fig. 8. Apparent molar heat capacity for $\text{MgCl}_2(\text{aq})$ as a function of concentration at: (a) $P = 0.1$ MPa and $T = 298.15$ K; (b) $P = 0.35$ MPa and $T = 278.15$ K. Main data sources: Perron et al. (1974, 1981), Holmes et al. (1997), Call et al. (2000). Curves show models optimised over the

range $P = (0.1 \text{ to } 100) \text{ MPa}$, $T = (273 \text{ to } 573) \text{ K}$, $m = (0 \text{ to } 6) \text{ mol kg}^{-1}$. Normal FIZ weights for all data (dashed line); reduced weights on data at $T \geq 523 \text{ K}$ (solid line).

To understand why the Pitzer model functions can fail so badly, it is helpful to remember that numerical problems of this kind have been observed before in a study confined to ambient conditions (May et al., 2010). The consequences of relatively small experimental errors can be dramatic even in two dimensions; a striking example is given in the Appendix. Obviously, there is an increased likelihood of such pathological effects occurring in multicomponent space, and greater difficulty with detecting them. To the best of our knowledge this serious limitation of the Pitzer equations has not been previously identified in the literature.

4.3. Case Study C: General regression of disparate literature data in binary systems

This Case Study shows that the Pitzer equations are inherently limited in their ability to distinguish between the merits of disparate sets of experimental data. Consequently, critical data evaluations become over-dependent on the subjective judgement of the assessor and full automation of the modelling process to achieve greater objectivity is precluded.

Pitzer parameters for activity and osmotic coefficients of $\text{MgCl}_2(\text{aq})$ from several sources, valid under ambient conditions, are given in Table 6. Solubility products for the formation of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}(\text{cr})$ at $m = 5.81 \text{ mol kg}^{-1}$ (Rard and Miller, 1981) have been calculated from each set of parameters. The critically evaluated solubility product of Wagman et al. (1982) is also included for comparison.

Table 6 Published Pitzer parameters for activity and osmotic coefficients of $\text{MgCl}_2(\text{aq})$ at $T = 298.15$ K. The solubility product, $\ln K_{sp}(\text{MgCl}_2 \cdot 6\text{H}_2\text{O}(\text{cr}))$, at $m = 5.81$ mol kg^{-1} is also shown.

Ref.	m_{max}	$\beta^{(0)}$	$\beta^{(1)}$	C^ϕ	$\ln K_{sp}$
Pitzer and Mayorga (1973)	4.5	0.3524	1.682	0.00519	10.38
Rard and Miller (1981)	4.0	0.3509	1.651	0.00651	10.53
Kim and Frederick (1988)	5.75	0.3557	1.617	0.00474	10.37
Holmes et al. (1997)	5.9	0.3559	1.608	0.00459	10.34
Christov (2009b)	m_{sat}	0.3619	1.581	0.00238	10.15
This work	5.9	0.3553	1.644	0.00510	10.43
Wagman et al. (1982)					10.24

Each of the parameterizations in the literature is based upon different datasets and methods. Pitzer and Mayorga (1973) based their optimization on the critically-evaluated data of Robinson and Stokes (1965), while Kim and Frederick's (1988) parameterization is based on the critical evaluation of Goldberg and Nuttall (1978). Other workers used various weighting schemes to reconcile the numerous sources of activity and osmotic coefficient data for optimization. Christov (2009a) appears to be the only worker to have relied so heavily on solubility data to parameterize his model for $\text{MgCl}_2(\text{aq})$, which may explain his rather different values for C^ϕ and $\ln K_{sp}$. The different sets of data chosen and the different optimization strategies employed means that, for example, osmotic coefficients calculated using alternative parameter sets display large deviations from one another (Fig. 9). For example, Christov's (2009a) model deviates considerably from the experimental data of Rard and Miller (1981) at high concentrations. The

remaining models differ by up to 0.02 in ϕ in their region of applicability. This is much larger than the uncertainty of 0.1—0.2% attributed to Rard and Miller's (1981) data.

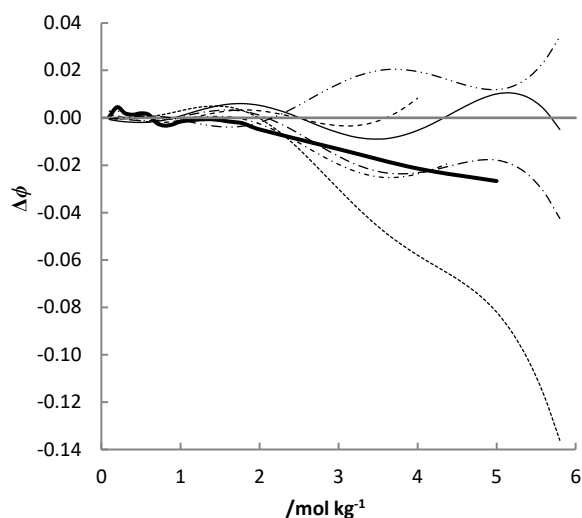


Fig. 9. Deviations of the osmotic coefficient for $\text{MgCl}_2(\text{aq})$ between various calculations and the experimental values of Rard and Miller (1981) as a function of concentration at $T = 298.15 \text{ K}$, showing critically-evaluated experimental values of Robinson and Stokes (1970) (thick solid line) and different Pitzer models: Pitzer (1973) (short dash-dot lines); Rard and Miller (1981) (dashed); Kim and Frederick (1988) (dash-dot-dot); Holmes et al. (1997) (long dash-dot); Christov (2009a) (dotted); this work (thin solid).

Some immediate observations present themselves regarding the nature of Pitzer equations. First, it is evident that the function provides no real assistance in identifying the better of disparate datasets – different experts have optimized different datasets without issue. Second, the characteristic, S-shaped distribution of all residual sets shown in Fig. 9 is indicative of some sort of incorrect (probably over-fitted) model behaviour, or of systematic errors in the data, or both. At the same time, it is worth noting that while the usual three Pitzer parameters suffice to fit the data within ± 0.01 in ϕ over the entire range of experimental data (Fig. 9, this work), extended Pitzer models involving up to six ion-interaction parameters(!) have been employed (Pitzer et al.,

1999) to reduce the deviations to less than ± 0.005 in ϕ . Such extensions are rarely justified (NaCl(aq) is a possible exception) given the differences between independent measurements but, worse, they conjure up a picture of agreement between observed data and model calculations which depends upon the data selected and which is subjective and non-trivial to verify independently (Rowland and May, 2013).

4.4. Case Study D: General regression of disparate literature data for mixtures

This Case Study shows that differences among the data sets and models are exacerbated when mixtures are considered. Recognising aberrant behaviour is more difficult and, consequently, robust thermodynamic modelling of multicomponent electrolyte solutions as an ambition remains remote.

Fig. 10a displays the mean activity coefficients of NaCl(aq) in mixtures of NaCl(aq) + MgCl₂(aq) at a constant stoichiometric ionic strength of $I = 6 \text{ mol kg}^{-1}$ (in other words for mixtures of $m = 6 \text{ mol kg}^{-1}$ NaCl(aq) and $m = 2 \text{ mol kg}^{-1}$ MgCl₂(aq)). The points at $y_{\text{MgCl}_2} = 1$, where $y_{\text{MgCl}_2} = 3m_{\text{MgCl}_2}/(3m_{\text{MgCl}_2} + m_{\text{NaCl}})$ is the ionic strength fraction of MgCl₂ in the mixtures, therefore correspond to γ_{NaCl}^t , the trace activity coefficient of NaCl(aq) in $m = 2 \text{ mol kg}^{-1}$ MgCl₂(aq). These values, obtained from various models, vary within a 5 % range in γ_{NaCl}^t . The variation of $\gamma_{\text{MgCl}_2}^t$ in $m = 6 \text{ mol kg}^{-1}$ NaCl(aq) is even larger (Fig. 10b).

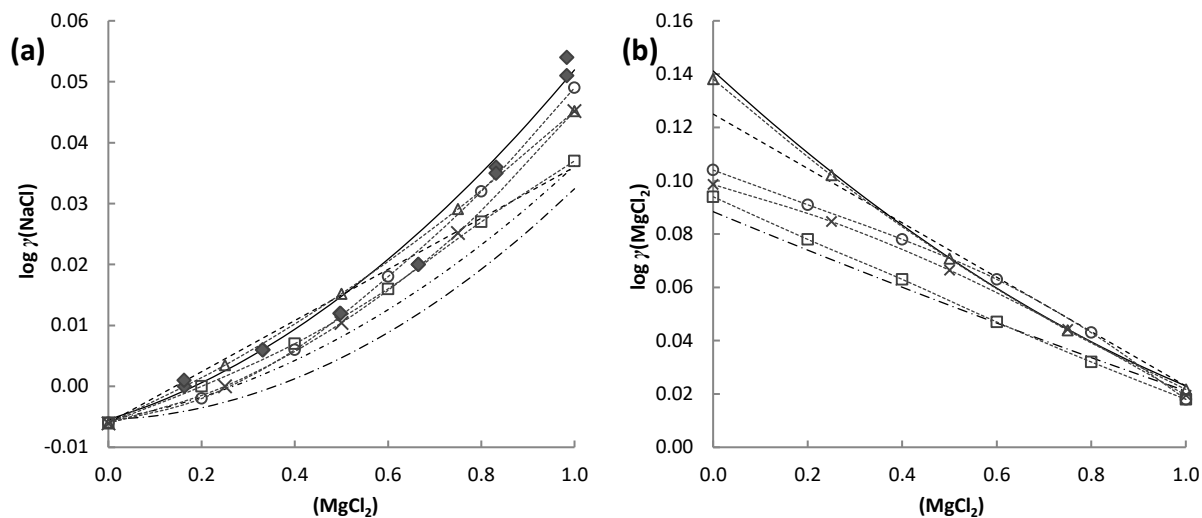


Fig. 10 Mean activity coefficients of (a) NaCl(aq); and (b) MgCl₂(aq), as a function of y_{MgCl_2} , the ionic strength fraction of MgCl₂(aq) in NaCl(aq) + MgCl₂(aq) mixtures, at $I = 6 \text{ mol kg}^{-1}$ and $t = 298.15 \text{ K}$. Potentiometric results from Lanier (1965) (filled symbols). Pitzer models: Pitzer and Mayorga (1973) and Pitzer (1975) (short dash-dot lines); Rard and Miller (1987) (solid); Holmes et al. (1997) (long dash-dot). Harned's rule (dashed lines). McKay-Perring (Platford, 1968) (squares), Scatchard (Platford, 1968) (circles), Pitzer ($\theta = \psi = 0$) (Rard and Miller, 1987) (triangles), Scatchard (Rard and Miller, 1987) (crosses).

The Pitzer model for NaCl(aq) + MgCl₂(aq) mixtures (with non-zero θ and ψ terms) reported by Rard and Miller (1981, 1987) is distinctly different from the other models, including Rard and Miller's own calculations using Pitzer ($\theta = \psi = 0$) and Scatchard models (Rard and Miller, 1987), although it is in reasonable agreement with Lanier's (1965) potentiometric data for γ_{NaCl} . On the other hand, Platford's isopiestic data for NaCl(aq) + MgCl₂(aq) mixtures (Platford, 1968) appear to be inconsistent with those of Rard and Miller. It is unclear why Platford's parameterization of the Scatchard model (using his data) yields results that are close to the Rard and Miller values for γ_{NaCl} but not those for γ_{MgCl_2} . Essentially opposite behaviour is observed for the Harned-rule model of Wu et al. (1968), which is close to Rard and Miller's (1987) prediction for γ_{MgCl_2} but not for γ_{NaCl} .

Activity coefficients derived from NaCl(s) solubility data from various sources show an even larger scatter (Fig. 11) than the differences among the various Pitzer models based on osmotic coefficients. Such data are therefore, at least for this system, hardly suitable for the optimization of mixing parameters.

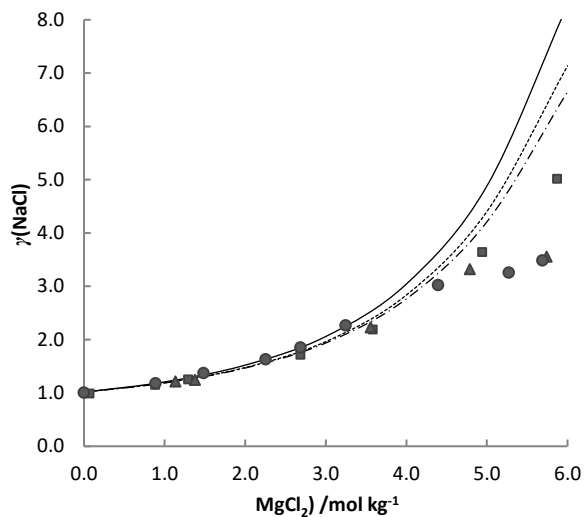


Fig. 11. Mean activity coefficient of NaCl(aq) at NaCl(s) saturation in solutions of MgCl₂(aq) at $T = 298.15$ K as a function of the MgCl₂(aq) molality. Experimental data: Kurnakov and Zemczny (1924) (circles); Keitel (1923) (triangles); Takegami (1921) (squares). Pitzer models: Pabalan and Pitzer (1987) (dotted line); Rard and Miller (1987) (solid); Holmes et al. (1997) (dash-dot).

5. DISCUSSION

While recognising the significant advances that had taken place in semi-empirical ('engineering') models for electrolyte solution properties since the mid-1980s, Loehe and Donohue (1997) pleaded for "a cessation of what has become the practice of promoting an equation's strengths without a discussion of its limitations". Regarding the strengths of the Pitzer equations specifically, Fernández-Prini et al. (1992, p. 103) give a thorough account of the framework's fundamental origins and subsequent development. In essence, Pitzer recognised the correctness of the Debye-Hückel screened potential concept and linearized the ion pair distribution function. The resulting equations, linear with respect to all adjustable parameters, offer considerable innate benefits including ionic additivity of parameters and a natural extension to multicomponent systems. Issues arising from the non-linear nature of an adjustable parameter in the denominator of the Debye-Hückel term, particularly regarding thermodynamic inconsistency in modelling electrolyte mixtures (Robinson and Stokes, 1970, p. 435), are thus bypassed. On the other hand, it should be remembered that the extended Debye-Hückel theory is innately inconsistent (Fernández-Prini et al., 1992, p. 103) in respect of both electroneutrality requirements and the second moment condition. It follows that thermodynamic 'purity' in any model based upon the Debye-Hückel theory is something of a chimera. Nonetheless, as shown in Case Study A, eminently satisfactory fits can be achieved using the Pitzer equations over restricted ranges of conditions when there are sufficient numbers of coherent data. Good agreement with experimental data can often be achieved up to concentrations of about 6 mol.kg^{-1} and even higher, by sacrificing accuracy in the more dilute range (Prausnitz et al., 1999, p. 546).

A key advantage of the Pitzer equations is their ability to describe the variation of the excess thermodynamic functions over wide ranges of composition, temperature and pressure in a self-consistent manner, with the quantities being related exactly in accord with the axiomatic functions of thermodynamics. Specifically, this means that the temperature dependence of the (excess) Gibbs energy must be consistent with independently measured (excess) enthalpy and heat capacity; the pressure dependence of G (or G^E) must be consistent with observed volume and compressibility changes, and so on. Unlike individual property functions which are combined arbitrarily (Loehe and Donohue, 1997), any Pitzer model with a given parameter set is inherently thermodynamically consistent (Pitzer, 1984) because all calculated solution properties derive from the same basic equation for the excess Gibbs energy (Eq. (1)). This consistency has been used, for instance, to extend such models to high temperatures and pressures by employing heat capacity and density data (Pitzer, 1986; Pabalan and Pitzer, 1987; Archer, 1992; Königsberger et al., 2009; Schrödle et al., 2010). However, the algebraic flexibility of the Pitzer equations that allows them to follow physicochemical property changes so closely is, at the same time, the reason for their basic weakness. Since the temperature and pressure dependences of the Pitzer equations are entirely empirical, the presence of incoherent data in the parameter optimization can compromise the fit to other data either under different conditions or for different properties (Case Study B (this work), Pitzer et al. (1984) and Rard and Archer (1995)). Empiricism was also found necessary by Pitzer in respect of the ionic strength dependence of B_{ca} (Eq. 2). All of the problems found in the present case studies can ultimately be traced back to empirical (over-)flexibility.

The Pitzer functions thus perform badly when dealing with data which, because of poorly-judged weighting, or gaps, or inaccuracies, do not constrain the empirical functions tightly enough. The Appendix provides a specific instance involving activity coefficients; similarly, in a previous investigation of binary electrolyte solutions at $P = 0.1$ MPa and $T = 298.15$ K (May et al., 2011) it was found that the extrapolation of ${}^\phi C_p$ and ${}^\phi V$ to infinite dilution was, for practical purposes, not sufficiently constrained by the Debye-Hückel behaviour embedded in the Pitzer equations (at low concentrations) to determine the standard partial molar quantities C_p^0 and V^0 . This is due directly to the empirical terms in these (derivative) equations, which even allow a reversal of function slope (e.g., Fig. 8) at concentrations as low as $m = 10^{-4}$ mol kg $^{-1}$. It is in contrast to the fundamentally sound behaviour of, say, the Redlich-Rosenfeld-Meyer equation (Redlich and Meyer, 1964), which has fewer (and therefore better behaved) parameters. Given that the experimental uncertainty of apparent/partial molar quantities increases very rapidly with decreasing concentration, the present observations belie the number of significant figures reported for C_p^0 and V^0 from the Pitzer fits of measured data. Typical examples of overly-optimistic precision appear in Krumgalz et al. (1995, 1996a, 1996b, 2000), where V^0 values are given to three decimal places. The excessive flexibility of the Pitzer equations, which is exacerbated by the facile introduction of purely empirical extensions, inevitably promotes chaotic effects and thus impedes development in the longer term of coherent and robust models. The growing practice of improving fits simply by adding basis functions (thereby increasing the number of adjustable parameters) should therefore be depreciated.

As is evident in the present case studies, profound difficulties can arise in the use of Pitzer functions because of variation in the sensitivity of those functions to values of different

physicochemical properties. These have been poorly recognised hitherto and do not seem amenable to any straightforward solution. For example, the sequence of published parameters (Case Study C) for $\text{MgCl}_2(\text{aq})$ seems to reflect to an uncomfortable extent individual assessments of the available data. While personal judgements are unavoidable in any critical assessment of experimental measurements, confidence in geochemical models depends on a rational basis for the weighting of data and on collective, independent and open processes of review and selection, leading to a general consensus.

With regard to ternary Pitzer parameters, numerous workers have followed the advice of Pabalan and Pitzer (1991): “because the terms which include ψ ... involve the second power of molality, this quantity is best determined by measurements at the highest concentration, i.e., in saturated solutions. Hence, some of the best values of ψ for many electrolyte mixtures come from solubility data”. There has thus been a tendency to fit Pitzer mixing parameters exclusively to solubility data. In doing so, the data have frequently been taken from just one source (usually that of the authors of the particular study) and the goodness of fit to those data taken as proof of the model’s predictive capability (Li et al, 2006; Li et al., 2010; Yang and Li, 2010). Given the real uncertainties in solubility measurements (Hefter and Tomkins, 2003) it is completely unsatisfactory to assess the quality of a model in such a self-referencing manner. Meinrath and colleagues (Meinrath, 2002; Spitzer et al., 2011) claim, with good justification, that many mixing interactions in electrolyte solutions are not statistically significant. While some researchers contest this view, there can be little doubt that the experimental uncertainties are considerably greater than are commonly assumed. Distinguishing real mixing interactions from systematic

experimental errors remains a profound challenge. Unfortunately, greater rigour is generally precluded by a lack of sufficient high-quality independently-confirmed experimental data.

A further important and general limitation of the Pitzer equations is that data from different databases cannot easily be combined or interchanged in a thermodynamically consistent way. The principles conferring thermodynamic consistency described above have a corollary that is often overlooked: Pitzer equations parameterized over different ranges of conditions, or using different data sets, or with different basis functions, are *inherently* inconsistent and, having more empirical parameters, they are worse affected than simpler theoretical frameworks. For example, this issue affects the recent Pitzer model for seawater by Waters and Millero (2013) who apply inconsistently-determined parameters without comment. Numerous ‘extended’ Pitzer equations, employing up to nine (*cf.* Pitzer’s original 3) ion-interaction parameters (Pitzer et al., 1999) have been proposed for particular binary systems at a given temperature. In addition, some of the fixed parameters proposed by Pitzer (1991) have been adjusted by some researchers to achieve better fits to experimental data, e.g., β_0 in the ionic-strength dependent terms, *cf.* Eq. (2) (Holmes and Mesmer, 1996). Rard and Wijesinghe (2003, 2008) and Wijesinghe and Rard (2005) developed formulae for converting parameters of certain extended Pitzer models to those of the standard Pitzer model (Eq. (1)) but found that the latter only worked satisfactorily when the β_0 parameters in the ionic-strength dependent terms of the second virial coefficient were optimised.

Another form of inconsistency between Pitzer models occurs because there is no fundamental (theory-based) temperature or pressure dependence of Pitzer parameters. Hence, a large number of different functions have been described in the literature (Eq. (3) is a single instance). For example, isothermal fits of ϕC_p and ϕV for NaOH(aq) and its mixtures with NaAl(OH)₄(aq),

measured to $T = 573.15$ K at $P = 10.0$ MPa, have been performed recently (Hnedkovsky et al., 2007; Schrödle et al., 2008; Hnedkovsky et al., 2010; Schrödle et al., 2010). When these results were fitted to temperature functions, error propagation led to model uncertainties which significantly exceeded the experimental precision of the measured data. This problem could only be addressed by using a multiple-fit procedure in which the standard molar quantities were fixed to the exact values obtained from their temperature functions. These observations bear on both the difficulty of determining meaningful parameter values in the Pitzer theoretical framework (van Gaans, 1991) and the more general assertion that temperature dependence of thermodynamic quantities cannot be accurately characterised by analytical functions, such as polynomials (Wood, 1976).

When the components of an electrolyte solution include both multiple cations and multiple anions, the number of required parameters increases very rapidly (Voigt, 2011). It is thus self-evidently difficult and laborious to construct large Pitzer models for multicomponent mixtures for non-ambient conditions without depending on subsets of data and/or parameters that are incompatible with one another. The enormity of the task of checking large multicomponent Pitzer models to ensure that they behave realistically over the whole multidimensional space of compositions, temperature and pressure is clear from Case Study D and has serious implications. For example, the popular Harvie-Møller-Weare (1984) seawater model, which is widely implemented in codes used by the geochemical community, was based on incorrect experimental data for gypsum solubilities in magnesium sulfate solutions (Marion and Farron, 1999). This led to long-undetected incorrect solubility predictions for multicomponent solutions and required updating to be consistent with more recent experimental results (Voigt, 2011).

6. CONCLUSIONS

Many of the issues described in this paper could, of course, be overcome by additional and more accurate experimental data. The need for good physicochemical property models is nonetheless assured by the many geochemical systems of interest and the wide range of conditions that still remain to be studied for almost all of them.

Unfortunately, at present, there is no universal, *validated* capability for modelling the thermodynamic properties of multicomponent electrolyte solutions. Theoretical limitations necessitate widespread resort to empirical or so-called ‘semi-empirical’ functions. Amongst the many such approaches now available, the Pitzer equations remain, with good reason, pre-eminent (May et al., 2011). No theoretical framework for aqueous solution thermodynamics available at present exhibits a more powerful combination of generality, reach and accuracy.

However, the Pitzer modelling process is generally sensitive to small perturbations, tends to be tailored to individual systems and often must resort to using poorly-sourced thermodynamic parameters. Despite recent technological developments allowing storage and processing of very large physicochemical property and parameter data sets, the present results suggest that the fitting process cannot be generalised to achieve an objective, reproducible description of measured multicomponent thermodynamic systems. Moreover, since the parameter sets available in the literature typically cannot be updated as necessary, thermodynamic inconsistencies,

associated with the particular ranges of conditions over which the published fits have been obtained, are for all practical purposes unavoidable.

Consequently, aqueous solution chemistry models are often found to be irreproducible and lack the reliability necessary for many practical applications. As a particular case in point, it remains extremely challenging even to calculate quantitatively the measured solubilities for mixed inorganic electrolyte systems available from sources such as Linke (1958, 1965). This goal cannot generally be achieved without invoking empirical parameters and other regressed correlations fitted individually to each chemical system.

To understand why progress is proving so difficult, this work offers a critique of the limitations associated with the parameterization of Pitzer models. It seems more than likely that the general conclusions drawn here apply also to other less-often-used, semi-empirical electrolyte models such as eNRTL (Song and Chen, 2009), MSA (Triolo et al., 1976), MSA-NRTL (Papaiconomou et al., 2002), UNIQUAC (Iliuta, 2002) or the ‘mixed solvent electrolyte model’ (MSE) implemented by OLI (Wang et al, 2002; Wang et al., 2004). The temptation to improve the fitting of thermodynamic property models by repeatedly introducing new variants with system-specific basis functions and additional adjustable parameters is not confined to the Pitzer equations (e.g. see Partanen, 2012). It is important to remember that these other theoretical approaches have so far only been tested in rather narrow ways (Lin et al., 2010) compared to the multicomponent modelling applications which have been based on the Pitzer framework.

Any framework requiring dozens of empirical parameters to be determined simultaneously in order to define the excess Gibbs energy surface over practical ranges of concentration, temperature and pressure will likely suffer from difficulties with numerical processing and validation. The ability to distinguish between good data and bad is nullified by the multiplicity of parameters involved. As von Neumann famously remarked, "With four parameters I can fit an elephant, and with five I can make him wiggle his trunk." (Dyson, 2004). There is little practical advantage gained by introducing *arbitrary* empirical parameters, in addition to those given in Eq. (1), so that the Pitzer equations fit the data of any given chemical system to specified precision. Yet, on the other hand, modelling functions possessing fewer parameters than the Pitzer equations, and which are consequently less precise, offer no better solution. To advance aqueous solution chemistry modelling, the implications of this dilemma need to be far better understood. Only then can they be addressed. Until that time, the Pitzer equations (used with appropriate caution) will remain a useful tool in the characterization and harmonization of aqueous physicochemical properties (May et al., 2011; Rowland and May, 2013).

APPENDIX

Fig. A1 shows the Pitzer fit to Robinson and Stokes' (1970) mean activity coefficient data for $\text{Al}_2(\text{SO}_4)_3(\text{aq})$. After slightly altering the activity coefficient values at the two lowest concentrations (Table A1), the data were re-fitted (same Pitzer model function but allowing different parameters). The change in the way that the two curves extrapolate to infinite dilution is remarkable, regardless of the actual physicochemical behaviour. Thermodynamic frameworks with less flexibility, such as the Hückel equation (Partanen, 2012; Rowland and May, 2014),

would not be so susceptible to error. Issues similar to those seen in Case Study B (Fig. 8) can thus arise even in a much simpler context. A major distinction between the two examples, of course, is that such misbehaviour is considerably less discernible in a multi-dimensional space.

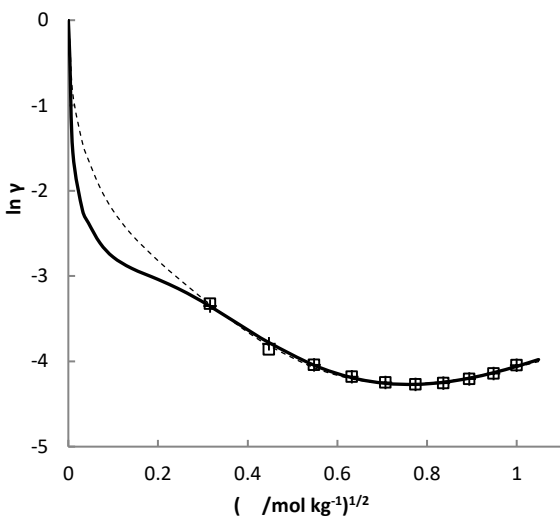


Fig. A1 Mean activity coefficient (as natural logarithm) of $\text{Al}_2(\text{SO}_4)_3(\text{aq})$ at $T = 298.15 \text{ K}$; symbols are original (pluses) and modified (squares) data from Robinson and Stokes (1970) - see Table A1. Pitzer models: fit to original data (solid line); fit to modified data (dashed).

Table A1

Mean activity coefficients of $\text{Al}_2(\text{SO}_4)_3(\text{aq})$ from Robinson and Stokes (1970) and modified versions of the same data, as used to produce Fig. A1.

m (mol kg^{-1})	[70RoS_12002]	(modified)
0.1	0.0350	0.0360
0.2	0.0225	0.0210
0.3	0.0176	0.0176
0.4	0.0153	0.0153
0.5	0.0143	0.0143
0.6	0.0140	0.0140
0.7	0.0142	0.0142
0.8	0.0149	0.0149
0.9	0.0159	0.0159
1.0	0.0175	0.0175

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