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Aqueous electrolyte solution modelling: Some 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 deprecated 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; recent examples include the publications of 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 the various approaches proposed none has been more widely adopted than that of Pitzer (1973). This is because the Pitzer equations (Pitzer, 1991) enable convenient calculation of a comprehensive suite of aqueous solution thermodynamic properties for strong electrolytes and their mixtures, with unmatched precision over wide ranges of temperature and pressure (Grenthe et al., 1997, p. 355). In addition to its breadth and precision, the Pitzer formalism has also attracted interest ever since Harvie and Weare (1980) and Harvie et al. (1984) showed that it could be used to predict the successive precipitation of salts from evaporating seawater. Consequently, Pitzer equations have been widely adopted for aqueous geochemical and other modelling, and have been included in a number of software packages such as EQ3/6 (Wolery, 1992), The Geochemist's Workbench (Bethke, 1998), PHREEQC (Parkhurst and Appelo, 1999) and OLI Analyser (Reddy and Lewis, 2006). 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, 2011). The Pitzer framework is even being used in the development of traceable chemical activity determination (Berdat et al., 2009), including suggestions for improving the determination of pH (Buck et al., 2002; Waters and Millero, 2013). Such efforts have significant implications for a major multinational effort that is underway to assess the long-term risks of radioactive waste disposal (Baechler et al., 2012; Kim et al., 2010). These developments might give the impression that modelling the thermodynamic properties of electrolyte solutions using the Pitzer equations is without significant problems, but this is not so. In fact, progress since the 1980s towards a comprehensive, integrated and predictive thermodynamic modelling capability via the Pitzer equations, or any other model, has been limited. This reflects persistent deficiencies in theory. For example, 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. 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), including Pitzer; and the need to rely on approximate methods for making temperature corrections to thermodynamic data (Puigdomenech et al., 1997). More subtle difficulties have also started to become apparent. One is the combinatorial explosion of function parameters that arises with multicomponent mixtures (Voigt, 2011). This is implicit in Brönsted's specific ion interaction theory (Brönsted, 1922a, 1922b; Guggenheim, 1935) but even more strongly manifest in the Pitzer formalism. Others are the ongoing limitations of the

availability of reliable experimental data for function-parameter regression (Voigt, 2011) and the prohibitive burden of critical data assessment and fitting (Archer, 1990).

This paper describes a systematic investigation of the use of the Pitzer equations for modelling binary and ternary aqueous electrolyte solutions over wide ranges of composition, temperature and pressure. Both the strengths *and* weaknesses of the Pitzer approach are considered, so as to establish its limitations and to explore ways by which it might be more effectively applied. The approach employed has been as general as possible, covering data sets from widespread sources. Perhaps most importantly the approach is free from the subjective assessments that inevitably arise when new modelling functions are being proposed or are being applied to newly-measured experimental results.

2. THEORY

The original Pitzer equations and their many subsequent variants have been described in detail elsewhere (Archer, 1992; Pitzer, 1991) 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)):

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

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} , $\Phi_{cc'}$, $\Phi_{aa'}$, $\psi_{cc'a}$ and $\psi_{caa'}$ 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 I (Eq. (2)), whereas the third virial coefficient C_{ca} is independent of I .

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

In the original Pitzer equations, α_1 and α_2 are temperature- and pressure-independent theory-based coefficients; $\alpha_1 = 2.0$ (kg mol⁻¹)^{1/2} and $\alpha_2 = 0$ (kg mol⁻¹)^{1/2} (i.e., $\beta_{ca}^{(2)}$ is not needed) unless both ions are divalent (when $\alpha_1 = 1.4$ (kg mol⁻¹)^{1/2} and $\alpha_2 = 12$ (kg mol⁻¹)^{1/2}) or more highly charged (e.g., $\alpha_1 = 2.0$ (kg mol⁻¹)^{1/2} and $\alpha_2 = 50$ (kg mol⁻¹)^{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 $\beta_{ca}^{(0)}$, $\beta_{ca}^{(1)}$, $\beta_{ca}^{(2)}$ and C_{ca} per *binary* electrolyte solution.

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 ($\Phi_{cc'}$, $\psi_{cc'a}$) or a common cation ($\Phi_{aa'}$, $\psi_{caa'}$). 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, ${}^E\theta_{ij}$, 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 Φ_{ij} , which is then given by $\Phi_{ij} = \theta_{ij} + {}^E\theta_{ij}$ (Pitzer, 1991). Thus, at fixed pressure and temperature, G^E is expressed in terms of (an extra) two adjustable parameters, θ_{ij} and ψ_{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 by the fitting of reliable experimental data is now 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. By way of example, 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). 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 \bar{V}° and partial molar heat capacity \bar{C}_p° can have complex temperature dependences (Archer, 1992; Archer and Carter, 2000; Rogers and Pitzer, 1982). 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 (ϕV , ϕC_p) of a binary solute to be relative to a non-zero reference molality (Archer and Carter, 2000)

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

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:

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

As described by Archer (1992), the functional form of $C_p(m_r)n_r^{-1}$ 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

Some limitations of the Pitzer equations are well known (Section 1) so this paper focuses on four ‘Case Studies’ that, taken together, provide insights into other 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) extensive, high-quality data are available for them, particularly under non-ambient conditions; (b) they have relatively high solubilities; and (c) they feature prominently in natural brine solutions. A selection of literature Pitzer models for these electrolyte solutions is shown in Table 1 (Table A1 of Appendix A gives similar details for other multidimensional chemical systems).

Table 1 Literature sources of multidimensional Pitzer models for binary solutions of 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
Gruskiewicz and Simonson (2005) ^a	273—573	<i>P</i> _{sat}	<i>m</i> _{sat}

^a Using various extended forms of the original Pitzer equations; ^b At $T \leq 373.15$, K $P_{\text{sat}} = 0.1$ MPa; at $T > 373.15$, $P = P_{\text{sat}}$

Most of the present work was performed using the JESS (Joint Expert Speciation System) software package (May and Murray, 1991, 2001; May et al., 2010, 2011; Rowland and May, 2010, 2012, 2013, 2014). 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 not previously practicable (May et al., 2010; Rowland and May, 2013). Most importantly, for meaningful analysis of modelling functions, it is necessary to have systems, such as NaCl(aq), MgCl₂(aq) and CaCl₂(aq), that have been measured sufficiently often by independent investigators to permit a realistic assessment of experimental errors (Rowland and May, 2013).

In Case Studies A and B, the full range of relevant physicochemical property data for the three binary 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 was applied (May et al., 2010), a computational technique that avoids numerical ill-conditioning and minimizes the impacts of correlation (Press et al., 1992).

With Case Studies C and D, all thermodynamic properties were calculated using the Gibbs-energy minimizer incorporated into the ChemSage/FactSage/ChemApp software family (Bale et al., 2009; Eriksson and Hack, 1990; Eriksson and Königsberger, 2008; Petersen and Hack, 2007). 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 well-established literature data at non-ambient conditions

This Case Study confirms, as is well known, that the Pitzer equations in their standard form can accurately describe the physicochemical properties of numerous binary electrolyte solutions over wide ranges of conditions when the experimental 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) over suitable sets of conditions (Table 2). The upper temperature limit, $T \leq 523$ K, was imposed on MgCl₂(aq) and CaCl₂(aq) because of well-known difficulties in the data 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 arbitrarily 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 (May et al., 2010) data from the JESS Pitzer models

System	Conditions	$\ln \gamma$	ϕ	ϕL ^a	ΔH_{dil} ^{a,b}	ϕC_p ^c	ϕV ^d
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

4.1.1 NaCl(aq)

As would be expected from the previous work of Pitzer et al. (1984) and Archer and Carter (2000), the representation of the thermodynamic properties of NaCl(aq) by the Pitzer equations over the given conditions was highly satisfactory. The activity and osmotic coefficients were particularly 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 ϕL was anomalously large (Table 3). 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).

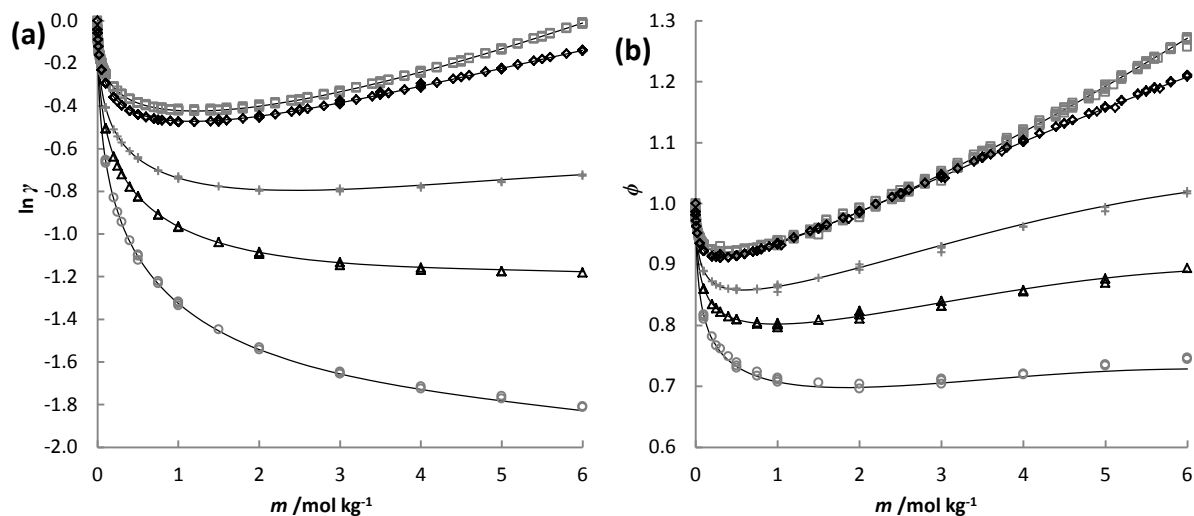


Fig. 1. (a) Activity coefficients and (b) osmotic coefficients of NaCl(aq) as a function of concentration at: $T/\text{K} \approx 298$ (squares), 373 (diamonds), 473 (pluses), 523 (triangles) and 573 (circles). Pressure is the greater of saturation vapour pressure or 0.1 MPa. Main data sources: Pitzer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

Table 4 Comparison of apparent molar volumes from literature studies 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 ^a
Rogers and Pitzer (1982)	-34.4
Pitzer et al. (1984)	-34.4
Majer et al. (1988)	-40.8
Archer (1992)	-39.9

^a Experimental determination at $t = 572.08$ K

Some systematic deviations in ϕC_p between Archer's (1992) critical review and this work are also evident (Fig. 2) at high pressures. However, there are no reliable supporting experimental (as opposed to simulated) data to lend favour to one model or the other.

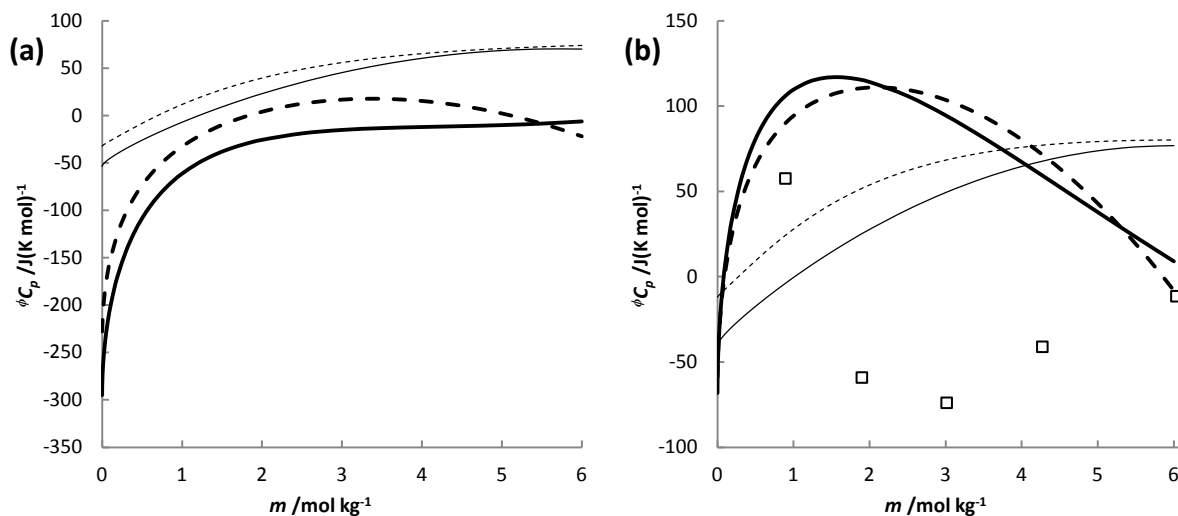


Fig. 2 Apparent molar heat capacity of NaCl(aq) as a function of concentration at pressures of: (a) 80 MPa and (b) 100 MPa, with $T/\text{K} = 273.15$ (thin lines) and 573.15 (thick lines). Dashed lines are from the correlation of Archer (1992). Solid lines are from the present JESS Pitzer model. Points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

4.1.2 MgCl₂(aq)

The MgCl₂(aq) activity and osmotic coefficients are also described with impressive accuracy (Fig. 3) using the standard form of the Pitzer equations. The standard deviations of the fit to ϕV were $0.52 \text{ cm}^3 \text{ mol}^{-1}$ for $T \leq 373.15$ K, and $0.97 \text{ cm}^3 \text{ mol}^{-1}$ for $T > 373.15$ 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. 4.

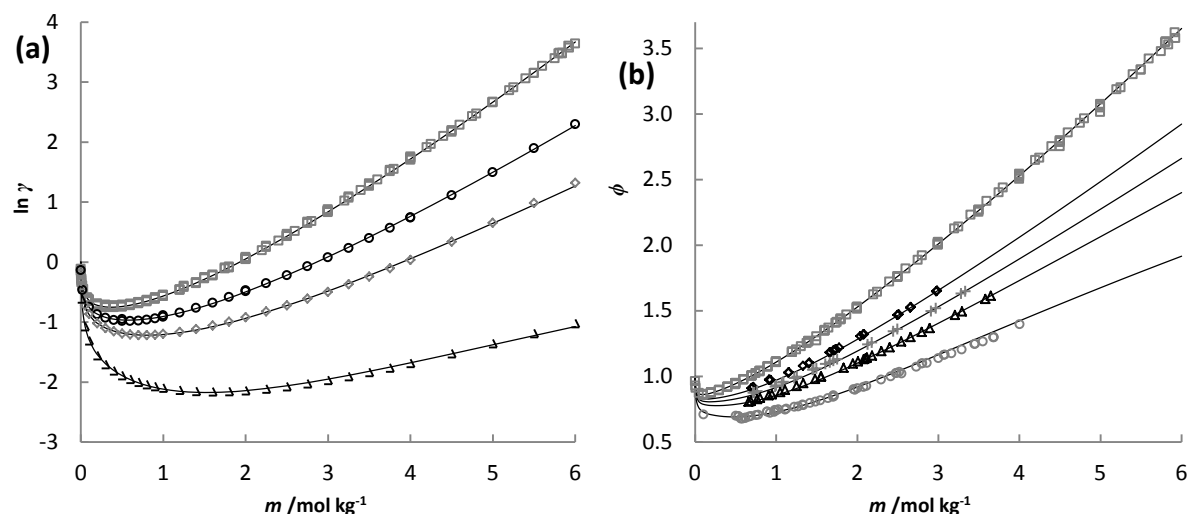


Fig. 3 (a) Activity coefficients of MgCl₂(aq) as a function of concentration at $T/\text{K} \approx 298$ (squares), 373 (circles), 423 (diamonds) and 523 (triangles). Main data sources: Goldberg and Nuttall (1978), Wang et al. (1998) and Christov (2009b). (b) Osmotic coefficients of MgCl₂(aq) as a function 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.

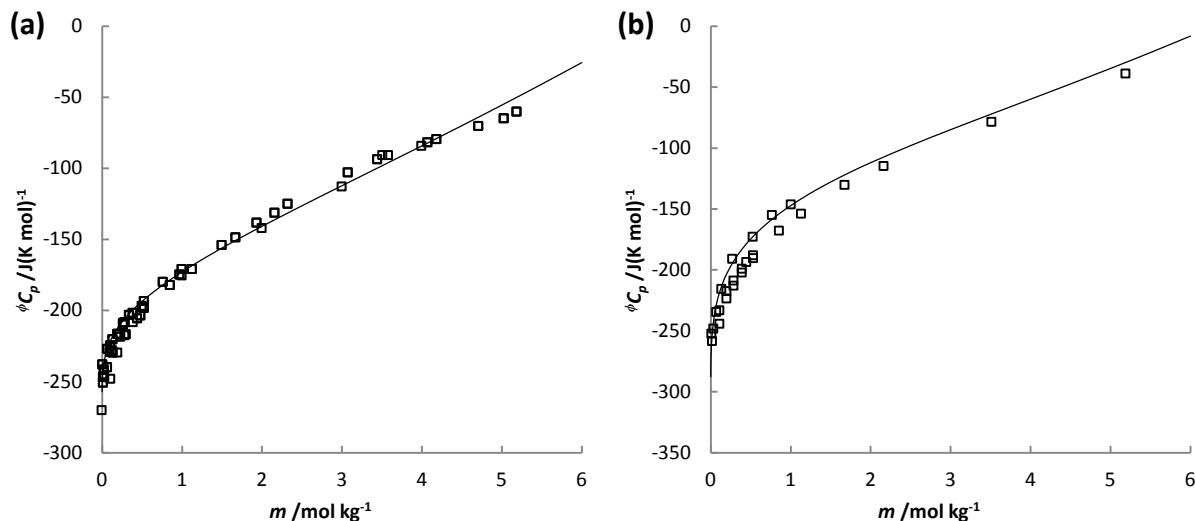


Fig. 4 Apparent molar heat capacities of MgCl₂(aq) as a function of concentration at: (a) $T = 298.15 \text{ K}$; (b) $T = 373.15 \text{ K}$. Main data sources: Perron et al. (1974, 1981), Saluja and LeBlanc (1987), Saluja et al. (1995), Holmes et al. (1997) and Call et al. (2000). Lines from the JESS Pitzer model.

4.1.3 CaCl₂(aq)

For CaCl₂(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. 5). 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 $12 \text{ J}(\text{K mol})^{-1}$ for $T \leq 373.15 \text{ K}$ and $33 \text{ J}(\text{K mol})^{-1}$ for $T > 373.15 \text{ K}$.

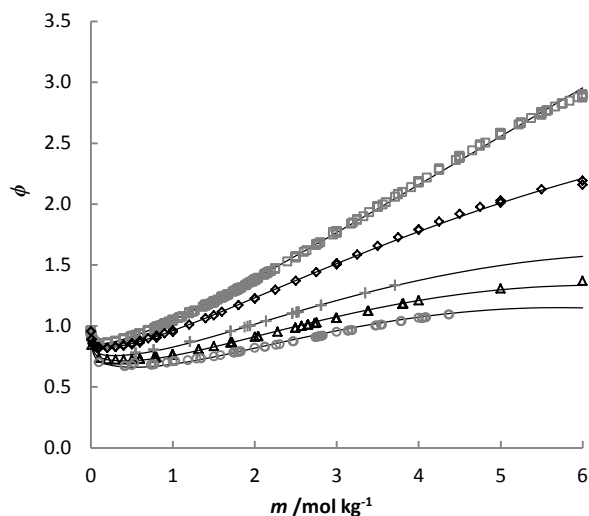


Fig. 5 Osmotic coefficients of CaCl₂(aq) as a function of concentration at: $T / \text{K} \approx 298$ (squares), 373 (diamonds), 443 (pluses), 473 (triangles) and 498 (circles). Main data sources: Rard and

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 fitting with the Pitzer model data sets that are incomplete and/or thermodynamically inconsistent. The numerical pathologies produced are not always easily detectable and 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)	N_d
White et al. (1988)	ϕC_p	549.0	10.1—17.9	0.03—2.26	46
	ϕC_p	573.5	17.9	0.03—2.26	23
Holmes and Mesmer (1996)	ϕ	524	P_{sat}	0.42—3.95	21
Obšil et al. (1997)	ϕV	572.6	10.4—30.3	0.03—3.04	28
Wang et al. (1998)	γ	573	P_{sat}	0.001—6	32
	ϕ	573	P_{sat}	0.001—6	32
	ϕV	573	10—30	0.001—3	72

Pitzer parameters were thus determined for MgCl₂(aq) over a range of conditions spanning $P = (0.1 \text{ to } 100)$ MPa, $T = (273 \text{ to } 573)$ K and $m = (0 \text{ to } 6)$ 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 MgCl₂(aq) from the Pitzer model optimised to $T = 573$ K. Numbers in bold are those that are significantly ($> 30\%$) greater than corresponding values in Table 3.

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

^a Units: kJ mol⁻¹; ^b Units: J K⁻¹ mol⁻¹; ^c Units: cm³ mol⁻¹

Although the high-temperature data were poorly represented (Table 6), for example with a spurious minimum in $\phi C_p(T)$ (Fig. 6), more striking were the large deviations in $\phi C_p(m)$ arising at low temperatures (Fig. 7, dashed lines) that were previously well fitted (Fig. 4) when the data were restricted to $T \leq 523$ K.

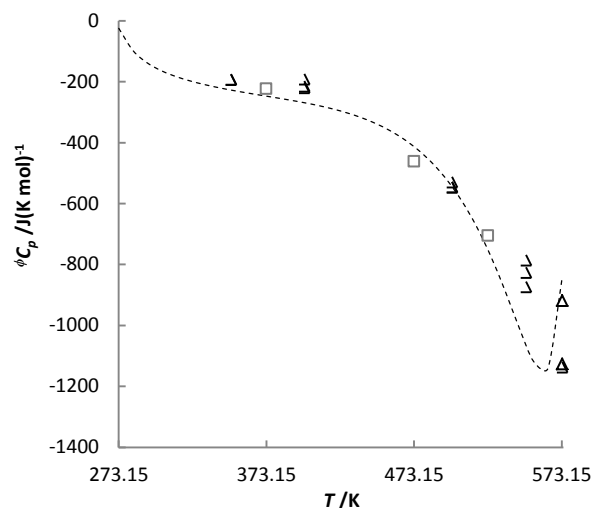


Fig. 6. Apparent molar heat capacity of $\text{MgCl}_2(\text{aq})$ as a function of temperature at $P \approx 17.9$ MPa and $m = 0.03$ mol kg^{-1} . Data sources: White et al. (1988) (triangles) and Wang et al. (1998) (squares). Line from the JESS Pitzer model to $T = 573$ K.

The effect in Fig. 6 illustrates the critical dependence of the fit both on the weights given to data for a particular property and for different ranges of conditions, neither of which can be established objectively.

The theoretical Debye-Hückel limiting slope for ϕC_p is positive under the conditions of temperature and pressure considered in this work. However, the slope of $\phi C_p(m)$ calculated from the Pitzer equations was negative in dilute electrolyte solutions in some cases (e.g. Fig. 7). The cause of this non-physical behaviour is the attempt to constrain a large number of empirical parameters using incoherent (high-temperature) data. Since this kind of behaviour may occur in regions of the multidimensional space where no data are available, it is often only detected via close human inspection of the model rather than its adverse effect on the residuals.

A noticeable improvement in the correlation of $\phi C_p(m)$ at near-ambient temperatures (Fig. 7, solid lines) was achieved by lowering the weights of the high-temperature data. However, the selection of appropriate weights inevitably involves some degree of human expertise making the resulting models inherently subjective. Neither has it entirely cured the flexing characteristic of overfitted functions.

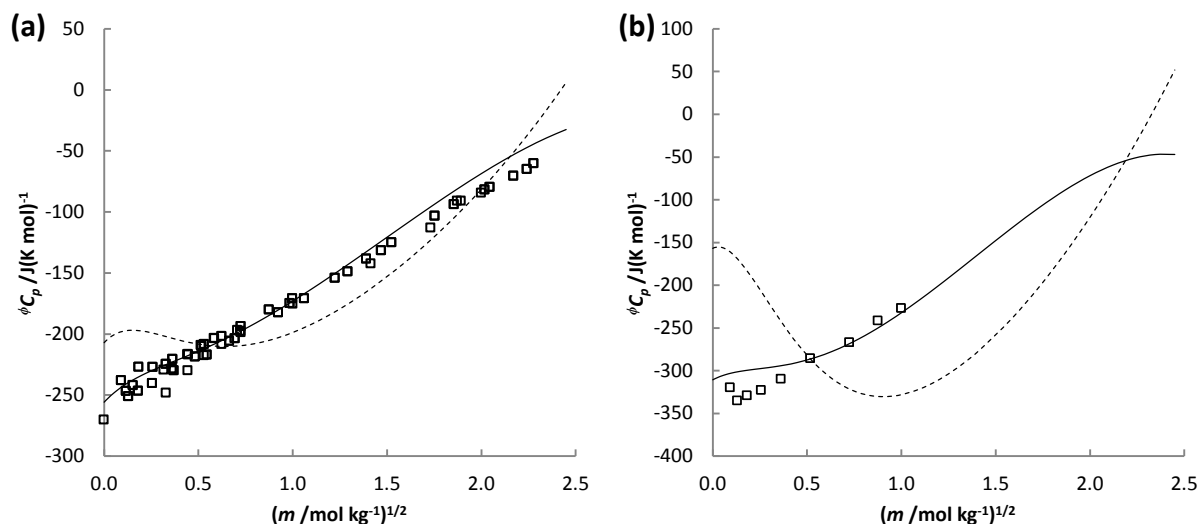


Fig. 7. Apparent molar heat capacity for $\text{MgCl}_2(\text{aq})$ as a function of concentration at: (a) $P = 0.1$ MPa and $T = 298.15$ K; (b) $P = 0.35$ MPa and $T = 278.15$ K. Main data sources: Perron et al. (1974, 1981), Holmes et al. (1997), Call et al. (2000). Curves show models optimised over the range $P = (0.1 \text{ to } 100)$ MPa, $T = (273 \text{ to } 573)$ K, $m = (0 \text{ to } 6)$ mol kg^{-1} . Normal FIZ weights for all data (dashed line); reduced weights on data at $T \geq 523$ K (solid line).

To understand why the Pitzer model functions can fail so badly, as illustrated in Figs. 6 and 7, 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). In other words, the consequences of relatively small experimental errors can be dramatic. This is so even in two dimensions (a striking example is given in Appendix A). The likelihood of such pathological effects increases in multidimensional space, as does the difficulty in detecting them.

4.3 Case Study C: General regression of disparate literature datasets 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. Full automation of the modelling process to achieve greater objectivity is also precluded.

It might be expected that the fitting of thermodynamic data for any given chemical system would improve progressively over time or, at least, not deteriorate. Unfortunately, this is not necessarily what is observed. $\text{MgCl}_2(\text{aq})$ was chosen as a chemical system for this Case Study since it is well-characterised experimentally to concentrations that should be possible to analyse satisfactorily using the standard form of the Pitzer equations.

Pitzer parameters for activity and osmotic coefficients of $\text{MgCl}_2(\text{aq})$ from several sources for ambient conditions are given in Table 7. Solubility products for the formation of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}(\text{cr})$ at $m = 5.81$ 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 7 Published Pitzer parameters for activity and osmotic coefficients of $\text{MgCl}_2(\text{aq})$ at $T = 298.15$ K from different literature sources (see text). The solubility product, $\ln K_{sp}(\text{MgCl}_2 \cdot 6\text{H}_2\text{O}(\text{cr}))$, applies to $m = 5.81 \text{ mol kg}^{-1}$.

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 (2009a)	m_{sat}	0.3619	1.581	0.00238	10.15
This work	5.8	0.3553	1.644	0.00510	10.43
Wagman et al. (1982)					10.24

Each of the parameterizations in the literature shown in Table 7 is based upon different datasets and methods. Pitzer and Mayorga (1973) based their optimization on the critically-evaluated data of Robinson and Stokes (1970), 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 numerous sources of activity and osmotic coefficient data for optimization. Christov (2009a) appears to be alone in relying 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. 8). 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 to 0.2)% attributed to Rard and Miller's (1981) data.

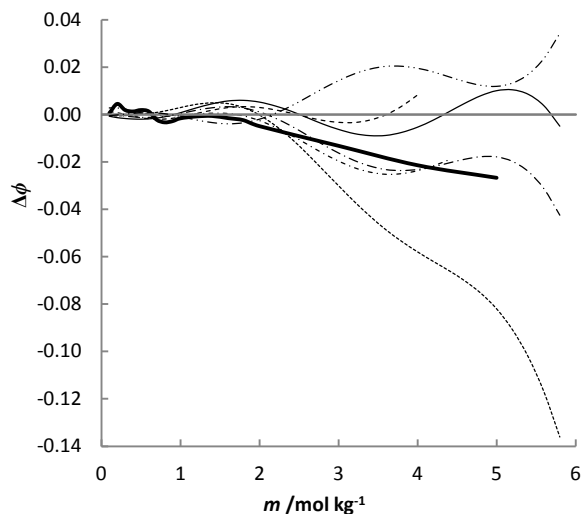


Fig. 8. Deviations of the osmotic coefficient for $\text{MgCl}_2(\text{aq})$ between various literature models and the experimental values of Rard and Miller (1981) (indicated by the horizontal line) as a function of concentration at $T = 298.15$ K. Model of Robinson and Stokes (1970) (thick solid line) 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 inferences can be drawn from Fig. 8. First, it is evident that the Pitzer function provides no real assistance in identifying the better datasets – different experts have arrived at significantly different parameters and fits without issue. Second, the S-shaped distribution of **all** residual sets shown in Fig. 8 is characteristic 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. 8, 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 that 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 electrolyte mixtures

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

The mixtures chosen to illustrate these problems are among the best-characterised systems available. Fig. 9a 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). The values of γ_{NaCl}^t obtained from various models vary by up to 5 %. The variation of $\gamma_{\text{MgCl}_2}^t$ in $m = 6 \text{ mol kg}^{-1}$ NaCl(aq) is even larger (Fig. 9b).

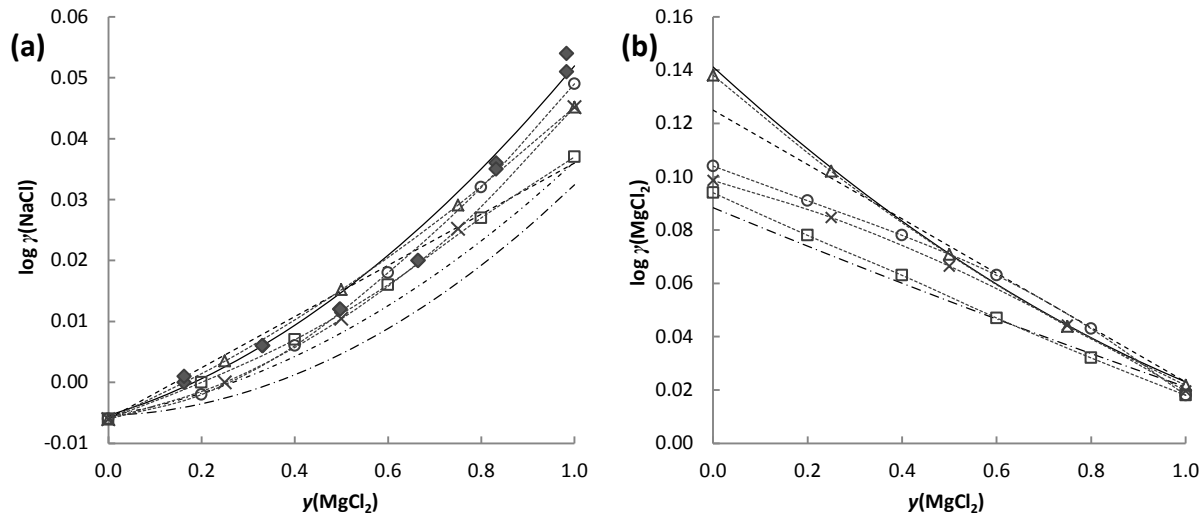


Fig. 9. Mean activity coefficients of (a) NaCl(aq); and (b) MgCl₂(aq), as a function of y_{MgCl_2} , the ionic strength fraction of MgCl₂(aq) in NaCl(aq) + MgCl₂(aq) mixtures, at $I = 6 \text{ mol kg}^{-1}$ and $T = 298.15 \text{ K}$. Potentiometric results from Lanier (1965) (filled symbols). Pitzer 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).

Several mean activity coefficient models are compared with experimental data (Lanier, 1965) in Fig. 9. The Pitzer model for NaCl(aq) + MgCl₂(aq) mixtures (with non-zero θ and ψ terms) reported by Rard and Miller (1981, 1987) is in good agreement with Lanier's (1965) potentiometric data for γ_{NaCl} , but is distinctly different from the other models, including Rard and Miller's own calculations using both Pitzer ($\theta = \psi = 0$) and Scatchard models (Rard and Miller, 1987). It is unclear to us why Platford's (1968) parameterization of the Scatchard model (using his isopiestic data for NaCl(aq) + MgCl₂(aq) mixtures) 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} .

Pitzer (1991) has emphasised the importance of solubility data as a means of anchoring isothermal activity and osmotic coefficients to a single well-defined point. Various Pitzer models based primarily on osmotic coefficient data are compared with mean activity coefficients of NaCl(aq) derived from solubility data in Fig. 10. The datasets are in good agreement with one another and with the Pitzer models when the molality of MgCl₂(aq) is less than 3 mol kg^{-1} . At higher concentrations, all models deviate systematically from the data and the data show larger scatter. It therefore seems that these data are unsuitable for the optimization of mixing parameters for this system, compared to the large body of isopiestic measurements.

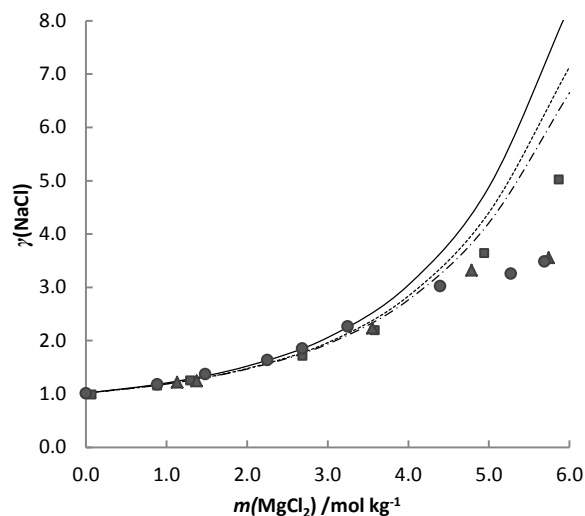


Fig. 10. Mean activity coefficient of NaCl(aq) at NaCl(s) saturation in solutions of MgCl₂(aq) at $T = 298.15$ K as a function of the MgCl₂(aq) molality. Experimental data: Kurnakov and Zemczny (1924) (circles); Keitel (1923) (triangles); Takegami (1921) (squares). Pitzer models: Pabalan and Pitzer (1987b) (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 Fernández-Prini et al. (1992, p. 106), flexible correlation of high-temperature data 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 inherently 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 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).

5.1 Comparison between the standard Pitzer equations, variants of the Pitzer equations, and other theoretical frameworks

Various forms of the Pitzer equations have been used to correlate thermodynamic properties for more than 20 different binary electrolyte solutions over wide ranges of temperature (Table A1). Over time, extended variants of the Pitzer equations have tended to appear more frequently than the standard form. A key reason for this gain in popularity is that the increased number of parameters permit more accurate reproduction of available data over wider concentration ranges than the standard form. One of the most popular of the extended forms is due to Archer (1991), who introduced ionic-strength dependence into the third virial coefficient C^ϕ . Other extensions have increased the number of virial terms (Ananthaswamy and Atkinson, 1985) or introduced a temperature-dependent α_1 parameter (Holmes et al., 1997). The additional flexibility of these extended equations can be problematic: extra parameters make the optimisation numerically more complicated (Holmes et al., 1994; Pitzer et al., 1999) and models can no longer be combined consistently (Clegg and Whitfield, 1991). Many other variations of Pitzer's original equations have been presented in the literature, including forms with electrolyte-specific b (Pérez-Villaseñor et al., 2002) or on the mole fraction basis (Pitzer and Simonson, 1986). The different Pitzer equation variants littering the literature pose a serious impediment to developing a general electrolyte solution modelling capability.

An important reason for using a clear-cut expression for the Gibbs energies as developed by Pitzer is that subsequent application to chemical systems in general is relatively straightforward. The same cannot be said for the theoretical framework due to Helgeson et al. (1981) where the validity of certain assumptions, such as the form of the concentration dependence of the dielectric constant, are difficult to judge and the extension to multicomponent systems is problematic (Grenthe et al., 1997, p. 346).

5.2 Strengths and weaknesses arising from algebraic flexibility of the Pitzer equations

A key advantage of the Pitzer equations is their ability to describe the variation of 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 (excess) Gibbs energies must be consistent with independently measured (excess) enthalpies and heat capacities. Similarly, the pressure dependence of G (or G^E) must be consistent with observed volume and compressibility changes, and so on. This consistency has been used, for instance, to extend such models to high temperatures and pressures by employing heat capacity and density data (Archer, 1992; Königsberger et al., 2009; Pabalan and Pitzer, 1987b; Pitzer, 1986; Schrödle et al., 2010). On the other hand, the algebraic flexibility of the Pitzer equations that allows them to follow physicochemical property changes so closely is, at the same time, 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 (see Case Study B, 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). Unfortunately, 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 sufficiently the empirical functions. Appendix A 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 reliably the standard partial molar quantities \bar{C}_p^o and \bar{V}^o . This is due directly to the empirical terms in these (derivative) equations, which can even allow a reversal of function slope (e.g., Fig. 7) at concentrations as low as $m = 10^{-4}$ mol kg⁻¹. This contrasts with 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 often reported for \bar{C}_p^o and \bar{V}^o from the Pitzer fits of measured data. Typical examples of overly-optimistic precision appear in Krumgalz et al. (1995, 1996a, 1996b, 2000), where \bar{V}^o values are given to three decimal places when it seems probable that the real uncertainty is at least an order of magnitude larger. The excessive flexibility of the Pitzer equations, which is exacerbated by the facile introduction of purely empirical extensions, promotes chaotic effects and thus impedes development of more coherent and robust models. The growing practice of improving fits simply by adding basis functions (thereby increasing the number of adjustable parameters) is therefore to be deprecated.

5.3 Sensitivity of Pitzer functions

As is evident from the present case studies, profound difficulties can arise in the use of Pitzer functions because of variations in the sensitivity of those functions to the values of different physicochemical properties. These differing sensitivities have been poorly recognised and do not seem to be amenable to straightforward solution. For example, the sequence of published parameters (Case Study C) for MgCl₂(aq) seems to reflect, to an uncomfortable extent, individual assessments of the quality/reliability 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.

With regard to ternary Pitzer parameters, numerous workers have followed the advice of Pabalan and Pitzer (1991, p. 460): “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 that 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, 2013; 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 have applied inconsistently-determined parameters without comment. Numerous ‘extended’ Pitzer equations, employing up to nine (*cf.* Pitzer’s original three) 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., α_i 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 α_i 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 example). For instance, isothermal fits of ${}^\phi C_p$ and ${}^\phi V$ 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, 2010; Schrödle et al., 2008, 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 multiple numbers of cations and 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 reportedly (Marion and Farren, 1999) based on incorrect experimental data for gypsum solubilities in magnesium sulfate solutions. 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 resolved 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 semi-empirical functions. Amongst the many such approaches now available the Pitzer equations remain pre-eminent, with good reasons (Section 1; 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, requires tailoring 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 results presented in this paper suggest that the fitting process cannot be generalised to achieve an objective, reproducible description of measured multicomponent thermodynamic data. 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 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 in this area, this work has offered a critique of the limitations associated with the parameterization of Pitzer models. It seems more than likely that the 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 et al., 2002) or the 'mixed solvent electrolyte model' (MSE) implemented by OLI (Wang et al, 2002, 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 composition, 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 limited 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 a 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 better understood. Only then can they be better 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

Table A1 lists some Pitzer equation models covering wide ranges of temperature. Most of the models published after 1990 use one of many extended variants of the Pitzer equations (c.f. Section 5.1). As such, maintaining thermodynamic consistency is problematic. Caution should be exercised before combining models from different sources to describe multicomponent electrolyte solutions.

Table A1

Survey of binary electrolyte systems described in the literature by multidimensional Pitzer models.

Electrolyte	Conditions	Ref.
HCl	298–647 K, 7–40 MPa, 2 mol kg ⁻¹ ^a	Simonson et al. (1990)
LiCl	0–250 °C, P_{sat} , 6 mol kg ⁻¹	Holmes and Mesmer (1983)
Li ₂ SO ₄	0–225 °C, P_{sat} , 3 mol kg ⁻¹	Holmes and Mesmer (1986)
NaOH	0–300 °C, <400 bar, 10 mol kg ⁻¹	Pabalan and Pitzer (1987a)
	298–523 K, <40 MPa, 6.3 mol kg ⁻¹ ^b	Simonson et al. (1989)
NaBr	260–623 K, <150 MPa, 8 mol kg ⁻¹ ^b	Archer (1991)
	260–623 K, <150 MPa, 8 mol kg ⁻¹ ^b	Rard and Archer (1995)
NaNO ₃	236–425 K, P_{sat} , min(m_{sat} ; 25 mol kg ⁻¹) ^b	Archer (2000)
Na ₂ SO ₄	0–225 °C, P_{sat} , 3 mol kg ⁻¹	Holmes and Mesmer (1986)
	0–200 °C, 100 bar, <1 mol kg ⁻¹	Phutela and Pitzer (1986)
KOH	273–573 K, P_{sat} , m_{sat} ^b	Li and Pitzer (1996)
KF	298–473 K, <30 MPa, 2.5 mol kg ⁻¹	Das and Pitzer (2001)

KCl	0–250 °C, P_{sat} , 6 mol kg ⁻¹ 273–573 K, <500 bar, 4.5 mol kg ⁻¹ 260–420 K, P_{sat} , m_{sat} ^b	Holmes and Mesmer (1983) Pabalan and Pitzer (1988) Archer (1999)
K ₂ SO ₄	0–225 °C, P_{sat} , 2 mol kg ⁻¹ 0–225 °C, 300 bar, 0.65 mol kg ⁻¹ 271–500 K, P_{sat} , 2.5 mol kg ⁻¹ ^b	Holmes and Mesmer (1986) Das and Pitzer (1999) Palmer et al. (2002)
CsCl	0–250 °C, P_{sat} , 6 mol kg ⁻¹	Holmes and Mesmer (1983)
Cs ₂ SO ₄	0–225 °C, P_{sat} , 6 mol kg ⁻¹	Holmes and Mesmer (1986)
BaCl ₂	273–523 K, <40 MPa, 4.1 mol kg ⁻¹ ^b	Holmes et al. (1997)
MgSO ₄	298–473 K, 20 bar, 3 mol kg ⁻¹	Phutela and Pitzer (1986)
Ca(NO ₃) ₂	298.15–373 K, 0.1 MPa, 8 mol kg ⁻¹ ^b	Oakes et al. (2000)
SrCl ₂	273–473 K, P_{sat} , 1 mol kg ⁻¹ 273–523 K, <40 MPa, 5.5 mol kg ⁻¹ ^b	Phutela et al. (1987) Holmes et al. (1997)
NdCl ₃	298–372 K, 0.1–0.5 MPa, m_{sat} ^b	Oakes et al. (2004)

At $T \leq 373.15$ K, $P_{\text{sat}} = 0.1$ MPa; at $T > 373.15$, $P = P_{\text{sat}}$.^a Ion-association model; ^b Using various extended forms of the original Pitzer equations;

Fig. A1 shows the Pitzer fit to Robinson and Stokes' (1970) mean activity coefficient values for $\text{Al}_2(\text{SO}_4)_3(\text{aq})$. After slightly altering the activity coefficients at the two lowest concentrations (Table A2), the values were re-fitted using the same Pitzer model function but allowing the parameter values to vary. 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. 7) 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.

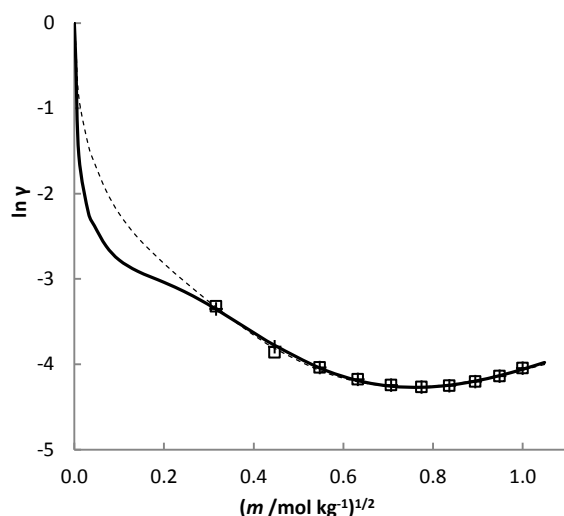


Fig. A1 Mean activity coefficient (as natural logarithm) of $\text{Al}_2(\text{SO}_4)_3(\text{aq})$ at $T = 298.15 \text{ K}$; symbols are original (pluses) and modified (squares) data from Robinson and Stokes (1970) - see Table A2. Pitzer models fit to: original data (solid line); modified data (dashed).

Table A2

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 (shown in bold), as used to produce Fig. A1.

$m \text{ (mol kg}^{-1}\text{)}$	$\gamma \text{ (Robinson and Stokes, 1970)}$	$\gamma \text{ (modified)}$
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

REFERENCES

- Afanas'ev V. N. (2011) Solvation of Electrolytes and Nonelectrolytes in Aqueous Solutions, *J. Phys. Chem.* **B115**, 6541-6563.
- Ananthaswamy J. and Atkinson G. (1985) Thermodynamics of Concentrated Electrolyte Mixtures. 5. A Review of The Thermodynamic Properties of Aqueous Calcium Chloride in the Temperature Range 273.15-373.15 K. *J. Chem. Eng. Data* **30**, 120-128.
- Archer D. G. (1990) Effect of Revisions of Debye-Hückel Limiting Law Coefficients on the Thermodynamic Parameters for Strong-Electrolyte Solutions, *J. Chem. Eng. Data* **35**, 340-344.
- Archer D. G. (1991) Thermodynamic Properties of the NaBr + H₂O System. *J. Phys. Chem. Ref. Data* **20**, 509-555.
- Archer D. G. (1992) Thermodynamic Properties of the NaCl + H₂O System. II. Thermodynamic Properties of NaCl(aq), NaCl·2H₂O(cr), and Phase Equilibria. *J. Phys. Chem. Ref. Data* **21**, 793-829.
- Archer D. G. (1999) Thermodynamic Properties of the KCl + H₂O System. *J. Phys. Chem. Ref. Data* **28**, 1-17.
- Archer D. G. (2000) Thermodynamic Properties of the NaNO₃ + H₂O System. *J. Phys. Chem. Ref. Data* **29**, 1141-1156.
- Archer D. G. and Carter R. W. (2000) Thermodynamic Properties of the NaCl+H₂O System. 4. Heat Capacities of H₂O and NaCl(aq) in Cold-Stable and Supercooled States. *J. Phys. Chem.* **B104**, 8563-8584.
- Baechler S., Croise J. and Altmann S. (2012) Modelling Coupled Chemico-osmotic and Advective-diffusive Transport of Nitrate Salts in the Callovo-Oxfordian Clay, *Advances in Water Resources* **49**, 76-85.
- Bale C. W., Belisle E., Chartrand P., Deckerov S. A., Eriksson G., Hack K., Jung I.-H., Kang Y. B., Melancon J., Pelton A. D., Robelin C. and Petersen S. (2009) FactSage Thermochemical Software and Databases – Recent Developments. *CALPHAD: Comput. Coupling Phase Diagrams Thermochem.* **33**, 295-311.
- Berdat D., Andres H. and Wunderli S. (2009) Development of Suitable ISE Measurement Procedures for SI-Traceable Chemical Activity Determination. *Chimia* **63**, 670-677.
- Bethke C. M. (1998) The Geochemist's Workbench, Ver. 3.0, Univ. Illinois, Urbans-Champaign, IL, U.S.A.
- Brönsted J. N. (1922a) Studies on Solubility. IV. The Principle of the Specific Interaction of Ions. *J. Am. Chem. Soc.* **44**, 877-898.
- Brönsted J. N. (1922b) Calculation of the Osmotic and Activity Functions in Solution of Uni-univalent Salts. *J. Am. Chem. Soc.* **44**, 938-948.
- Buck R. P., Rondinini S., Covington A. K., Baucke F. G., Brett C. M. A., Camoes M. F., Milton M. J. T., Mussini T., Naumann R., Pratt K. W., Spitzer P. and Wilson G. S. (2002) Measurement of pH. Definition, Standards and Procedures. *Pure Appl. Chem.* **74**, 2169-2200.
- Busey R. H., Holmes H. F. and Mesmer R. E. (1984) The Enthalpy of Dilution of Aqueous Sodium Chloride to 673 K Using a New Heat-Flow and Liquid-Flow Microcalorimeter. Excess Thermodynamic Properties and Their Pressure Coefficients. *J. Chem. Thermodyn.* **16**, 343-372.
- Call T. G., Ballerat-Busserolles K., Origlia M. L., Ford T. D. and Woolley E. M. (2000) Apparent Molar Volumes and Heat Capacities of Aqueous Magnesium Chloride and Cadmium Chloride at Temperatures from 278.15 K to 393.15 K at the Pressure 0.35 MPa: A Comparison of Ion-ion Interactions. *J. Chem. Thermodyn.* **32**, 1525-1538.
- Christov C. (2009a) Isopiestic Determination of the Osmotic Coefficients of an Aqueous MgCl₂ + CaCl₂ Mixed Solution at (25 and 50) °C. Chemical Equilibrium Model of Solution Behavior and Solubility in the MgCl₂ + H₂O and MgCl₂ + CaCl₂ + H₂O Systems to High Concentration at (25 and 50) °C. *J. Chem. Eng. Data* **54**, 627-635.
- Christov C. (2009b) Chemical Equilibrium Model of Solution Behavior and Bishofite (MgCl₂·6H₂O(cr)) and Hydrogen-Carnallite (HCl·MgCl₂·7H₂O(cr)) Solubility in the MgCl₂ + H₂O and HCl-MgCl₂ + H₂O Systems to High Acid Concentration at (0 to 100) °C. *J. Chem. Eng. Data* **54**, 2599-2608.

Clegg S. L. and Whitfield M. (1991) Activity Coefficients in Natural Waters. In *Activity Coefficients in Electrolyte Solutions*, second ed. (ed. K. S. Pitzer). CRC Press, Boca Raton, Florida, USA, pp. 279-434.

Das B. and Pitzer K. S. (1999) Thermodynamic Properties of Aqueous Potassium Sulfate under Superambient Conditions. *J. Solution Chem.* **28**, 283-289.

Das B. and Pitzer K. S. (2001) Thermodynamic Properties of Aqueous Potassium Fluoride under Superambient Conditions. *J. Solution Chem.* **30**, 489-496.

Dyson F. (2004) Quote attributed to von Neumann by Enrico Fermi, in "A meeting with Enrico Fermi". *Nature* **427**, p. 297.

Eriksson G. and Hack K. (1990) ChemSage - A Computer Program for the Calculation of Complex Chemical Equilibria. *Mettl. Trans.* **21B**, 1013-1023.

Eriksson G. and Königsberger, E. (2008) FactSage and ChemApp: Two Tools for the Prediction of Multiphase Chemical Equilibria in Solutions, *Pure Appl. Chem.* **80**, 1293-1302.

Fernández D. P., Goodwin A. R. H., Lemmon E. W., Levelt Sengers J. M. H. and Williams R. C. (1997) A Formulation for the Static Permittivity of Water and Steam at Temperatures from 238 K to 873 K at Pressures up to 1200 MPa, including Derivatives and Debye-Huckel Coefficients. *J. Phys. Chem. Ref. Data* **26**, 1125-1166.

Fernández-Prini R. J., Corti H. R. and Japas M. L. (1992) *High-Temperature Aqueous Solutions: Thermodynamic Properties*, CRC Press, Boca Raton, U.S.A.

Fraenkel D. (2011) Monoprotic Mineral Acids Analyzed by the Smaller-Ion Shell Model of Strong Electrolyte Solutions, *J. Phys. Chem.* **B115**, 557-568.

Goldberg R. N. and Nuttall R. L. (1978) Evaluated Activity and Osmotic Coefficients for Aqueous Solutions: The Alkaline Earth Metal Halides. *J. Phys. Chem. Ref. Data* **7**, 263-310.

Grant-Taylor D. F. (1981) Partial Molar Volumes of Sodium Chloride Solutions at 200 bar, and Temperatures from 175 to 350 °C, *J. Solution Chem.* **10**, 621-630.

Grenthe I., Plyasunov A. V. and Spahiu K. (1997) Estimation of Medium Effects on Thermodynamic Data. In *Modelling in Aquatic Chemistry* (eds. I. Grenthe and I. Puigdomenech). Nuclear Energy Agency, OECD, Paris, France, pp. 325-426.

Gruskiewicz M. S. and Simonson J. M. (2005) Vapor Pressures and Isopiestic Molalities of Concentrated CaCl₂(aq), CaBr₂(aq), and NaCl(aq) to T = 523 K. *J. Chem. Thermodyn.* **37**, 906-930.

Guggenheim E. A. (1935) The Specific Thermodynamic Properties of Aqueous Solutions of Strong Electrolytes. *Philos. Mag.* **19**, 588-643.

Haghtalab A., Shojaeian A. and Mazloumi S. H. (2011) Nonelectrolyte NRTL-NRF Model to Study Thermodynamics of Strong and Weak Electrolyte Solutions, *J. Chem. Thermodyn.* **43**, 354-363.

Harvie C. E. and Weare J. H. (1980) The Prediction of Mineral Solubilities in Natural Waters: The Na-K-Mg-Ca-Cl-SO₄-H₂O System from Zero to High Concentration at 25 °C. *Geochim. Cosmochim. Acta* **44**, 981-997.

Harvie C. E., Møller N. and Weare J. H. (1984) The Prediction of Mineral Solubilities in Natural Waters: The Na-K-Mg-Ca-H-Cl-SO₄-OH-HCO₃-CO₃-CO₂-H₂O System to High Ionic Strengths at 25 °C. *Geochim. Cosmochim. Acta* **48**, 723-751.

Hefter G. (2013) Some Highs and Lows (and in-betweens) of Solubility Measurements of Solid Electrolytes. *Pure Appl. Chem.* **85**, 2077-2087.

Hefter G. T. and Tomkins R. P. T., Eds. (2003) *The Experimental Determination of Solubilities*, Wiley, Chichester, UK.

Helgeson H. C., Kirkham D. H. and Flowers G. C. (1981) Theoretical Prediction of the Thermodynamic Behavior of Aqueous Electrolytes at High Pressures and Temperatures. IV. Calculation of Activity Coefficients, Osmotic Coefficients and Apparent Molal and Standard and Relative Partial Molal Properties to 600 °C and 5 kb. *Am. J. Sci.* **281**, 1249-1516.

Hnedkovsky L., Königsberger E., Cibulka I., Königsberger L.-C., Schrödle S., May P. M. and Hefter G. (2007) Densities of NaOH(aq) at Temperatures from (323 to 573) K and 10 MPa Pressure. *J. Chem. Eng. Data* **52**, 2237-2244.

- Hnedkovsky L., Königsberger E., Königsberger L.-C., Cibulka I., Schrödle S., May P. M. and Hefter G. (2010) Densities of Concentrated Alkaline Aluminate Solutions at Temperatures from (323 to 573) K and 10 MPa Pressure. *J. Chem. Eng. Data* **55**, 1173-1178.
- Holmes H. F. and Mesmer R. E. (1983) Thermodynamic Properties of Aqueous Solutions of the Alkali Metal Chlorides to 250 °C. *J. Phys. Chem.* **87**, 1242-1255.
- Holmes H. F. and Mesmer R. E. (1986) Thermodynamics of Aqueous Solutions of the Alkali Metal Sulfates. *J. Solution Chem.* **15**, 495-518.
- Holmes H. F. and Mesmer R. E. (1996) Aqueous Solutions of the Alkaline-earth Metal Chlorides at Elevated Temperatures. Isopiestic Molalities and Thermodynamic Properties. *J. Chem. Thermodyn.* **28**, 1325-1358.
- Holmes H. F., Busey R. H., Simonson J. M. and Mesmer R. E. (1994) CaCl₂(aq) at Elevated Temperatures. Enthalpies of Dilution, Isopiestic Molalities, and Thermodynamic Properties. *J. Chem. Thermodyn.* **26**, 271-298.
- Holmes H. F., Simonson J. M. and Mesmer R. E. (1997) Aqueous Solutions of the Alkaline Earth Metal Chlorides. Corrected Constants for the Ion-Interaction Model. *J. Chem. Thermodyn.* **29**, 1363-1373.
- Hsieh M.-T. and Lin S.-T. (2011) A Predictive Model for the Excess Gibbs Free Energy of Fully Dissociated Electrolyte Solutions, *AIChE J.* **57**, 1061-1074.
- Hu Y.-F., Chu H.-D., Li J.-G., Liu Z.-C., Peng X.-M., Ling S. and Zhang J.-Z. (2011) Extension of the Simple Equations for Prediction of the Properties of Mixed Electrolyte Solutions to the Mixed Ionic Liquid Solutions, *Ind. Eng. Chem. Res.* **50**, 4161-4165.
- Iliuta M. C., Thomsen, K. and Rasmussen, P. (2002) Modeling of Heavy Metal Salt Solubility Using the Extended UNIQUAC Model. *AIChE J.* **48**, 2664-2689.
- Keitel H. (1923) The System KCl-MgCl₂-H₂O and NaCl-MgCl₂-H₂O. *Kali Steinsalz* **17**, 261-265.
- Kim B. Y., Oh J. Y., Baik M. H. and Yun J. -I. (2010) Effect of Carbonate on the Solubility of Neptunium in Natural Granitic Groundwater, *Nucl. Engin. Technol.* **42**, 552-561.
- Kim H.-T. and Frederick W. J. Jr. (1988) Evaluation of Pitzer Ion Interaction Parameters of Aqueous Electrolytes at 25 °C. 1. Single Salt Parameters, *J. Chem. Eng. Data* **33**, 177-184.
- Königsberger E. and Eriksson G. (1995) A New Optimization Routine for ChemSage. *CALPHAD: Comput. Coupling Phase Diagrams Thermochem.* **19**, 207-214.
- Königsberger E., Eriksson G., May P. M. and Hefter G. (2005) Comprehensive Model of Synthetic Bayer Liquors. Part 1. Overview. *Ind. Eng. Chem. Res.* **44**, 5805-5814.
- Königsberger E., Hefter G. and May P. M. (2009) Solubility and Related Properties in Hydrometallurgy. *Pure Appl. Chem.* **81**, 1537-1545.
- Königsberger E., Bochmann S., May P. M. and Hefter G. (2011) Thermodynamics of Impurities in Hydrometallurgical Processes. *Pure Appl. Chem.* **83**, 1075-1084.
- Krumgalz B. S., Pogorelsky R. and Pitzer K. S. (1995) Ion Interaction Approach to Calculations of Volumetric Properties of Aqueous Multiple-Solute Electrolyte Solutions. *J. Solution Chem.* **24**, 1025-1038.
- Krumgalz B. S., Pogorelsky R. and Pitzer K. S. (1996a) Volumetric Properties of Single Aqueous Electrolytes from Zero to Saturation Concentration at 298.15 K Represented by Pitzer's Ion-Interaction Equations. *J. Phys. Chem. Ref. Data* **25**, 663-689.
- Krumgalz B. S., Pogorelsky R. and Pitzer K. S. (1996b) Erratum: Volumetric Properties of Single Aqueous Electrolytes from Zero to Saturation Concentration at 298.15 K Represented by Pitzer's Ion-Interaction Equations. *J. Phys. Chem. Ref. Data* **25**, 1389.
- Krumgalz B. S., Pogorelsky R., Sokolov A. and Pitzer K. S. (2000) Volumetric Ion Interaction Parameters for Single-Solute Aqueous Electrolyte Solutions at Various Temperatures. *J. Phys. Chem. Ref. Data* **29**, 1123-1139.

- Kunz W. and Neueder R. (2010) An Attempt of a General Overview. In *Specific Ion Effects* (ed. W. Kunz). World Scientific Publ. Co. Pte. Ltd., Singapore, pp. 3-54.
- Kurnakov N. and Zemczny S. F. (1924) Equilibria in the Reciprocal System Sodium Chloride-Magnesium Sulfate with Particular Reference to Natural Brines. *Z. Anorg. Allg. Chem.* **140**, 149-182.
- Lamperski S. and Pluciennik M. (2011) Individual Activity Coefficients of a Solvent Primitive Model Electrolyte Calculated from the Inverse Grand-Canonical Monte Carlo Simulation and MSA Theory, *Mol. Phys.* **109**, 49-54.
- Lanier R. D. (1965) Activity Coefficients of Sodium Chloride in Aqueous Three-component Solutions by Cation-sensitive Glass Electrodes. *J. Phys. Chem.* **69**, 3992-3998.
- Li Z. and Pitzer K. S. (1996) Thermodynamics of Aqueous KOH over the Full Range to Saturation and to 573 K. *J. Solution Chem.* **25**, 813-823.
- Li M.-Y., Wang L.-S. and Gmehling J. (2011) Thermodynamics of Phase Equilibria in Aqueous Strong Electrolyte Systems, *Ind. Eng. Chem. Res.* **50**, 3621-3631.
- Li Y., Song P., Xia S., Li W. C. and Gao S.-y. (2006) Solubility Prediction for the HCl-MgCl₂-H₂O System at 40 °C and Solubility Equilibrium Constant Calculation for HCl-MgCl₂·7H₂O at 40 °C. *CALPHAD: Comput. Coupling Phase Diagrams Thermochem.* **30**, 61-64.
- Li Z., Deng T. and Liao M. (2010) Solid-liquid metastable equilibria in the quaternary system Li₂SO₄ + MgSO₄ + Na₂SO₄ + H₂O at T = 263.15K. *Fluid Phase Equilib.* **293**, 42-46.
- Lin Y., ten Kate A., Mooijer M., Delgado J., Fosbol P. L. and Thomsen K. (2010) Comparison of Activity Coefficient Models for Electrolyte Systems. *AIChE J.* **56**, 1334-1351.
- Linke W. F. (1958) *Solubilities, Inorganic and Metal-Organic Compounds, Vol. 1*, American Chemical Society, Washington DC, U.S.A.
- Linke W. F. (1965) *Solubilities, Inorganic and Metal-Organic Compounds, Vol. 2*, American Chemical Society, Washington DC, U.S.A.
- Loehe J. R. and Donohue M. D. (1997) Recent Advances in Modeling Thermodynamic Properties of Aqueous Strong Electrolyte Systems. *AIChE J.* **43**, 180-195.
- Majer V., Gates J. A., Inglese A. and Wood R. H. (1988) Volumetric Properties of Aqueous NaCl Solutions from 0.0025 to 5.0 mol.kg⁻¹, 323 to 600 K and 0.1 to 40 MPa, *J. Chem. Thermodyn.* **20**, 949-968.
- Marion G. M. and Farren R. E. (1999) Mineral Solubilities in the Na-K-Mg-Ca-Cl-SO₄-H₂O System: A Re-evaluation of the Sulfate Chemistry in the Spencer-Møller-Weare Model, *Geochim. Cosmochim. Acta* **63**, 1305-1318.
- Marshall S. L., May P. M. and Hefter G. T. (1995) Least-Squares Analysis of Osmotic Coefficient Data at 25 °C According to Pitzer's Equation. 1. 1:1 Electrolytes. *J. Chem. Eng. Data* **40**, 1041-1052.
- May P. M. and Murray K. (1991) JESS, A Joint Expert Speciation System - I. Raison d'Être. *Talanta* **38**, 1409-1417.
- May P. M. and Murray K. (2001) Database of Chemical Reactions Designed to Achieve Thermodynamic Consistency Automatically. *J. Chem. Eng. Data* **46**, 1035-1040.
- May P. M., Rowland D., Königsberger E. and Hefter G. (2010) JESS, a Joint Expert Speciation System - IV: A Large Database of Aqueous Solution Physicochemical Properties with an Automatic Means of Achieving Thermodynamic Consistency. *Talanta* **81**, 142-148.
- May P. M., Rowland D., Hefter G. and Königsberger E. (2011) A Generic and Updatable Pitzer Characterization of Aqueous Binary Electrolyte Solutions at 1 bar and 25 °C. *J. Chem. Eng. Data* **56**, 5066-5077.
- Meinrath G. (2002) Extended Traceability of pH: an Evaluation of the Role of Pitzer's Equations. *Anal. Bioanal. Chem.* **374**, 796-805.

- Millero F. J. and Pierrot D. (1998) A Chemical Equilibrium Model for Natural Waters. *Aquat. Geochem.* **4**, 153-199.
- Oakes C. S., Felmy A. R. and Sterner S. M. (2000) Thermodynamic Properties of Aqueous Calcium Nitrate $\{Ca(NO_3)_2\}$ to the Temperature 373 K including New Enthalpy of Dilution Data. *J. Chem. Thermodyn.* **32**, 29-54.
- Oakes C. S., Rard J. A. and Archer D. G. (2004) Enthalpies of Dilution of $NdCl_3(aq)$ at Temperatures from 297.89 K to 372.08 K and an Extended Pitzer Ion-Interaction Model for the $NdCl_3 + H_2O$ System. *J. Chem. Eng. Data* **49**, 313-325.
- Obšil M., Majer V., Hefter G. T. and Hynek V. (1997) Volumes of $MgCl_2(aq)$ at Temperatures from 298 K to 623 K and Pressures up to 30 MPa. *J. Chem. Thermodyn.* **29**, 575-593.
- Pabalan R. T. and Pitzer K. S. (1987a) Thermodynamics of $NaOH(aq)$ in Hydrothermal Solutions. *Geochim. Cosmochim. Acta* **51**, 829-837.
- Pabalan R. T. and Pitzer K. S. (1987b) Thermodynamics of Concentrated Electrolyte Mixtures and the Prediction of Mineral Solubilities to High Temperatures for Mixtures in the System $Na-K-Mg-Cl-SO_4-OH-H_2O$. *Geochim. Cosmochim. Acta* **51**, 2429-2443.
- Pabalan R. T. and Pitzer K. S. (1988) Apparent Molar Heat Capacity and Other Thermodynamic Properties of Aqueous KCl Solutions to High Temperatures and Pressures. *J. Chem. Eng. Data* **33**, 354-362.
- Pabalan R. T. and Pitzer K. S. (1991) *Activity Coefficients in Electrolyte Solutions*, second ed. (ed. K. S. Pitzer). CRC Press, Boca Raton, Florida, USA, pp. 435-490.
- Palmer D. A., Archer D. G. and Rard J. A. (2002) Isopiestic Determination of the Osmotic and Activity Coefficients of $K_2SO_4(aq)$ at the Temperatures 298.15 and 323.15 K and Revision of the Thermodynamic Properties of the $K_2SO_4 + H_2O$ System. *J. Chem. Eng. Data* **47**, 1425-1431.
- Papaiconomou N., Simonin J.-P., Bernard O. and Kunz W. (2002) MSA-NRTL Model for the Description of the Thermodynamic Properties of Electrolyte Solutions. *Phys. Chem. Chem. Phys.* **4**, 4435-4443.
- Parkhurst D. L. and Appelo C. A. J. (1999) Water-Resources Investigations Rep. 99-4259, User's Guide to PHREEQC (Version 2) - A Computer Program for Speciation, Batch-reaction, One-dimensional Transport, and Inverse Geochemical Calculations, U.S. Dept. Interior, U.S. Geol. Surv., Denver, Colorado, U.S.A.
- Partanen J.I. (2012) Re-evaluation of the Thermodynamic Activity Quantities in Pure Aqueous Solutions of Chlorate, Perchlorate, and Bromate Salts of Lithium, Sodium or Potassium Ions at 298.15 K. *J. Solution Chem.* **41**, 271-293.
- Pérez-Villaseñor F., Iglesias-Silva G. A. and Hall K. R. (2002) Osmotic and Activity Coefficients: Using a Modified Pitzer Equation for Strong Electrolytes 1:1 and 1:2 at 298.15 K. *Ind. Eng. Chem. Res.*, **41**, 1031-1037.
- Perron G., Desnoyers J. E. and Millero F. J. (1974) Apparent Molal Volumes and Heat Capacities of Alkaline Earth Chlorides in Water at 25 °C. *Can. J. Chem.* **52**, 3738-3741.
- Perron G., Roux A. and Desnoyers J. E. (1981) Heat Capacities and Volumes of $NaCl$, $MgCl_2$, $CaCl_2$, and $NiCl_2$ up to 6 molal in Water. *Can. J. Chem.* **59**, 3049-3054.
- Petersen S. and Hack K. (2007) The Thermochemistry Library ChemApp and Its Applications. *Int. J. Mater. Res* **98**, 935-945.
- Phutela R. C. and Pitzer K. S. (1983) Thermodynamics of Aqueous Calcium Chloride. *J. Solution Chem.* **12**, 201-207.
- Phutela R. C. and Pitzer K. S. (1986) Densities and Apparent Molar Volumes of Aqueous Magnesium Sulfate and Sodium Sulfate to 473 K and 100 Bar. *J. Chem. Eng. Data* **31**, 320-327.
- Phutela R. C., Pitzer K. S. and Saluja P. P. S. (1987) Thermodynamics of Aqueous Magnesium Chloride, Calcium Chloride, and Strontium Chloride at Elevated Temperatures. *J. Chem. Eng. Data* **32**, 76-80.
- Pitzer K. S. (1973) Thermodynamics of Electrolytes. I. Theoretical Basis and General Equations. *J. Phys. Chem.* **77**, 268-277.
- Pitzer K. S. (1975) Thermodynamics of Electrolytes. V. Effects of Higher-Order Electrostatic Terms. *J. Solution Chem.* **4**, 249-265.

Pitzer K. S. (1986) Theoretical Considerations of Solubility with Emphasis on Mixed Aqueous Electrolytes. *Pure Appl. Chem.* **58**, 1599-1610.

Pitzer K. S. (1991) Ion Interaction Approach: Theory and Data Correlation. In *Activity Coefficients in Electrolyte Solutions*, second ed. (ed. K. S. Pitzer). CRC Press, Boca Raton, Florida, USA, pp. 75-153.

Pitzer K. S. and Mayorga G. (1973) Thermodynamics of Electrolytes. II. Activity and Osmotic Coefficients for Strong Electrolytes with One or Both Ions Univalent. *J. Phys. Chem.* **77**, 2300-2308.

Pitzer K. S. and Simonson J. M. (1986) Thermodynamics of Multicomponent, Miscible, Ionic Systems: Theory and Equations. *J. Phys. Chem.* **90**, 3005-3009.

Pitzer K. S., Peiper J. C. and Busey R. H. (1984) Thermodynamic Properties of Aqueous Sodium Chloride Solutions. *J. Phys. Chem. Ref. Data* **13**, 1-102.

Pitzer K. S., Wang P., Rard J. A. and Clegg S. L. (1999) Thermodynamics of Electrolytes. 13. Ionic Strength Dependence of Higher-Order Terms; Equations for CaCl_2 and MgCl_2 . *J. Solution Chem.* **28**, 265-282.

Platford R. F. (1968) Isopiestic Measurements on the System Water-Sodium Chloride-Magnesium Chloride at 25 °C. *J. Phys. Chem.* **72**, 4053-4057.

Prausnitz J. M., Lichtenthaler R. N. and de Azevedo E. G. (1999) *Molecular Thermodynamics of Fluid-Phase Equilibria*, Prentice Hall PTR, New Jersey, U.S.A.

Press W. H., Teukolsky S. A., Vetterling W. T. and Flannery B. P. (1992) *Numerical Recipes in FORTRAN*, second ed., Cambridge Univ. Press, Cambridge, U.K.

Puchkov L. V., Styazhkin P. S. and Federov M. K. (1976) Specific Heat Capacities of Aqueous NaCl Solutions at Temperatures up to 350 °C and Pressures up to 1000 kg/cm². *J. Appl. Chem. (USSR)* **49**, 1268-1271.

Puigdomenech I., Rard J. A., Plyasunov A. V. and Grenthe I. (1997) Temperature Corrections to Thermodynamic Data and Enthalpy Calculations. In *Modelling in Aquatic Chemistry* (eds. I. Grenthe and I. Puigdomenech). Nuclear Energy Agency, OECD, Paris, France, pp. 427-493.

Rard J. A. and Archer D. G. (1995) Isopiestic Investigation of the Osmotic and Activity Coefficients of Aqueous NaBr and the Solubility of $\text{NaBr}\cdot 2\text{H}_2\text{O}(\text{cr})$ at 298.15 K: Thermodynamic Properties of the $\text{NaBr} + \text{H}_2\text{O}$ System over Wide Ranges of Temperature and Pressure, *J. Chem. Eng. Data* **40**, 170-185.

Rard J. A. and Miller D. G. (1981) Isopiestic Determination of the Osmotic and Activity Coefficients of Aqueous MgCl_2 Solutions at 25 °C. *J. Chem. Eng. Data* **26**, 38-43

Rard J. A. and Miller D. G. (1987) Isopiestic Determination of the Osmotic and Activity Coefficients of Aqueous Mixtures of Sodium Chloride and Magnesium Chloride at 25 °C. *J. Chem. Eng. Data* **32**, 85-92.

Rard J. A. and Spedding F. H. (1977) Isopiestic Determination of the Osmotic Coefficients of Aqueous CaCl_2 Solutions at 25 °C. *J. Chem. Eng. Data* **22**, 56-58.

Rard J. A. and Wijesinghe A. M. (2003) Conversion of Parameters between Different Variants of Pitzer's Ion-interaction Model, both with and without Ionic Strength Dependent Higher-order Terms. *J. Chem. Thermodyn.* **35**, 439-473.

Rard J. A. and Wijesinghe A. M. (2008) Conversion of Parameters Among Variants of Scatchard's Neutral-Electrolyte Model for Electrolyte Mixtures that Have Different Numbers of Mixing Terms. *J. Solution Chem.* **37**, 1149-1185.

Reddy S. T. and Lewis A. E. (2006) Water Recovery and Salt Recovery from Brine Solutions. Proc. 13th Int. Workshop Industrial Crystallization Univ. Technol., Delft, The Netherlands, pp. 328.

Redlich O. and Meyer D. M. (1964) The Molal Volumes of Electrolytes, *Chem. Rev.* **64**, 221-227.

Robinson R. A. and Stokes R. H. (1970) *Electrolyte Solutions*, second ed. revised, Butterworth and Co., London.

Rogers P. S. Z. and Pitzer K. S. (1982) Volumetric Properties of Aqueous Sodium Chloride Solutions. *J. Phys. Chem. Ref. Data* **11**, 15-81.

- Rowland D. and May P. M. (2010) JESS, a Joint Expert Speciation System - V: Approaching Thermodynamic Property Prediction for Multicomponent Concentrated Aqueous Electrolyte Solutions. *Talanta* **81**, 149-155.
- Rowland D. and May P. M. (2012) An Investigation of Zdanovskii's Rule for Predicting the Water Activity of Multicomponent Aqueous Strong Electrolyte Solutions, *J. Chem. Eng. Data* **57**, 2589-2602.
- Rowland D. and May P. M. (2013) A Pitzer-based Characterization of Aqueous Magnesium Chloride, Calcium Chloride and Potassium Iodide Solution Densities to High Temperature and Pressure, *Fluid Phase Equilib.* **338**, 54-62.
- Rowland D. and May P.M. (2014) Thermodynamics of strong aqueous electrolyte solutions at $t = 25\text{ }^{\circ}\text{C}$ described by the Hückel equations. *J. Chem. Eng. Data* **59**, 2030-2039.
- Saluja P. P. S. and LeBlanc J. C. (1987) Apparent Molar Heat Capacities and Volumes of Aqueous Solutions of MgCl_2 , CaCl_2 , and SrCl_2 at Elevated Temperatures. *J. Chem. Eng. Data* **32**, 72-76.
- Saluja P. P. S., Jobe D. J., LeBlanc J. C. and Lemire R. J. (1995) Apparent Molar Heat Capacities and Volumes of Mixed Electrolytes [$\text{NaCl}(\text{aq}) + \text{CaCl}_2(\text{aq})$], [$\text{NaCl}(\text{aq}) + \text{MgCl}_2(\text{aq})$], and [$\text{CaCl}_2(\text{aq}) + \text{MgCl}_2(\text{aq})$]. *J. Chem. Eng. Data* **40**, 398-406.
- Schrödle S., Königsberger E., May P. M. and Hefter G. (2008) Heat Capacities of Aqueous Solutions of Sodium Hydroxide and Water Ionization up to $300\text{ }^{\circ}\text{C}$ at 10 MPa. *Geochim. Cosmochim. Acta* **72**, 3124-3128
- Schrödle S., Königsberger E., May P. M. and Hefter G. (2010) Heat Capacities of Aqueous Sodium Hydroxide / Aluminate Mixtures and Prediction of the Solubility Constant of Boehmite up to $300\text{ }^{\circ}\text{C}$. *Geochim. Cosmochim. Acta* **74**, 2368-2379.
- Simonson J. M., Mesmer R. E. and Rogers P. S. Z. (1989) The Enthalpy of Dilution and Apparent Molar Heat Capacity of $\text{NaOH}(\text{aq})$ to 523 K and 40 MPa. *J. Chem. Thermodyn.* **21**, 561-584.
- Simonson J. M., Holmes H. F., Busey R. H., Mesmer R. E., Archer D. G. and Wood R. H. (1990) Modeling of the Thermodynamics of Electrolyte Solutions to High Temperatures Including Ion Association: Application to Hydrochloric Acid. *J. Phys. Chem.* **94**, 7675-7681.
- Song Y. and Chen C.-C. (2009) Symmetric Electrolyte Nonrandom Two-Liquid Activity Coefficient Model. *Ind. Eng. Chem. Res.* **48**, 7788-7797.
- Spitzer P., Fisticaro P., Meinrath G. and Stoica D. (2011) pH Buffer Assessment and Pitzer's Equations. *Accred. Qual. Assur.* **16**, 191-198.
- Sun R. and Dubessy J. (2012) Prediction of Vapor-Liquid Equilibrium and PVTx Properties of Geological Fluid System with SAFT-LJ EOS Including Multi-Polar Contribution. Part II: Application to $\text{H}_2\text{O}-\text{NaCl}$ and $\text{CO}_2-\text{H}_2\text{O}-\text{NaCl}$ System, *Geochim. Cosmochim. Acta* **88**, 130-145.
- Takegami S. (1921) Reciprocal Salt Pairs: $\text{Na}_2\text{Cl}_2 + \text{MgSO}_4$ and $\text{Na}_2\text{SO}_4 + \text{MgCl}_2$ at $25\text{ }^{\circ}\text{C}$. *Memoirs College Sci. Kyoto Imperial Univ.* **4**, 317-342.
- Tian P., Ning P., Cao H. and Li Z. (2012) Determination and Modeling of Solubility for $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} - \text{NH}_4^+ - \text{Cl}^- - \text{SO}_4^{2-} - \text{NO}_3^- - \text{H}_2\text{O}$ System, *J. Chem. Eng. Data* **57**, 3664-3671.
- Triolo R., Grigera J. R. and Blum L. (1976) Simple Electrolytes in the Mean Spherical Approximation. *J. Phys. Chem.* **80**, 1858-1861.
- van Gaans P. F. M. (1991) Extracting Robust and Physically Meaningful Pitzer Parameters for Thermodynamic Properties of Electrolytes from Experimental Data. Ridge Regression as an Aid to the Problem of Intercorrelation, *J. Solution Chem.* **20**, 703-730.
- Voigt W. (2011) Chemistry of Salts in Aqueous Solutions: Applications, Experiments, and Theory. *Pure Appl. Chem.* **83**, 1015-1030.
- Wagman D. D., Evans W. H., Parker V. B., Schumm R. H., Halow I., Bailey S. M., Churney K. L. and Nuttall R. L. (1982) *J. Phys. Chem. Ref. Data* **11**, Suppl. 2.

- Wang P., Pitzer K. S. and Simonson J. M. (1998) Thermodynamic Properties of Aqueous Magnesium Chloride Solutions from 250 to 600 K and to 100 MPa. *J. Phys. Chem. Ref. Data* **27**, 971-991.
- Wang P., Anderko A. and Young R. D. (2002) A Speciation-based Model for Mixed-Solvent Electrolyte Systems. *Fluid Phase Equilib.* **203**, 141-176.
- Wang P., Springer R. D., Anderko A. and Young R. D. (2004) Modeling Phase Equilibria and Speciation in Mixed-Solvent Electrolyte Systems. *Fluid Phase Equilib.* **222-223**, 11-17.
- Waters J.F. and Millero F.J. (2013) The Free Proton Concentration Scale for Seawater pH. *Marine Chemistry* **149**, 8-22.
- White D. E., Gates J. A., Tillet D. M. and Wood R. H. (1988) Heat Capacity of Aqueous MgCl_2 from 349 to 598 K. *J. Chem. Eng. Data* **33**, 485-490.
- Wijesinghe A. M. and Rard J. A. (2005) Conversion and Optimization of the Parameters from an Extended Form of the Ion-interaction Model for $\text{Ca}(\text{NO}_3)_2(\text{aq})$ and $\text{NaNO}_3(\text{aq})$ to those of the Standard Pitzer Model, and an Assessment of the Accuracy of the Parameter Temperature Representations. *J. Chem. Thermodyn.* **37**, 1196-1218.
- Wolery T. J. (1992) EQ3NR User's Guide, Pt. I, Version 7.0, EQ3/6, A Software Package for Geochemical Modeling of Aqueous Systems: Package Overview and Installation Guide Report UCRL-MA-110662, Pt I, Lawrence Livermore National Laboratory, Livermore, U.S.A.
- Wood J. R. (1976) Thermodynamics of Brine-salt Equilibria. II. The System $\text{NaCl-KCl-H}_2\text{O}$ from 0 to 200 °C. *Geochim. Cosmochim. Acta* **40**, 1211-1220.
- Wu Y. C., Rush R. M. and Scatchard G. (1968) Osmotic and Activity Coefficients for Binary Mixtures of Sodium Chloride, Sodium Sulfate, Magnesium Sulfate, and Magnesium Chloride in Water at 25 °C. I. Isopiestic Measurements on the Four Systems with Common Ions. *J. Phys. Chem.* **72**, 4048-4053.
- Xiao T. and Song X. (2011) A Molecular Debye-Hückel Theory and Its Applications to Electrolyte Solutions, *J. Chem. Phys.* **135**, 104104-(1-14).
- Yang J.-M. and Li J. (2010) Solubility in the Ternary System $\text{LiCl} + \text{MgCl}_2 + \text{H}_2\text{O}$ at 60 and 75 °C. *Russ. J. Phys. Chem.* **84**, 1169-1173.