Thermodynamically-robust Pitzer equations for volumetric properties of electrolyte solutions

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Abstract

Pitzer equations are widely employed to correlate and predict the volumetric properties of aqueous electrolyte solutions over broad ranges of pressure and temperature. However, the currently-used pressure and temperature terms are empirical and tend to violate known thermodynamic behaviour. Three functional constraints have been identified that overcome this problem.

Pitzer equations are the most accurate and commonly-used framework for modelling the thermodynamics of high ionic-strength solutions relevant in geochemical, industrial, nuclear waste repository and atmospheric applications [1]. They are also the preferred thermodynamic framework for the upcoming Scientific Committee on Oceanic Research project on chemical speciation in seawater (Working Group 145) which will model $CO_2(g)$ uptake by the ocean (including effects of acidification and of rising global temperatures on trace metal equilibria). It is even hoped that Pitzer equations will be included in the IUPAC Standard for pH measurement [2]. Together, these varied applications span wide ranges of temperature and pressure but, since no adequate fundamental theory exists [1], the dependence of the Pitzer equations on temperature and pressure has had to be purely empirical [3], with problematic consequences.

The effect of pressure on the density of aqueous electrolyte solutions is typically smooth, regular and always increasing (Figure SI1), the last of these effects being expressed mathematically as:

$$(\partial \rho / \partial p)_{t,m} > 0 \quad (1).$$

Surprisingly, many published models for density violate this simple thermodynamic relationship. Such failures include several based on the Pitzer equations, for example, the model for KCl(aq) by Pabalan and Pitzer [4] (as described in ref [6]) and the models for $MgCl_2(aq)$ and $SrCl_2(aq)$ by Holmes *et al.* [5] (Figure SI2). A method that guarantees thermodynamic rigour, reduces the need for time-consuming manual inspection of the model results and yields more robust predictions outside the range of available experimental measurements is thus urgently needed. In particular, reliable solution density models are essential for accurate predictions of all thermodynamic behaviour, *e.g.* solubility and phase equilibria, at high pressure [7].

This is not a straightforward problem due primarily to its multi-dimensional nature. It transpires that eq 1 is a necessary but not sufficient condition. None of the published methods for optimising Pitzer parameters appears to guarantee reliable predictions, depending instead on tedious manual searching of the whole space to detect and find ways to repair aberrant behaviour. This concern applies equally to the ordinary least-squares methods, either linear [8] or non-linear (*e.g.* ref [9]), and to the more sophisticated approaches such as ridge regression [10] and Bayesian analysis [11].

To find ways of constraining the optimization more effectively, volumetric property values for well-characterized electrolyte solutions were analysed in detail using the current JESS database of physicochemical property values [12]. Volumetric quantities for over 300 binary electrolyte solutions were considered. First, it emerged that apparent molar volumes, V_ϕ, of binary aqueous electrolyte solutions – without known exception – increase with pressure over wide ranges of temperature and concentration (Figure 1) *i.e.* $(\partial V_\phi / \partial p)_{t,m} > 0$. This is all the more interesting because it is somewhat counter-intuitive, but (probably) reflects that the solvent is more compressible than the solute. Second, the apparent molar volume also always follows the relation $(\partial^2 V_\phi / \partial t^2)_{p,m} < 0$ for 'structure-breaking' aqueous electrolytes [13; 14, fig.

7a; 15, figs. 9-10]. Third, the extrapolation of apparent molar volumes to infinite dilution must be in accord with Debye-Hückel theory, requiring that $(\partial V_\phi/\partial m)_{p,t} > 0$ at low m.

The identified constraints were accordingly included in the parameter optimization scheme by discretization at a series of nodes (p_i, t_j, m_k) designed to span approximately-evenly the multidimensional space (Table 1), yielding the following linear inequalities:

$$\rho(p_i + \Delta p, t_j, m_k) > \rho(p_i, t_j, m_k)$$
$$V_\phi(p_i + \Delta p, t_j, m_k) > V_\phi(p_i, t_j, m_k)$$
$$2V_\phi(p_i, t_j, m_k) > V_\phi(p_i, t_j + \Delta t, m_k) + V_\phi(p_i, t_j - \Delta t, m_k)$$
$$V_\phi(p_i, t_j, m_k + \Delta m) > V_\phi(p_i, t_j, m_k)$$

where, in this work, $\Delta p = 50$ bar, $\Delta t = 0.5$ °C and $\Delta m = 0.1$ mol kg^{-1}.

Table 1. Node locations used to constrain the optimization of the Pitzer parameters for volume. Each node comprises a (p, t, m) triplet. Models 1 and 2 were each optimized using 1000 nodes.

p /bar [a]	t /°C	m /mol kg^{-1} [b,c]
1.00	0	0
375.75	27.27	0.375
750.50	54.54	1.500
1125.25	81.81	3.375
1500.00	109.09	6.000
	136.36	
	163.64	
	190.91	
	218.18	
	245.45	
	272.73	
	300.00	

[a] Nodes with $p = 1.00$ bar only for $t < 100$ °C. [b] $(\partial\rho/\partial p)_{t,m}$ only constrained for $m > 1.0$ mol kg^{-1}. [c] For electrolyte solutions such as HClO$_4$(aq), the relation $V_\phi(p_i, t_j, m_k + \Delta m) > V_\phi(p_i, t_j, m_k)$ might be valid only to $m \sim 1.0$ mol kg^{-1}.

The exact node locations are not crucial to the outcome of the optimization, nor the values of Δp, Δt and Δm, these latter selected to yield sufficiently different calculated property values on the left and right sides of the inequalities.

Least-squares optimization subject to linear inequalities is Problem LSI of Lawson and Hanson [18]. The JESS software suite (ref [19] and references therein) contains Fortran 77 optimization routines that follow those in the SLATEC Common Mathematical Library, Version 4.1 (www.netlib.org/slatec/). The computations were verified against the results of subroutine *lsqlin* from MATLAB [20]. This set of constraints was found to be satisfactory for a variety of uni-univalent electrolytes including all the alkali metal halides and nitrates.

KCl(aq) serves to illustrate the advantages of the proposed approach (in contrast to the difficulties experienced by Pabalan and Pitzer [4] for this significant system). Three separate optimizations of volumetric property values for (0 to 300) °C and (0 to 6) mol kg^{-1} are compared: Model 1 – in which all available data from (1 to 1500) bar are optimized subject to all constraints; Model 2 – in which only data from (1 to 200) bar are optimized while subject to all constraints; and Model 3 – in which the data from (1 to 200) bar were optimized without constraints. The optimized parameter values for each model are given in Table SI1 and the results of Models 1–3 are compared graphically in Figure 2.

It is evident that Model 1 agrees well with all of the most-accurate data from the literature and that Model 2, despite being based on fewer data, compares favourably with Model 1. Model 2 even gives physically-plausible extrapolations for pressure and concentration and it only deviates from the high-pressure (> 200 bar) data to an extent which is generally on the order of experimental uncertainty (Figures 2b-d). On the other hand, Model 3 (optimized against the same dataset as Model 2) gives reasonable agreement with the data at 200 bar but without the identified constraints it fluctuates wildly in its extrapolation to infinite dilution (Figure 2a) and it has very poor predictive capability at pressures outside the range of optimized data, exhibiting extremely large residuals (Figures 2b,c) and unrealistic physical trends (Figures 2c,d).

Similar results were found with the other uni-univalent electrolyte solutions suggesting that the method is generally applicable. However, the ranges over which the constraints can be applied may need to be tailored to specific electrolyte solutions, especially those of higher valency. This issue is currently being investigated.

Conclusions

Notwithstanding their popularity, current implementations of the Pitzer equations are unstable at non-ambient temperatures and pressures due to their empirical nature. By enforcing physically-realistic behaviour on such models in the form of three novel constraints, electrolyte solution properties can be predicted with considerably greater confidence.

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