

Thermodynamics of strong aqueous electrolyte solutions at $t = 25\text{ }^{\circ}\text{C}$ described by the Hückel equations

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Abstract

A theoretical framework based on the Hückel equation for activity coefficients has been developed and the physicochemical properties of 57 binary strong electrolyte solutions at $t = 25\text{ }^{\circ}\text{C}$ have been correlated. These properties include the activity and osmotic coefficients, apparent molar relative enthalpies, apparent molar heat capacities and apparent molar volumes. The correlating equations agree well with property values from the literature up to concentrations of $m = 2.0\text{ mol kg}^{-1}$ for 1:1 electrolytes and $m = 0.5\text{ mol kg}^{-1}$ for 2:1, 1:2 and 3:1 electrolytes. Certain electrolytes could not be satisfactorily represented, including polyprotic acids, 2:2 electrolytes and the zinc and cadmium halides. In addition to quantifying Hückel equation parameters that can be used for the convenient calculation of physicochemical property values, the results provide a benchmark against which other theoretical frameworks with few adjustable parameters can be compared.

KEYWORDS: Hückel equation, aqueous electrolytes, activity coefficients, apparent molar relative enthalpy, apparent molar volume

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Introduction

Although many theoretical frameworks for modelling aqueous electrolyte solutions have been proposed and developed more recently (e.g. the mean spherical approximation^{1,2}), empirical extensions of Debye-Hückel theory remain popular due to their relative simplicity and because calculated values can be compared directly with experimental data. Equations containing arbitrary numbers of extended terms in increasing powers of m (the solute molality) have been used to review critically the activity and osmotic coefficients of some 1:1³ and 2:1⁴⁻⁶ aqueous electrolyte solutions at $t = 25$ °C. Equations with one or two extended terms have also been investigated for selected electrolyte solutions by Partanen and co-workers (e.g.⁷⁻¹⁰).

Absent from these works are properties related to the derivatives of the equations for the activity and osmotic coefficients with respect to temperature and pressure, including for example, the enthalpy, heat capacity and volume. Equations for these thermodynamic properties appeared in the literature soon after it was accepted that the Debye-Hückel theory described adequately activity coefficient data for binary aqueous strong electrolyte solutions.¹¹ However, the equations were laborious¹² and were seldom used.¹³ To the present authors' knowledge, a systematic study of the ability of a simple and general extension of Debye-Hückel theory to correlate multiple thermodynamic properties beyond activity and osmotic coefficients of aqueous electrolyte solutions has never appeared in the literature. Filling this gap motivates the present work. This is important because, with few parameters, the Hückel equations have less empirical flexibility than, say, their more popular Pitzer equation counterparts.

A thermodynamically-consistent framework is developed to correlate simultaneously data for activity coefficients, osmotic coefficients, apparent relative molar enthalpies, apparent molar heat capacities and apparent molar volumes. Best-fitting parameters valid at $t = 25$ °C are reported for 57 aqueous binary electrolyte solutions.

Theory

The Debye-Hückel formula for the activity coefficient of a single electrolyte in aqueous solution is¹⁵

$$\ln \gamma_{\pm} = -3A_{\phi}|z_+z_-|\sqrt{I}/(1 + Ba\sqrt{I}) \quad (1)$$

where A_{ϕ} is the Debye-Hückel coefficient, z_+ and z_- are the algebraic charges on the cation and anion respectively, $I = 0.5\nu|z_+z_-|m$ is the stoichiometric ionic strength of the solution expressed in molal concentration units, ν is the number of moles of ions in solution when one mole of the electrolyte completely dissociates, $B\sqrt{I}$ is a fundamental quantity of interionic attraction theory and a is the ‘distance of closest approach’ of the ions.¹⁴ From theory, the temperature variation of B is proportional to $(\epsilon T)^{-1/2}$, where ϵ is the dielectric permittivity of the solvent.¹⁴ In early works the parameter a was taken independent of temperature¹² and pressure.¹¹ However, when compared against more accurate data, the need for temperature and pressure dependence became apparent.^{13,16,17} Since both B and a may vary with temperature and pressure, eq 1 can be simplified using the definition $\dot{a} \equiv Ba$.

A simple empirical extension to eq 1¹⁸ was proposed by Hückel:¹⁹

$$\ln \gamma_{\pm} = -3A_{\phi}|z_+z_-|\sqrt{I}\eta(\dot{a}\sqrt{I}) + Cm \quad (2)$$

where $\eta(x) = 1/(1+x)$. Only two adjustable parameters, \dot{a} and C , are required for each electrolyte. Various forms of this equation have appeared in the chemical literature. For example, setting \dot{a} equal to 1 or 1.5 $(\text{kg mol}^{-1})^{1/2}$ gives Guggenheim’s equation²⁰ or the Specific Ion-interaction Theory (SIT) equation²¹ respectively.

The consistent equation for the osmotic coefficient is obtained by solving the Gibbs-Duhem relation and has the form

$$\phi = 1 - A_{\phi}|z_+z_-|\sqrt{I}\sigma(\dot{a}\sqrt{I}) + Cm/2 \quad (3)$$

where $\sigma(x) = 3[1+x - (1+x)^{-1} - 2\ln(1+x)]/x^3$. Substituting eqs 2 and 3 into the relation for

the excess Gibbs energy, G^{ex} ,²² gives

$$G^{\text{ex}}/w_w = \nu mRT[A_\phi|z_+z_-|\sqrt{I}(\sigma - 3\eta) + Cm/2] \quad (4)$$

where w_w is the mass of solvent in kilograms, $R = 8.314 \text{ J(K mol)}^{-1}$ is the gas constant and T is the temperature in Kelvin. Appropriate differentiation of the Gibbs energy yields the apparent molar relative enthalpy ${}^\phi L$, apparent molar heat capacity ${}^\phi C_p$ and the apparent molar volume ${}^\phi V$ ²²

$${}^\phi L = -\nu|z_+z_-|\sqrt{I}f^L - \frac{\nu RT^2}{2} \frac{\partial C}{\partial T} m \quad (5)$$

$${}^\phi C_p = {}^\phi C_p^\circ - \nu|z_+z_-|\sqrt{I}f^J - \frac{\nu RT^2}{2} \left(\frac{2}{T} \frac{\partial C}{\partial T} + \frac{\partial^2 C}{\partial T^2} \right) m \quad (6)$$

$${}^\phi V = {}^\phi V^\circ - \nu|z_+z_-|\sqrt{I}f^V + \frac{\nu RT}{2} \frac{\partial C}{\partial p} m \quad (7)$$

where the f^X ($X \in \{L, J, V\}$) are given by

$$f^L = \left[\frac{A_L}{4}(\sigma - 3\eta) + A_\phi RT^2 \frac{\partial}{\partial T}(\sigma - 3\eta) \right] \quad (8)$$

$$f^J = \left\{ \frac{1}{4} \left[A_J(\sigma - 3\eta) + 2A_L \frac{\partial}{\partial T}(\sigma - 3\eta) \right] \right. \quad (9)$$

$$\left. + A_\phi RT^2 \left[\frac{2}{T} \frac{\partial}{\partial T}(\sigma - 3\eta) + \frac{\partial^2}{\partial T^2}(\sigma - 3\eta) \right] \right\} \quad (10)$$

$$f^V = \left[-\frac{A_V}{4}(\sigma - 3\eta) + A_\phi RT \frac{\partial}{\partial p}(\sigma - 3\eta) \right] \quad (11)$$

and A_L , A_J and A_V are the Debye-Hückel coefficients for the enthalpy, heat capacity and volume respectively.

The derivatives of $(\sigma - 3\eta)$ with respect to T and p (in MPa) are given by

$$\frac{\partial}{\partial T}(\sigma - 3\eta) = \sqrt{I} \frac{\partial \dot{a}}{\partial T} \left(\frac{\partial \sigma}{\partial x} - 3 \frac{\partial \eta}{\partial x} \right) \quad (12)$$

$$\frac{\partial^2}{\partial T^2}(\sigma - 3\eta) = \sqrt{I} \frac{\partial^2 \dot{a}}{\partial T^2} \left(\frac{\partial \sigma}{\partial x} - 3 \frac{\partial \eta}{\partial x} \right) + \left(\sqrt{I} \frac{\partial \dot{a}}{\partial T} \right)^2 \left(\frac{\partial^2 \sigma}{\partial x^2} - 3 \frac{\partial^2 \eta}{\partial x^2} \right) \quad (13)$$

$$\frac{\partial}{\partial p}(\sigma - 3\eta) = \sqrt{I} \frac{\partial \dot{a}}{\partial p} \left(\frac{\partial \sigma}{\partial x} - 3 \frac{\partial \eta}{\partial x} \right) \quad (14)$$

Formulae for calculating $\partial\eta/\partial x$, $\partial\sigma/\partial x$ etc. are given in the Appendix.

Equations similar to eq 5 have appeared in Owen and Brinkley,¹¹ Guggenheim and Prue,²³ Jongenburger and Wood²⁴ and Helgeson and Kirkham.²⁵ However, the following simplifications were made in these works: Owen and Brinkley assumed a independent of temperature;¹¹ Guggenheim and Prue²³ and Helgeson and Kirkham²⁶ used $\dot{a} = 1 \text{ (kg mol}^{-1}\text{)}^{1/2}$ following Guggenheim;²⁰ and Jongenburger and Wood assumed \dot{a} independent of temperature and pressure but added a term in $m^{3/2}$. Nevertheless, these equations have been used quite often in the chemical literature, as for example in Refs.^{17,27-31} To be as general and thermodynamically consistent as possible, this work treats \dot{a} and its derivatives with respect to temperature and pressure occurring in eqs 2 to 7 as adjustable parameters, to be determined by comparison with physicochemical property values from the literature. The parameter C , its derivatives, ϕC_p° and ϕV° are determined in the same manner.

Methods

The JESS physicochemical property database³² contains data for more than 200 electrolytes in water at $t = 25 \text{ }^\circ\text{C}$. A representative selection of electrolytes was examined initially to determine suitable concentration limits for the optimization of \dot{a} , C and their derivatives using the Hückel equation framework. The following limits gave satisfactory agreement for the majority of strong electrolytes: 2.0 mol kg^{-1} for 1:1 electrolytes; 0.5 mol kg^{-1} for 2:1 (and 1:2) and 3:1 electrolytes. Although we have confined ourselves to these limits in this work for the sake of generality, it is important to note that some strong electrolytes can be described to much higher concentrations by the Hückel equations. On the other hand, 2:2 and higher valence electrolytes exhibit unmistakable ion-association in aqueous solution, even under moderately dilute conditions, and could not be described satisfactorily. Certain electrolytes of other valence types exhibit speciation changes at low concentrations or are not represented well by the Hückel equations for some other reason. These electrolyte solutions include those that were problematic in our corresponding optimization

of Pitzer parameters³³ (HF(aq), H₂SO₄(aq), H₃PO₄(aq), KHSO₄(aq), NaHSO₄(aq)) as well as the following electrolyte solutions: CdCl₂(aq), CdBr₂(aq), CdI₂(aq), ZnCl₂(aq), ZnBr₂(aq), ZnI₂(aq), Na₂MoO₄(aq) and K₂Cr₂O₇(aq).

The Debye-Hückel coefficients were calculated using the static permittivity formulation of Fernández et al.³⁴ and the thermodynamic properties of water from IAPWS 95.³⁵ The values at $t = 25$ °C are $A_\phi = 0.39126$ (kg mol⁻¹)^{1/2}, $A_L/RT = 0.79558$ (kg mol⁻¹)^{1/2}, $A_C/R = 3.8205$ (kg mol⁻¹)^{1/2} and $A_V = 1.8979$ cm³ kg^{1/2} mol^{-3/2}.

The values of the parameters \hat{a} and C (and their derivatives) and ϕC_p° and ϕV° were obtained by the method of least squares. The following physicochemical properties were used (literature references to the data sources can be seen at <http://jess.murdoch.edu.au/huckel.shtml>) : mean activity coefficients, osmotic coefficients, water activities, apparent molar relative enthalpies, apparent molar enthalpies of dilution, apparent molar heat capacities, apparent molar volumes, absolute densities, relative densities and specific volumes. Since \hat{a} and its derivatives occur non-linearly, the well-regarded³⁶ Levenberg-Marquardt method was used to obtain best-fitting parameter values. Initial estimates of zero were adequate for all parameters. The residuals between the model equations and the physicochemical property values were weighted using the scheme described in Ref.³⁷ The assigned weight (ranging from 1 to 9)³² was subtracted from 10 and multiplied by a scale factor to give the relative uncertainty of each datum (σ_i). The scale factors used were 0.001 for activity coefficients (as $\ln \gamma_\pm$) and osmotic coefficients, 20 J mol⁻¹ for apparent molar relative enthalpies, 2.0 J(K mol)⁻¹ for apparent molar heat capacities and 0.1 cm³ mol⁻¹ for apparent molar volumes.

Agreement between the model and the available physicochemical property values at $t = 25$ °C is measured by a normalized lack-of-fit statistic ($SSLF_{\text{dof}}$). The lack of fit is calculated as the difference between the total sum of squared residuals and the contribution of ‘pure error’ to the sum of squares ($SSPE$),³⁸ divided by the degrees of freedom (number of data N_D minus number of adjustable parameters N_P), i.e. $SSLF_{\text{dof}} = \{\sum_i [(y_i - y_{\text{model},i}) \sigma_i^{-1}]^2 - SSPE\} (N_D - N_P)^{-1}$. Typically, $SSPE$ is evaluated based only on ‘duplicate’ data³⁸ (for example, property values at the same con-

centration but possibly from different literature sources). An approach based on constrained linear splines is used in this work (see Appendix), giving more reasonable estimates for the minimum sum of squares that can be achieved when a simple model is used to correlate noisy data. Values of $SSLF_{\text{dof}}$ less than or approximately equal to unity reflect that the equations correlate the property values overall to within their relative uncertainty.

Results

There were 57 electrolytes for which the FIZ database contained sufficient reliable information at $t = 25\text{ }^{\circ}\text{C}$ to obtain values for \dot{a} and C (Table 1), their derivatives with respect to temperature and pressure (Table 2), and ${}^{\phi}C_p^{\circ}$ and ${}^{\phi}V^{\circ}$ (Table 3). The number of reported digits in the parameter values is generally one greater than necessary to reproduce the property values within their experimental variation. Lithium hydroxide has the largest $SSLF_{\text{dof}}$ value of any 1:1 electrolyte. The Hückel correlation is plotted against mean activity coefficient values in Figure 1. Even though this is the least well fitting uni-univalent salt, the model is in good agreement with the literature values. On the other hand, the SIT equation shows large systematic deviations from the activity coefficient values and has a lack-of-fit 100 times greater than the Hückel model (see Supporting Information). The JESS website (<http://jess.murdoch.edu.au>) features comprehensive graphical comparisons between the physicochemical property values from the literature from which the parameters were optimized. The resulting models (see <http://jess.murdoch.edu.au/huckel.shtml>) are also available. This may also be useful for verifying an implementation of the equations.

Comparable \dot{a} and C values taken from the literature are also shown (Table 1). Parameter values are only tabulated if they apply to equations having the same number of parameters as this work (i.e. linear in molality). In the case of Hamer and Wu,³ the values of the C parameters were adjusted from common (base 10) logarithms to natural logarithms. In general, the parameter values obtained in this work are in close agreement with their literature counterparts. Even in the case of LiCl(aq) where the \dot{a} values differ by more than $0.1\text{ (kg mol}^{-1}\text{)}^{1/2}$, the osmotic coef-

ficients evaluated from the two sets of parameters differ by less than 0.0035 up to $m = 1.2 \text{ mol kg}^{-1}$, the concentration limit determined by Partanen.³⁹ Presumably this is due to some correlation between the parameters. Since osmotic coefficient values derived from very accurate isopiestic measurements have an experimental uncertainty of about 0.003,⁵¹ this difference is as small as can reasonably be expected.

The \dot{a} and C values from this work are plotted in Figure 2. The parameters are correlated — but not strongly — and there are some noteworthy patterns. For example, the bi- and trivalent metal chloride, nitrate and perchlorate salts are loosely clustered near the points (1.6, 0.4), (1.6, 0.1) and (1.9, 1.0) respectively. We surmise that this clustering reflects the dominance of some common fundamental solution property, perhaps hydration or ion pairing.

The values of ϕC_p° and ϕV° that were obtained using the Hückel equations are compared to the values given by Marcus⁴⁸ in Table 3. Graphical comparisons are also shown in Figure 3 and Figure 4. The general agreement is considered satisfactory in both cases. However, there are some large differences. For example, Marcus' value of $-193 \text{ J(K mol)}^{-1}$ for $\text{Gd}(\text{ClO}_4)_3$ conflicts with the value in this work ($-157 \text{ J(K mol)}^{-1}$) and that of Criss and Millero ($-148.1 \text{ J(K mol)}^{-1}$).⁵² Improvements in both the reliability of available data since the Marcus evaluation (Marcus' ϕV° values are based mainly on values from Millero, 1971⁵³) and the analysis of the data seem likely to explain many of these differences.

Lack-of-fit statistics for different models are contained in the Supplementary Information. Comparison of the lack-of-fit values for the Hückel model, the model with electrolyte-specific \dot{a} independent of temperature and pressure and the model with $\dot{a} \equiv 1.5 \text{ (kg mol}^{-1}\text{)}^{1/2}$ for all electrolytes (SIT) indicates that the SIT equations are relatively poor at correlating the physicochemical properties of strong electrolyte solutions, with over 60% of systems investigated having lack-of-fit values more than 10 times larger than the corresponding Hückel equation. Although allowing \dot{a} to vary for each electrolyte significantly improves the agreement with data (more than half of the electrolytes have lack-of-fit less than two times the value of the Hückel model), there are more than five electrolytes where the lack of fit is considerably larger (around one order of magnitude)

than the Hückel model and some of the fits are almost as poor as the SIT equation. For example, the lack-of-fit value for $\text{Sm}(\text{NO}_3)_3$ is 1.26 when correlated using the Hückel equations, 12.0 when \dot{a} is independent of temperature and pressure and 13.1 when $\dot{a} = 1.5 \text{ (kg mol}^{-1}\text{)}^{1/2}$). The main reason for the relatively large lack-of-fit values is deficient modelling of apparent molar enthalpy of dilution data (Figure 5). The maximum deviation between the property values and SIT model or the model with \dot{a} independent of temperature and pressure is approximately 1.0 kJ mol^{-1} which is considerably larger than the stated uncertainty of (0.01 to 0.02) kJ mol^{-1} .⁵⁴

Some other systems where correlation of the apparent molar relative enthalpy values is problematic are shown in Figures 6 and 7.

Discussion

The correlation of thermodynamic properties of binary strong electrolyte solutions by the Hückel equations was generally satisfactory. These equations have the same capability to harmonize values for different thermodynamic properties as, for example, the Pitzer equations,³³ albeit to lower electrolyte concentrations. The limitation in respect of concentration is understandable because the Hückel equation framework presented here contains fewer adjustable parameters than the corresponding Pitzer framework. Indeed, the work at NBS^{3-6,57,58} and by Partanen and co-workers (e.g.⁴⁶) has shown that the Hückel equations for activity and osmotic coefficients can be extended readily with empirical terms in increasing powers of molality to cover wider ranges of concentration (greater than 20 mol kg^{-1} in some cases). Eqs 2 to 7 could be extended similarly to correlate data at higher concentrations.

Other properties could be incorporated into this framework without difficulty. For example, the apparent molar expansibility and the apparent molar compressibility are related to the derivatives of ϕV with respect to temperature and pressure respectively. These properties were not considered in the present work since the number of binary electrolyte systems for which data are available is small in comparison to the number of electrolyte systems for which enthalpies, heat capacities and

volumes have been experimentally characterized. Prediction of property values under temperature and pressure conditions outside the range of the regressed property values proved less useful than might be expected because the functional dependence of \hat{a} and C with respect to temperature and pressure is not known and the correlation between the parameters increases the uncertainty of the predictions.

Although the equations for the activity and osmotic coefficients are simple, the non-linear nature of the adjustable parameter \hat{a} means that the derivatives of the Gibbs excess energy become increasingly complicated, e.g. they contain multiple Debye-Hückel coefficients. Prior to the electronic computer era, this meant that simpler equations for the apparent molar quantities were preferred. For example, the Masson equation,⁵⁹ the Redlich-Rosenfeld-Meyer equation^{60,61} or polynomial functions. Such equations are useful for data interpolation and smoothing.¹⁷ However, they are flawed because they either are not consistent with equations for activity coefficients or do not adhere to the correct limiting slope (e.g. Masson).⁶²

The simpler form of equations considered in this work, having \hat{a} constant for all electrolytes or independent of temperature and pressure are found to be less capable at correlating the strong electrolyte solution property values than the Hückel equation where \hat{a} and its derivatives are adjustable. In particular, the apparent molar relative enthalpy proved problematic unless \hat{a} was temperature dependent. A constant value of \hat{a} is not able to correlate values for different physicochemical properties satisfactorily unless the equations are extended with extra terms in increasing powers of molality, as is done by, for example, Jongenburger and Wood.²⁴

Theoretically, the parameter \hat{a} can be related to the size of hydrated ions in solution.⁴⁵ However, the optimized value of \hat{a} tends to vary when the limit of concentration changes,¹⁴ the calculated property values are insensitive to the exact value of \hat{a} within experimental error,³ and some experimental datasets can be best-described using negative values of \hat{a} (e.g. PbCl_2 ⁵⁸). As well as being physically unrealistic, negative values of \hat{a} lead to numerical issues such as division by zero or taking the logarithms of negative numbers.⁵⁸ This suggests that some of the assumptions underlying the empirical extension of the Debye-Hückel theory, for example that the ions are spheres of

equal radii,⁶³ have been invalidated. For these reasons, the adjustable parameters are typically not considered to have physical significance.^{3,17}

One of the key disadvantages of the Hückel equations is that they do not apply readily to mixed electrolyte solutions, since the cross-differentiation rule places restrictions on the allowed parameter values.⁶⁴ However, attempts have been made to generalize eq 2 to mixtures of electrolytes^{65–67} and mixing rules such as that of Harned or Zdanovskii/Stokes and Robinson^{68,69} can be used to overcome this limitation.

Conclusion

A thermodynamically-consistent framework for calculating activity coefficients, osmotic coefficients, apparent molar enthalpies, heat capacities and volumes of binary strong electrolyte solutions was developed. Parameters for calculating property values at $t = 25$ °C for 57 electrolytes were presented. All 1:1 electrolytes were correlated successfully up to $m = 2.0$ mol kg⁻¹ and other electrolyte types to $m = 0.5$ mol kg⁻¹. This work establishes for the first time the widespread applicability of the Hückel equations for describing strong aqueous electrolyte solution thermodynamics, not only for the correlation of activity and osmotic coefficients but also for other key physicochemical properties such as the enthalpy, heat capacity and volume.

The results reported in this paper provide a benchmark against which other theoretical frameworks with few parameters (such as SIT) can be compared. This should help to reduce the effort expended on models which are advocated in the literature but are actually less general and less accurate. Our results also support the use of the Hückel equation, properly used, for critical data assessment purposes. The Hückel equation does not merely achieve a ‘better description’, as has been suggested,⁷¹ but rather helps to elucidate the type and number of factors determining the way physicochemical properties change. In contrast, the use of the SIT equation for modelling strong electrolyte solution data (as is done, for example, in Ref.⁷³) is not recommended. The Hückel equation is also less susceptible to systematic errors than the three-parameter Pitzer equations over

the restricted range of concentration. Although good optimization practice always seeks to avoid fitting more parameters than are justified, this can be surprisingly difficult to achieve when the available data are scattered or of low accuracy. This paper demonstrates that straightforward application of Debye-Hückel theory achieves remarkably good and general activity coefficient fits with binary strong electrolyte solutions (one salt plus water) to reasonable ionic strength without resort to equation extensions or the need for more than two adjustable parameters.

Appendix

Functions and their derivatives appearing in the Debye-Hückel terms

The following relations are required in the Debye-Hückel terms for activity coefficients, osmotic coefficients and apparent molar enthalpies, heat capacities and volumes.

$$\begin{aligned}\eta(x) &= 1/(1+x) \\ \partial\eta/\partial x &= -1/(1+x)^2 = -\eta^2 \\ \partial^2\eta/\partial x^2 &= 2/(1+x)^3 = 2\eta^3\end{aligned}$$

$$\begin{aligned}\sigma(x) &= 3[1+x - (1+x)^{-1} - 2\ln(1+x)]/x^3 = 3s/x^3 \\ \partial\sigma/\partial x &= \sigma[-3/x + (1+\eta(\eta-2))/s] \\ \partial^2\sigma/\partial x^2 &= (\partial\sigma/\partial x)^2/\sigma + \sigma\{2x\eta^3/s - [(1+\eta(\eta-2))/s]^2 + 3/x^2\}\end{aligned}$$

Estimating the ‘pure error’ of a dataset

For the purpose of comparison, this work determines the ‘pure error’³⁸ of the physicochemical property datasets for each electrolyte. This is achieved conveniently because most of the

physicochemical property values of interest here change in simple and predictable ways with respect to changes in concentration over the concentration ranges of interest, i.e., $\partial^2 \ln \gamma / \partial m^2 \geq 0$, $\partial^2 \phi / \partial m^2 \geq 0$, $\partial^2 \phi C_p^\circ / \partial m^2 \leq 0$ and $\partial^2 \phi V^\circ / \partial m^2 \leq 0$. The only properties which are not amenable to this technique are the apparent molar relative enthalpy and the apparent molar enthalpy of dilution, e.g., $\partial^2 \phi L / \partial m^2$ can take both positive and negative values even below $m = 2.0 \text{ mol kg}^{-1}$. Since the contribution to the pure error of the enthalpy data cannot be easily approximated, the overall estimate of the pure error is conservative.

Assume the following set of data is available: $(x_i, y_i \pm u_i)$ where i ranges from 1 to N , u_i is the uncertainty of the i^{th} datum and $x_1 < x_2 < \dots < x_N$. The x_i must be distinct since they serve as the locations of the spline nodes. At each node we seek to determine a_i , the value of the spline approximating y_i in a least-squares sense. Let the weighted residual between the i^{th} datum and its corresponding spline value be given by $r_i = (y_i - a_i) / u_i$. The spline values must be constrained in accordance with the relations regarding the signs of the second derivatives of the physicochemical property values with respect to molality given above. The following expressions are used when the second derivatives are assumed to be positive:

$$2 \frac{[(x_{i+1} - x_i)(a_i - a_{i+2}) + (x_{i+2} - x_i)(a_{i+1} - a_i)]}{[(x_{i+1} - x_i)(x_{i+2} - x_i)(x_{i+1} - x_{i+2})]} \geq 0 \quad i = 1 \quad (15)$$

$$2 \frac{[(x_{i+1} - x_i)(a_i - a_{i-1}) + (x_{i-1} - x_i)(a_{i+1} - a_i)]}{[(x_{i+1} - x_i)(x_{i-1} - x_i)(x_{i+1} - x_{i-1})]} \geq 0 \quad i = 2, \dots, N - 1 \quad (16)$$

$$2 \frac{[(x_{i-2} - x_i)(a_i - a_{i-1}) + (x_{i-1} - x_i)(a_{i-2} - a_i)]}{[(x_{i-2} - x_i)(x_{i-1} - x_i)(x_{i-2} - x_{i-1})]} \geq 0 \quad i = N \quad (17)$$

Using $a_i = y_i - r_i u_i$ in the above, the constraints can be put into matrix form and the problem expressed as

$$\text{minimize } \sum_i r_i^2 \quad \text{subject to } Ar \geq b \quad (18)$$

which can be solved using the Least Distance Programming algorithm.⁷⁴

An example spline is shown in Figure 8. The data were generated by the following code (in Matlab syntax)

```
x = -1:0.1:1;
y = x.^2 + 0.2*rand(size(x));
u = ones(size(x));
```

The sum of squares corresponding to the spline is 0.038. The best-fitting second-degree polynomial has sum of squares equal to 0.079. The lack-of-fit sum-of-squares³⁸ for the quadratic model is therefore 0.041.

Supporting Information Available

Tabulated lack-of-fit statistics for the different models analysed in this work. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

Notes and References

- (1) Blum, L.; Høye, J. S. Mean Spherical Model for Asymmetric Electrolytes. 2. Thermodynamic Properties and the Pair Correlation Function. *J. Phys. Chem.* **1977**, *81*, 1311–1316.
- (2) Blum, L.; Vericat, F.; Fawcett, W. R. On the Mean Spherical Approximation for Hard Ions and Dipoles. *J. Chem. Phys.* **1992**, *96*, 3039–3044.
- (3) Hamer, W. J.; Wu, Y. C. Osmotic Coefficients and Mean Ionic Activity Coefficients of Univalent Electrolytes in Water at 25 °C. *J. Phys. Chem. Ref. Data* **1972**, *1*, 1047–1099.
- (4) Goldberg, R. N.; Nuttall, R. L. Evaluated Activity and Osmotic Coefficients for Aqueous Solutions: The Alkaline Earth Metal Halides. *J. Phys. Chem. Ref. Data* **1978**, *7*, 263–309.
- (5) Goldberg, R. N. Evaluated Activity and Osmotic Coefficients for Aqueous Solutions: Bi-Univalent Compounds of Zinc, Cadmium, and Ethylene Bis(Trimethylammonium) Chloride and Iodide. *J. Phys. Chem. Ref. Data* **1981**, *10*, 1–52.
- (6) Goldberg, R. N. Evaluated Activity and Osmotic Coefficients for Aqueous Solutions: Thirty-Six Uni-Bivalent Electrolytes. *J. Phys. Chem. Ref. Data* **1981**, *10*, 671–764.

- (7) Partanen, J. I.; Covington, A. K. Re-evaluation of the Activity Coefficients of Aqueous Hydrochloric Acid Solutions up to a Molality of 2.0 Using Two-parameter Hueckel and Pitzer Equations. Part 1. Results at 25 °C. *J. Solution Chem.* **2002**, *31*, 187–196.
- (8) Partanen, J. I.; Covington, A. K. Re-evaluation of the Thermodynamic Activity Quantities in Aqueous Sodium and Potassium Chloride Solutions at 25 °C. *J. Chem. Eng. Data* **2009**, *54*, 208–219.
- (9) Partanen, J. I.; Makkonen, E. K.; Vahteristo, K. P. Re-Evaluation of Activity Coefficients in Dilute Aqueous Hydrobromic and Hydriodic Acid Solutions at Temperature from 0 to 60 °C. *J. Solution Chem.* **2013**, *42*, 190–210.
- (10) Partanen, J. I. Traceable Mean Activity Coefficients and Osmotic Coefficients in Aqueous Magnesium Chloride Solutions at $T = 298.15$ K up to a Molality of 3.0 mol kg^{-1} . *J. Chem. Thermodyn.* **2013**, *66*, 65–70.
- (11) Owen, B. B.; Brinkley Jr., S. R. Extrapolation of Apparent Molal Properties of Strong Electrolytes. *Ann. N. Y. Acad. Sci.* **1949**, *51*, 753–764.
- (12) Harned, H. S.; Ehlers, R. W. The Thermodynamics of Aqueous Hydrochloric Acid Solutions from Electromotive-force Measurements. *J. Am. Chem. Soc.* **1933**, *55*, 2179–2193.
- (13) Vanderzee, C. E.; Swanson, J. A. Heats of Dilution and Relative Apparent Molal Enthalpies of Aqueous Sodium Perchlorate and Perchloric Acid. *J. Phys. Chem.* **1963**, *67*, 285–291.
- (14) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions, 2nd Edn. Revised*; Butterworth and Co., London, 1970.
- (15) Ref. 14, p. 229.
- (16) Wirth, H. E.; Collier Jr., F. N. Apparent and Partial Molar Volumes of Sodium Perchlorate and Perchloric Acid Mixed Solutions. *J. Am. Chem. Soc.* **1950**, *72*, 5292–5296.

- (17) Spedding, F. H.; Pikal, M. J.; Ayers, B. O. Apparent Molal Volumes of Some Aqueous Rare Earth Chloride and Nitrate Solutions at 25 °C. *J. Phys. Chem.* **1966**, *70*, 2440–2449.
- (18) Ref. 14, p. 231.
- (19) Hückel, E. Theory of Concentrated Aqueous Solutions of Strong Electrolytes. *Phys. Z.* **1925**, *26*, 93–147.
- (20) Guggenheim, E. A. The Specific Thermodynamic Properties of Aqueous Solutions of Strong Electrolytes. *Philos. Mag.* **1935**, *19*, 588–643.
- (21) Bretti, C.; Foti, C.; Sammartano, S. A New Approach in the Use of SIT in Determining the Dependence on Ionic Strength of Activity Coefficients. Applications to Some Chloride Salts of Interest in the Speciation of Natural Fluids. *Chem. Speciation Bioavail.* **2004**, *16*, 105–110.
- (22) Pitzer, K. S. In *Activity Coefficients in Electrolyte Solutions*, 2nd. Edn.; Pitzer, K. S., Ed.; CRC Press, Boca Raton, Florida, USA, 1991; pp 75–153.
- (23) Guggenheim, E. A.; Prue, J. E. Heats of Dilution of Aqueous Electrolyte Solutions. *Trans. Faraday Soc.* **1954**, *50*, 710–718.
- (24) Jongenburger, H. S.; Wood, R. H. The Heats and Entropies of Dilution of the Perchlorates of Magnesium and Strontium. *J. Phys. Chem.* **1965**, *69*, 4231–4238.
- (25) Helgeson, H. C.; Kirkham, D. H. Theoretical Prediction of the Thermodynamic Behavior of Aqueous Electrolytes at High Pressures and Temperatures. II. Debye-Hückel Parameters for Activity Coefficients and Relative Partial Molal Properties. *Am. J. Sci.* **1974**, *274*, 1199–1261.
- (26) Ref. 25, p. 1211.
- (27) Ensor, D. D.; Anderson, H. L. Heats of Dilution of NaCl: Temperature Dependence. *J. Chem. Eng. Data* **1973**, *18*, 205–212.

- (28) Snipes, H. P.; Manly, C.; Ensor, D. D. Heats of Dilution of Aqueous Electrolytes: Temperature Dependence. *J. Chem. Eng. Data* **1975**, *20*, 287–291.
- (29) Leung, W. H.; Millero, F. J. The Enthalpy of Dilution of Some 1-1 and 2-1 Electrolytes in Aqueous Solution. *J. Chem. Thermodyn.* **1975**, *7*, 1067–1078.
- (30) Millero, F. J.; Duer, W. C.; Shepard, E.; Chetirkin, P. V. The Enthalpies of Dilution of Phosphate Solutions at 30 °C. *J. Solution Chem.* **1978**, *7*, 877–889.
- (31) Li, J.-C.; Wei, J.-H.; Gao, S. Y. Heats of Dilution, Heat Capacities and Apparent Molal Enthalpies of $\text{Li}_2\text{B}_4\text{O}_7\text{-Li}_2\text{SO}_4\text{-LiCl-H}_2\text{O}$ Systems at 298.15 K. *J. Therm. Anal.* **1998**, *52*, 497–504.
- (32) May, P. M.; Rowland, D.; Königsberger, E.; Hefter G. JESS, a Joint Expert Speciation System - IV: A Large Database of Aqueous Solution Physicochemical Properties with an Automatic Means of Achieving Thermodynamic Consistency. *Talanta* **2010**, *81*, 142–148.
- (33) May, P. M.; Rowland, D.; Hefter, G.; Königsberger, E. A Generic and Updatable Pitzer Characterization of Aqueous Binary Electrolyte Solutions at 1 bar and 25 °C. *J. Chem. Eng. Data* **2011**, *56*, 5066–5077.
- (34) Fernández, D. P.; Goodwin, A. R. H.; Lemmon, E. W.; Levelt Sengers, J. M. H.; Williams, R. C. 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-Hückel Coefficients. *J. Phys. Chem. Ref. Data* **1997**, *26*, 1125–1166.
- (35) Wagner, W.; Pruss, A. The IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use. *J. Phys. Chem. Ref. Data* **2002**, *31*, 387–535.
- (36) Press, W. H.; Teukolsky, S. A.; Vetterling, W. T.; Flannery, B. P. *Numerical Recipes in FORTRAN, 2nd Edn.*; Cambridge Univ. Press, Cambridge, U.K., 1992.

- (37) Rowland, D. An Investigation of Automated Physicochemical Property Modelling of Aqueous Strong Electrolyte Solutions and Their Mixtures. Ph.D. thesis, Murdoch University, Western Australia, 2013.
- (38) Neter, J.; Wasserman, W. *Applied Linear Statistical Models*; Richard D. Irwin, Inc., Homewood, Illinois, 1974; p 842.
- (39) Partanen, J. I. Re-Evaluation of the Thermodynamic Activity Quantities in Aqueous Lithium Chloride Solutions at 25 °C up to a Molality of 6.0 mol kg⁻¹. *J. Chem. Eng. Data* **2009**, *54*, 882–889.
- (40) Partanen, J. I. Re-Evaluation of the Thermodynamic Activity Quantities in Aqueous Alkali Metal Bromide Solutions at 25 °C. *J. Chem. Eng. Data* **2010**, *55*, 2202–2213.
- (41) Partanen, J. I. Re-evaluation of the Thermodynamic Activity Quantities in Aqueous Solutions of Silver Nitrate, Alkali Metal Fluorides and Nitrites, and Dihydrogen Phosphate, Dihydrogen Arsenate, and Thiocyanate Salts with Sodium and Potassium Ions at 25 °C. *J. Chem. Eng. Data* **2011**, *56*, 2044–2062.
- (42) Partanen, J. I. Re-evaluation of the Thermodynamic Activity Quantities in Aqueous Metal Iodide Solutions at 25 °C. *J. Chem. Eng. Data* **2010**, *55*, 3708–3719.
- (43) Partanen, J. I. 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.* **2012**, *41*, 271–293.
- (44) Partanen, J. I. Re-evaluation of the Thermodynamic Activity Quantities in Aqueous Rubidium and Cesium Chloride Solutions at 25 °C. *J. Chem. Eng. Data* **2010**, *55*, 249–257.
- (45) Partanen, J. I. Mean Activity Coefficients and Osmotic Coefficients in Aqueous Solutions of Salts of Ammonium Ions with Univalent Anions at 25 °C. *J. Chem. Eng. Data* **2012**, *57*, 2654–2666.

- (46) Partanen, J. I. Traceable Mean Activity Coefficients and Osmotic Coefficients in Aqueous Calcium Chloride Solutions at 25 °C up to a Molality of 3.0 mol kg⁻¹. *J. Chem. Eng. Data* **2012**, *57*, 3247–3257.
- (47) Partanen, J. I. Re-evaluation of the Mean Activity Coefficients of Strontium Chloride in Dilute Aqueous Solutions from (10 to 60) °C and at 25 °C up to the Saturated Solution Where the Molality is 3.520 mol kg⁻¹. *J. Chem. Eng. Data* **2013**, *58*, 2738–2747.
- (48) Marcus, Y. *Ion Properties*; Marcel Dekker Inc., New York, U.S.A., 1997.
- (49) Covington, A. K.; Ferra, M. I. A.; Robinson, R. A. Ionic Product and Enthalpy of Ionization of Water from Electromotive Force Measurements. *J. Chem. Soc., Faraday Trans. 1* **1977**, *73*, 1721–1730.
- (50) Zaytsev, I. D.; Aseyev, G. G. *Properties of Aqueous Solutions of Electrolytes*; CRC Press, Boca Raton, U.S.A., 1992.
- (51) Rard, J. A.; Platford, R. F. In *Activity Coefficients in Electrolyte Solutions, 2nd. Edn.*; Pitzer, K. S., Ed.; CRC Press, Boca Raton, Florida, USA, 1991; pp 209–277.
- (52) Criss, C. M.; Millero, F. J. Modeling Heat Capacities of High Valence-Type Electrolyte Solutions with Pitzer's Equations. *J. Solution Chem.* **1999**, *28*, 849–864.
- (53) Millero, F. J. The Molal Volumes of Electrolytes. *Chem. Rev.* **1971**, *71*, 147–176.
- (54) Spedding, F. H.; Derer, J. L.; Mohs, M. A.; Rard, J. A. Heats of Dilution of Some Aqueous Rare Earth Electrolyte Solutions at 25 °C. 2. Rare Earth Nitrates. *J. Chem. Eng. Data* **1976**, *21*, 474–488.
- (55) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *2-1*–2-392.
- (56) Holmes, H. F.; Mesmer, R. E. Thermodynamics of Aqueous Solutions of the Alkali Metal Sulfates. *J. Solution Chem.* **1986**, *15*, 495–518.

- (57) Staples, B. R.; Nuttall, R. L. The Activity and Osmotic Coefficients of Aqueous Calcium Chloride at 298.15 K. *J. Phys. Chem. Ref. Data* **1977**, *6*, 385–407.
- (58) Goldberg, R. N. Evaluated Activity and Osmotic Coefficients for Aqueous Solutions: Bi-Univalent Compounds of Lead, Copper, Manganese, and Uranium. *J. Phys. Chem. Ref. Data* **1979**, *8*, 1005–1048.
- (59) Masson, D. O. Solute Molecular Volumes in Relation to Solvation and Ionization. *Philos. Mag.* **1929**, *8*, 218–235.
- (60) Redlich, O.; Rosenfeld, P. The Partial Molar Volumes of Dissolved Electrolytes. *Z. Phys. Chem.* **1931**, *A155*, 65–74.
- (61) Redlich, O.; Meyer, D. M. The Molal Volumes of Electrolytes. *Chem. Rev.* **1964**, *64*, 221–227.
- (62) Krumgalz, B. S.; Pogorelsky, R.; Iosilevskii, Ya. A.; Weiser, A.; Pitzer, K. S. Ion Interaction Approach for Volumetric Calculations for Solutions of Single Electrolytes at 25 °C. *J. Solution Chem.* **1994**, *23*, 849–875.
- (63) Ref. 14, p. 231.
- (64) Ref. 14, p. 435.
- (65) Helgeson, H. C. Thermodynamics of Hydrothermal Systems at Elevated Temperatures and Pressures. *Am. J. Sci.* **1969**, *267*, 729–804.
- (66) Wood, J. R. Thermodynamics of Brine-salt Equilibria. I. The Systems NaCl-KCl-MgCl₂-CaCl₂-H₂O and NaCl-MgSO₄-H₂O at 25 °C. *Geochim. Cosmochim. Acta* **1975**, *39*, 1147–1163.
- (67) Wood, J. R. Thermodynamics of Brine-salt Equilibria. II. The System NaCl-KCl-H₂O from 0 to 200 °C. *Geochim. Cosmochim. Acta* **1976**, *40*, 1211–1220.

- (68) Zdanovskii, A. B. *Trudy Solvanoj Laboratorii (Trans. Salt Lab.) No. 6*; Akad. Nauk. SSSR, 1936.
- (69) Stokes, R. H.; Robinson, R. A. Interactions in Aqueous Nonelectrolyte Solutions. I. Solute-Solvent Equilibria. *J. Phys. Chem.* **1966**, *70*, 2126–2131.
- (70) Grenthe, I.; Plyasunov, A. V.; Spahiu, K. In *Modelling in Aquatic Chemistry*; Grenthe, I., Puigdomenech, I., Eds.; Nuclear Energy Agency, OECD, Paris, France, 1997; pp 325–426.
- (71) Ref. 70, p. 347.
- (72) Powell, K. J.; Brown, P. L.; Byrne, R. H.; Gajda, T.; Hefter, G.; Leuz, A. -K.; Sjoberg, S.; Wanner, H. Chemical Speciation of Environmentally Significant Heavy Metals with Inorganic Ligands. Part 5: The $\text{Zn}^{2+} + \text{OH}^-$, Cl^- , CO_3^{2-} , SO_4^{2-} , and PO_4^{3-} Systems (IUPAC Technical Report). *Pure Appl. Chem.* **2013**, *85*, 2249–2311.
- (73) Ref. 72, Appx. 1B.
- (74) Lawson, C. L.; Hanson, R. J. *Solving Least Squares Problems*; Society for Industrial and Applied Mathematics, 1995; p 337.

Table 1: Best-fitting values of \dot{a} and C using the Hückel equations for 57 aqueous electrolyte solutions. Parameter values taken from the literature are shown for comparison. The normalized sum-of-squares due to lack of fit, $SSLF_{\text{dof}}$, is also shown.

Electrolyte	$\dot{a} / (\text{kg mol}^{-1})^{1/2}$	$C / \text{kg mol}^{-1}$	$SSLF_{\text{dof}}$	Reference
HCl	1.394	0.282	0.03	this work
	1.4	0.3		7
HNO ₃	1.607	0.135	0.06	this work
HClO ₄	1.299	0.312	0.28	this work
LiOH	0.6078	0.0836	0.37	this work
LiCl	1.371	0.241	0.05	this work
	1.5	0.221		39
LiBr	1.311	0.295	0.28	this work
	1.3	0.29		40
NaOH	1.274	0.124	0.05	this work
NaF	1.258	-0.0374	0.01	this work
	1.25	-0.032		41
	1.28	-0.041		3
NaCl	1.321	0.0883	0.04	this work
	1.4	0.072		8
NaBr	1.375	0.125	0.07	this work
	1.45	0.113		40
NaI	1.477	0.174	0.05	this work
	1.6	0.15		42
NaNO ₃	1.167	-0.0534	0.04	this work
NaClO ₄	1.379	0.0336	0.04	this work
	1.4	0.028		43
Na ₂ SO ₄	1.213	-0.31	0.11	this work

Table 1: Continued

Electrolyte	$\hat{a} / (\text{kg mol}^{-1})^{1/2}$	$C / \text{kg mol}^{-1}$	$SSLF_{\text{dof}}$	Reference
Na(Acetate)	1.622	0.176	0.05	this work
NaClO ₃	1.274	-0.0159	0.04	this work
	1.17	0.0009		43
KOH	1.118	0.247	0.08	this work
KF	1.183	0.1	0.07	this work
	1.16	0.1		41
KCl	1.222	0.0265	0.02	this work
	1.3	0.011		8
KBr	1.278	0.0335	0.01	this work
	1.35	0.019		40
KI	1.417	0.0535	0.01	this work
	1.45	0.05		42
KNO ₃	0.8054	-0.166	0.13	this work
K ₂ SO ₄	1.015	-0.147	0.40	this work
	0.94	-0.089		6
RbF	1.605	0.105	0.06	this work
	1.5	0.12		41
RbCl	1.07	0.0254	0.07	this work
	1.04	0.033		44
RbBr	1.095	0.0126	0.01	this work
	1.19	-0.002		40
RbI	1.085	0.0126	0.01	this work
	1.12	-0.003		42
CsF	1.517	0.157	0.04	this work
	1.6	0.135		41

Table 1: Continued

Electrolyte	$\hat{a} / (\text{kg mol}^{-1})^{1/2}$	$C / \text{kg mol}^{-1}$	$SSLF_{\text{dof}}$	Reference
CsCl	0.8645	0.0252	0.05	this work
	0.84	0.034		44
NH ₄ Cl	1.252	0.02	0.03	this work
	1.3	0.009		45
NH ₄ NO ₃	0.9276	-0.0736	0.07	this work
	0.97	-0.08		45
BaCl ₂	1.38	0.253	0.23	this work
	1.37	0.273		4
CaCl ₂	1.549	0.372	0.06	this work
	1.55	0.377		46
CoCl ₂	1.632	0.375	0.25	this work
LaCl ₃	1.692	0.487	1.18	this work
La(NO ₃) ₃	1.671	0.0509	0.73	this work
La(ClO ₄) ₃	1.982	0.999	0.38	this work
MgCl ₂	1.629	0.444	0.21	this work
	1.67	0.448		10
Mg(NO ₃) ₂	1.486	0.512	0.31	this work
MnCl ₂	1.518	0.365	0.54	this work
Mn(ClO ₄) ₂	1.898	0.835	0.23	this work
NiCl ₂	1.581	0.409	0.11	this work
SrCl ₂	1.476	0.349	0.15	this work
	1.5	0.33		47
Sr(NO ₃) ₂	1.44	-0.127	0.65	this work
NdCl ₃	1.626	0.574	0.29	this work
Nd(NO ₃) ₃	1.546	0.148	0.32	this work

Table 1: Continued

Electrolyte	$\dot{a} / (\text{kg mol}^{-1})^{1/2}$	$C / \text{kg mol}^{-1}$	$SSLF_{\text{dof}}$	Reference
Nd(ClO ₄) ₃	1.913	1.01	0.31	this work
SmCl ₃	1.653	0.582	0.29	this work
Sm(NO ₃) ₃	1.54	0.151	1.26	this work
Sm(ClO ₄) ₃	1.923	1.05	0.40	this work
EuCl ₃	1.651	0.614	0.39	this work
GdCl ₃	1.693	0.59	0.60	this work
Gd(NO ₃) ₃	1.577	0.23	0.23	this work
Gd(ClO ₄) ₃	1.905	1.1	0.31	this work
PrCl ₃	1.721	0.491	0.71	this work
Pr(NO ₃) ₃	1.558	0.152	0.34	this work
Pr(ClO ₄) ₃	1.94	0.98	0.27	this work

Table 2: Values of $d\dot{a}/dT$, $d^2\dot{a}/dT^2$, $d\dot{a}/dp$, dC/dT , d^2C/dT^2 and dC/dp for use in the Hückel equations. The absence of a parameter value means that the available data were well-represented without it.

Electrolyte	Term	dX/dT	d^2X/dT^2	dX/dp
HCl	\dot{a}	0.000238	4.00E−6	8.24E−5
	C	−0.00101	−3.87E−6	6.21E−5
HNO ₃	\dot{a}	0.00165	−0.000146	0.000327
	C	0.000158	−	−9.35E−5
HClO ₄	\dot{a}	0.00415	−0.000138	0.000106
	C	0.000389	4.01E−6	−0.000128
LiOH	\dot{a}	0.000515	−5.47E−5	−9.37E−5
	C	−0.000549	−3.73E−6	0.000316
LiCl	\dot{a}	0.000996	−1.28E−5	0.000295

Table 2: Continued

Electrolyte	Term	dX/dT	d^2X/dT^2	dX/dp
	C	-0.000619	-	0.000145
LiBr	\dot{a}	0.00174	-2.51E-5	0.000241
	C	-0.000693	-	8.84E-5
NaOH	\dot{a}	0.00134	-0.000124	0.00118
	C	0.000574	-3.10E-5	0.000476
NaF	\dot{a}	-1.12E-5	-0.000184	0.00018
	C	0.000987	-	0.000498
NaCl	\dot{a}	0.00134	-6.64E-5	0.00054
	C	0.00107	-3.07E-5	0.000211
NaBr	\dot{a}	0.00182	-2.37E-5	0.000572
	C	0.00116	-4.35E-5	0.000167
NaI	\dot{a}	0.00154	-0.000226	0.000118
	C	0.00141	-	0.000169
NaNO ₃	\dot{a}	0.0048	-0.000215	0.000489
	C	0.00189	-1.68E-5	0.00024
NaClO ₄	\dot{a}	0.0055	-0.000312	0.000346
	C	0.00186	-	0.000229
Na ₂ SO ₄	\dot{a}	0.00202	-0.000172	0.00121
	C	0.00482	-	0.000747
Na(Acetate)	\dot{a}	-0.00226	-3.69E-5	0.00172
	C	-0.000264	-1.87E-5	0.000187
NaClO ₃	\dot{a}	0.00447	-0.000153	0.000447
	C	0.00168	-3.53E-5	0.000275
KOH	\dot{a}	0.00125	-0.000144	0.000573
	C	-0.000101	-	0.000452

Table 2: Continued

Electrolyte	Term	dX/dT	d^2X/dT^2	dX/dp
KF	\dot{a}	0.000695	-0.000112	0.00107
	C	0.000164	-	0.000233
KCl	\dot{a}	0.00177	-5.30E-5	0.000757
	C	0.000936	-2.31E-5	0.000185
KBr	\dot{a}	0.00227	4.17E-5	0.00036
	C	0.00123	-5.68E-5	0.000234
KI	\dot{a}	0.00263	-3.68E-5	-0.000114
	C	0.00162	-3.77E-5	0.00027
KNO ₃	\dot{a}	0.0104	-0.000183	0.000891
	C	0.00107	8.81E-6	2.68E-5
K ₂ SO ₄	\dot{a}	0.0028	-0.000103	0.00119
	C	0.00195	-	0.000429
RbF	\dot{a}	0.00196	-0.000155	-0.00083
	C	-0.000203	-	0.000886
RbCl	\dot{a}	0.00288	-0.000105	0.00066
	C	0.000761	-	0.000165
RbBr	\dot{a}	0.00384	-6.67E-5	0.000272
	C	0.00101	-2.80E-5	0.000217
RbI	\dot{a}	0.0045	-0.000145	0.000385
	C	0.00134	-	0.000119
CsF	\dot{a}	0.000235	-0.00012	0.000741
	C	3.37E-5	-	0.000346
CsCl	\dot{a}	0.00427	-7.59E-5	0.000416
	C	0.000641	-1.03E-5	0.000155
NH ₄ Cl	\dot{a}	0.00192	-1.90E-5	0.000293

Table 2: Continued

Electrolyte	Term	dX/dT	d^2X/dT^2	dX/dp
	<i>C</i>	5.71E-5	-1.83E-5	0.000131
NH ₄ NO ₃	<i>a</i>	0.00416	-7.63E-5	-5.09E-5
	<i>C</i>	0.00139	-2.07E-5	8.15E-5
BaCl ₂	<i>a</i>	0.000598	-6.22E-5	0.000858
	<i>C</i>	0.000906	-	-
CaCl ₂	<i>a</i>	0.000287	-3.28E-5	-0.000139
	<i>C</i>	-0.000556	-	0.000954
CoCl ₂	<i>a</i>	-0.000919	-3.02E-5	0.000641
	<i>C</i>	-0.00183	-	0.000371
LaCl ₃	<i>a</i>	-0.000205	-4.77E-5	0.00019
	<i>C</i>	-0.00129	-	0.00105
La(NO ₃) ₃	<i>a</i>	0.000862	-0.000131	0.00132
	<i>C</i>	0.00187	-	-
La(ClO ₄) ₃	<i>a</i>	0.00166	-7.96E-5	-0.000364
	<i>C</i>	0.000759	-	0.00123
MgCl ₂	<i>a</i>	0.000829	-1.97E-5	0.000116
	<i>C</i>	-0.00255	-	0.000728
Mg(NO ₃) ₂	<i>a</i>	0.00139	-6.88E-5	0.000337
	<i>C</i>	-0.000102	-	-
MnCl ₂	<i>a</i>	-0.0028	-	-0.000314
	<i>C</i>	-	-	0.0012
Mn(ClO ₄) ₂	<i>a</i>	0.000956	-	-0.0013
	<i>C</i>	0.000101	-	0.0012
NiCl ₂	<i>a</i>	-0.00125	-1.39E-5	2.57E-5
	<i>C</i>	-0.0017	-	0.00068

Table 2: Continued

Electrolyte	Term	dX/dT	d^2X/dT^2	dX/dp
SrCl ₂	\dot{a}	0.000867	-4.69E-5	-0.00011
	C	-0.00071	-	0.000865
Sr(NO ₃) ₂	\dot{a}	0.00404	-0.000197	0.000312
	C	0.00279	-	-
NdCl ₃	\dot{a}	0.000261	-3.74E-5	1.54E-5
	C	-0.0019	-	0.00126
Nd(NO ₃) ₃	\dot{a}	0.00163	-0.000118	0.00127
	C	0.00117	-	-
Nd(ClO ₄) ₃	\dot{a}	0.00189	-0.000127	0.000856
	C	0.000804	-	-
SmCl ₃	\dot{a}	0.00016	-5.40E-5	-6.42E-5
	C	-0.00224	-	0.00136
Sm(NO ₃) ₃	\dot{a}	0.00239	-0.000116	0.00108
	C	0.00032	-	-
Sm(ClO ₄) ₃	\dot{a}	0.00184	-0.00013	0.000867
	C	0.000553	-	-
EuCl ₃	\dot{a}	0.000202	-4.47E-5	0.000299
	C	-0.00271	-	0.00058
GdCl ₃	\dot{a}	0.000235	-5.52E-5	0.000505
	C	-0.00319	-	-
Gd(NO ₃) ₃	\dot{a}	0.0015	-0.000107	0.000733
	C	0.000913	-	-
Gd(ClO ₄) ₃	\dot{a}	0.00171	-5.68E-5	0.000742
	C	2.42E-5	-	-
PrCl ₃	\dot{a}	0.00019	-5.80E-5	8.66E-5

Table 2: Continued

Electrolyte	Term	dX/dT	d^2X/dT^2	dX/dp
	C	-0.00207	-	0.0013
Pr(NO ₃) ₃	\dot{a}	0.00125	-0.00013	0.00118
	C	0.0016	-	-
Pr(ClO ₄) ₃	\dot{a}	0.00187	-0.000142	0.00102
	C	0.000734	-	-

Table 3: Best-fitting values of ϕC_p° and ϕV° using the Hückel equations for 57 electrolyte solutions

Electrolyte	$\phi C_p^\circ / \text{J(K mol)}^{-1}$		$\phi V^\circ / \text{cm}^3 \text{mol}^{-1}$	
	this work	⁴⁸	this work	⁴⁸
HCl	-123.7	-127	17.82	17.8
HNO ₃	-72.61	-72	29.21	29.0
HClO ₄	-29.0	-25	43.8	44.1
LiOH	-78.19	-78	-4.51	-4.9
LiCl	-62.06	-65	16.94	16.9
LiBr	-65.07	-69	23.76	23.8
NaOH	-101	-97	-5.30	-5.2
NaF	-79.08	-73	-2.39	-2.4
NaCl	-84.43	-84	16.6	16.6
NaBr	-85.59	-88	23.44	23.5
NaI	-79.98	-78	34.99	35.0
NaNO ₃	-33.63	-29	28.08	27.8
NaClO ₄	7.96	18	43.0	42.9
Na ₂ SO ₄	-207.5	-194	11.59	11.6
Na(Acetate)	64.76	69	39.21	39.5
NaClO ₃	-20.6	-15	35.67	35.5

Table 3: Continued

Electrolyte	$\phi C_p^\circ / \text{J}(\text{K mol})^{-1}$		$\phi V^\circ / \text{cm}^3 \text{mol}^{-1}$	
	this work	⁴⁸	this work	⁴⁸
KOH	-133.9	-127	4.89	5.0
KF	-104.9	-103	7.60	7.8
KCl	-114.6	-114	26.79	26.8
KBr	-114.3	-118	33.74	33.7
KI	-104.3	-108	45.2	45.2
KNO ₃	-57.05	-59	38.2	38.0
K ₂ SO ₄	-262.4	-254	32.05	32.0
RbF	-125.8	-125	12.8	12.9
RbCl	-131.3	-136	31.89	31.9
RbBr	-133.8	-140	38.81	38.8
RbI	-128.8	-130	50.21	50.3
CsF	-138.6	-139	19.98	20.1
CsCl	-143.3	-150	39.18	39.1
NH ₄ Cl	-54.98	-57	35.89	35.7
NH ₄ NO ₃	-2.31	-2	47.26	46.9
BaCl ₂	-299.0	-300	22.94	23.1
CaCl ₂	-276.5	-281	17.72	17.7
CoCl ₂	-281.1	-281	10.12	11.6
LaCl ₃	-506	-507	14.4	14.3
La(NO ₃) ₃	-368.9	-342	47.06	47.9
La(ClO ₄) ₃	-202.3	-201	94.74	93.2
MgCl ₂	-263.7	-270	14.09	14.4
Mg(NO ₃) ₂	-165.7	-160	37.38	36.8
MnCl ₂	-258.9	-266	18.31	17.9

Table 3: Continued

Electrolyte	$\phi C_p^\circ / \text{J}(\text{K mol})^{-1}$		$\phi V^\circ / \text{cm}^3 \text{ mol}^{-1}$	
	this work	⁴⁸	this work	⁴⁸
Mn(ClO ₄) ₂	-55.63	-62	71.65	70.5
NiCl ₂	-296.8	-296	6.60	11.6
SrCl ₂	-285.7	-289	18.35	17.4
Sr(NO ₃) ₂	-201.4	-179	43.19	39.8
NdCl ₃	-495.3	-535	10.02	10.1
Nd(NO ₃) ₃	-355	-370	44.62	43.7
Nd(ClO ₄) ₃	-260.2	-229	87.31	89.0
SmCl ₃	-510.9	-530	11.08	11.1
Sm(NO ₃) ₃	-341.8	-365	45.55	44.7
Sm(ClO ₄) ₃	-257.6	-224	87.74	90.0
EuCl ₃	-478.3	-519	11.87	9.7
GdCl ₃	-495.4	-499	12.57	13.5
Gd(NO ₃) ₃	-328.6	-334	46.4	47.1
Gd(ClO ₄) ₃	-156.8	-193	89.79	92.4
PrCl ₃	-519.4	-546	10.79	10.9
Pr(NO ₃) ₃	-378.7	-381	45.52	44.5
Pr(ClO ₄) ₃	-279.3	-240	87.49	89.8

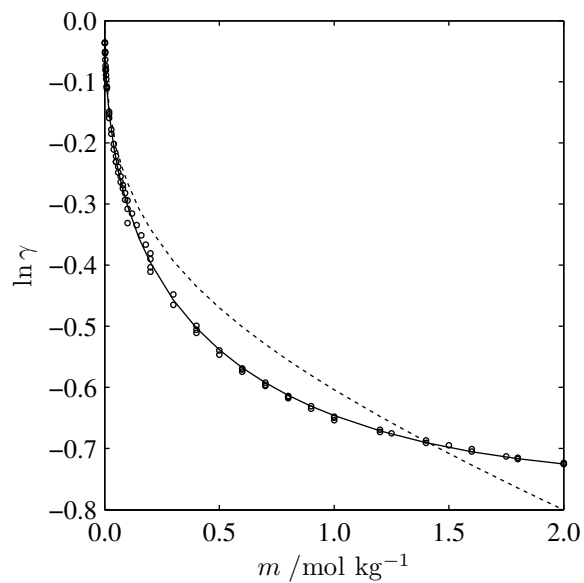


Figure 1: Mean activity coefficients (as $\ln \gamma$) for $\text{LiOH}(\text{aq})$ at $t = 25 \text{ }^\circ\text{C}$ from the literature,^{3,14,49,50} the Hückel equation (solid line) and the best-fitting SIT equation (dotted line) models from this work.

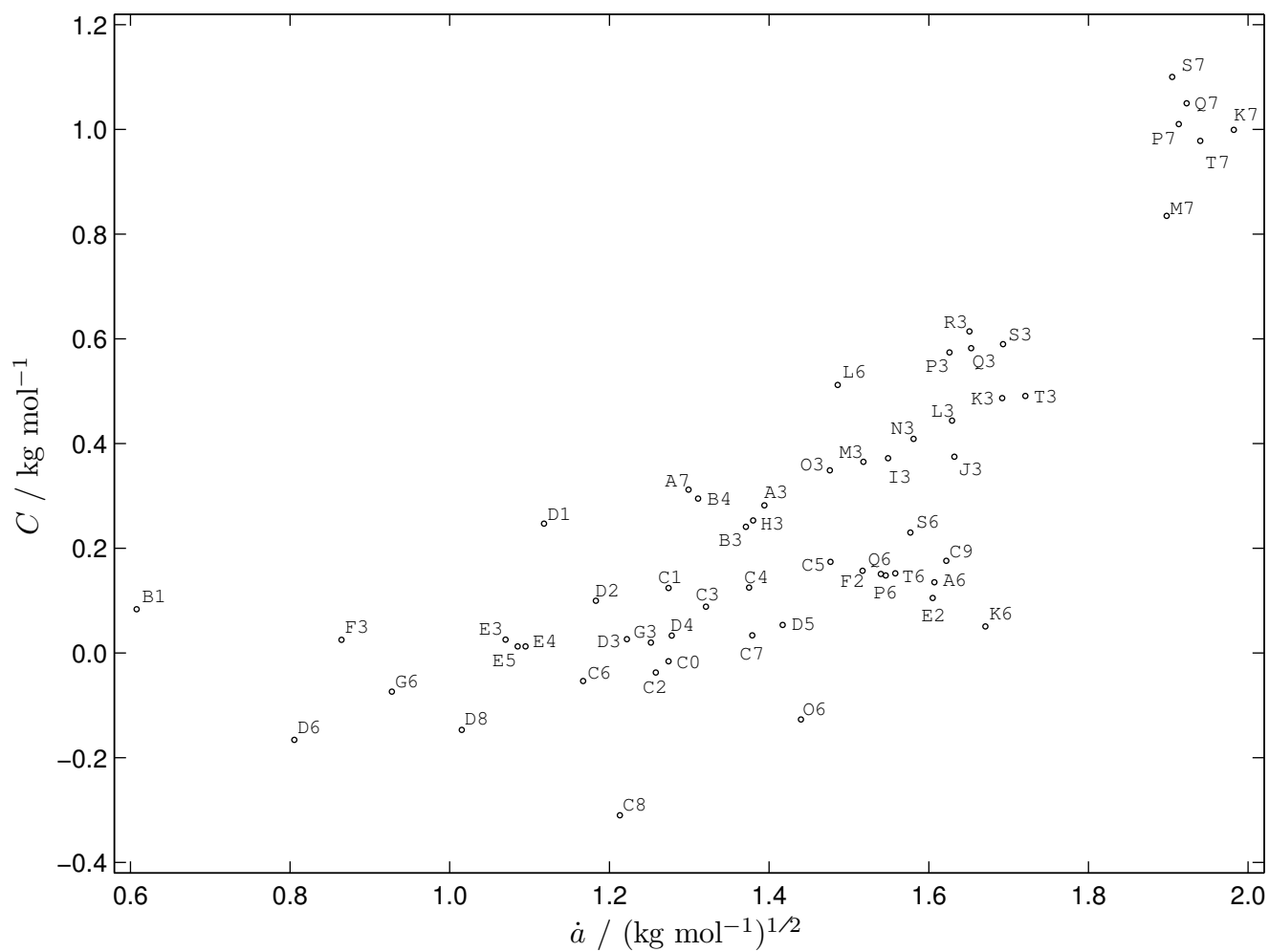


Figure 2: Optimized values of \dot{a} and C for 57 electrolytes in Table 1. Salts are indexed as X_n where X is the cation and n is the anion. $X = (A: H^+; B: Li^+; C: Na^+; D: K^+; E: Rb^+; F: Cs^+; G: NH_4^+; H: Ba^{2+}; I: Ca^{2+}; J: Co^{2+}; K: La^{3+}; L: Mg^{2+}; M: Mn^{2+}; N: Ni^{2+}; O: Sr^{2+}; P: Nd^{3+}; Q: Sm^{3+}; R: Eu^{3+}; S: Gd^{3+}; T: Pr^{3+})$. $n = (1: OH^-; 2: F^-; 3: Cl^-; 4: Br^-; 5: I^-; 6: NO_3^-; 7: ClO_4^-; 8: SO_4^{2-}; 9: Acetic^-; 0: ClO_3^-)$.

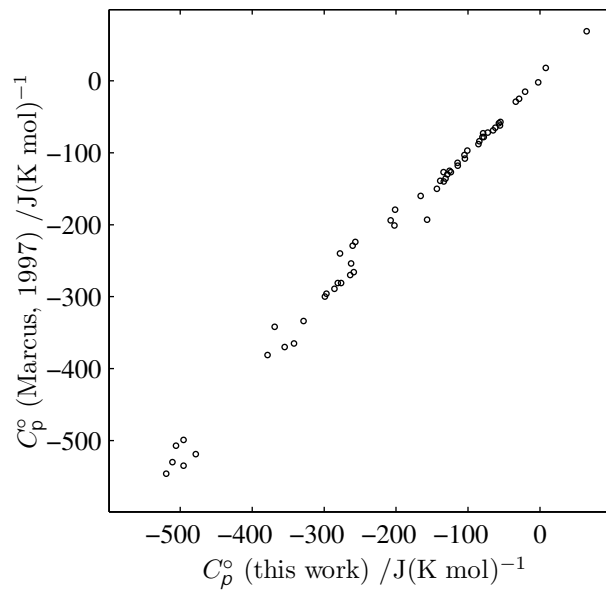


Figure 3: Comparison between the values of ϕC_p° obtained in this work and those of Marcus⁴⁸ for 57 electrolytes in Table 3.

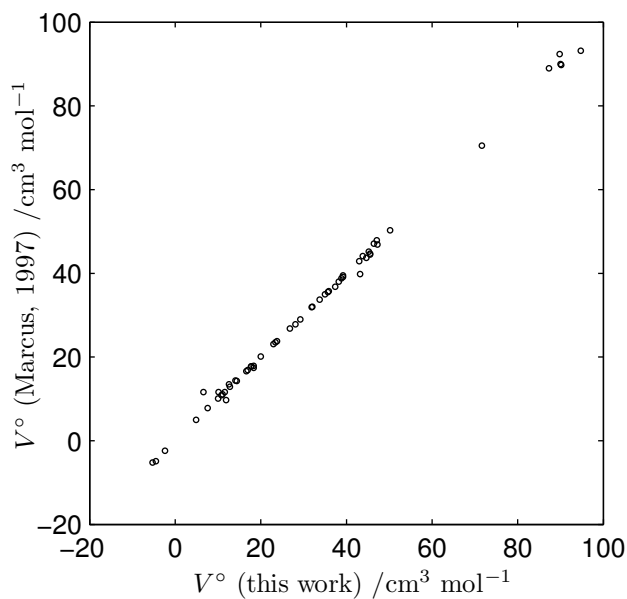


Figure 4: Comparison between the values of ϕV° obtained in this work and those of Marcus⁴⁸ for 57 electrolytes in Table 3.

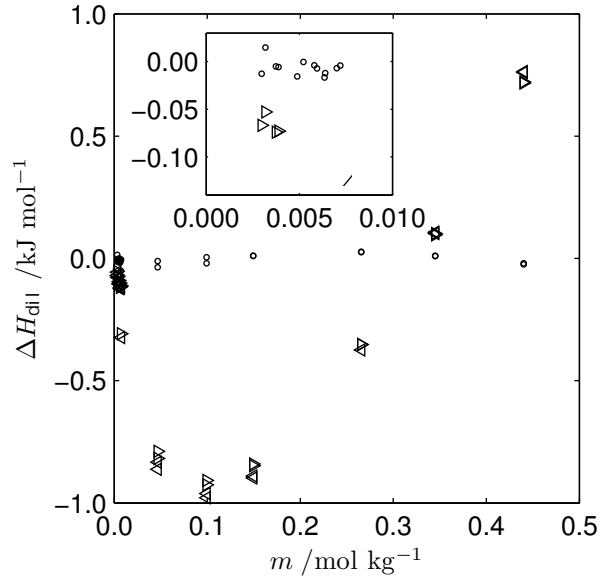


Figure 5: Deviations ΔH_{dil} of the experimental apparent molar enthalpy of dilution values of Spedding et al.⁵⁴ at $t = 25\text{ }^\circ\text{C}$ from the Hückel model (○), the model with \dot{a} independent of temperature and pressure (▷) and the SIT equation model with $\dot{a} = 1.5\text{ (kg mol}^{-1})^{1/2}$ (◄).

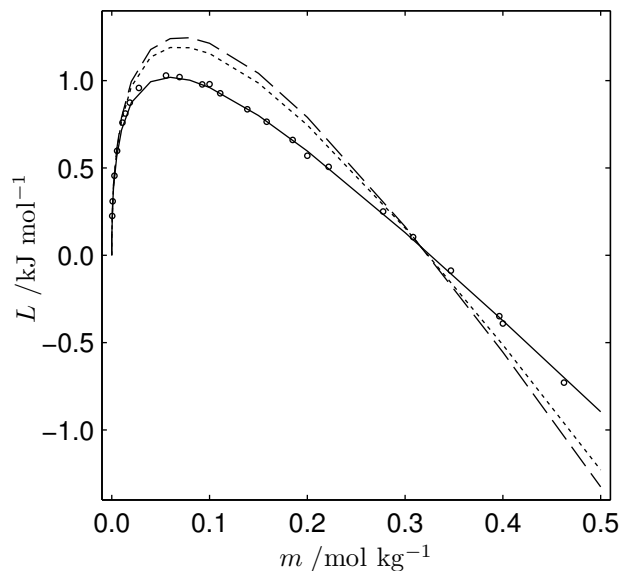


Figure 6: Apparent molar relative enthalpies for $\text{Na}_2\text{SO}_4(\text{aq})$ at $t = 25\text{ }^\circ\text{C}$ from the literature,^{55,56} the Hückel equation (solid line), the model with \dot{a} independent of temperature and pressure (dashed line) and the best-fitting SIT equation (dotted line) calculated from this work.

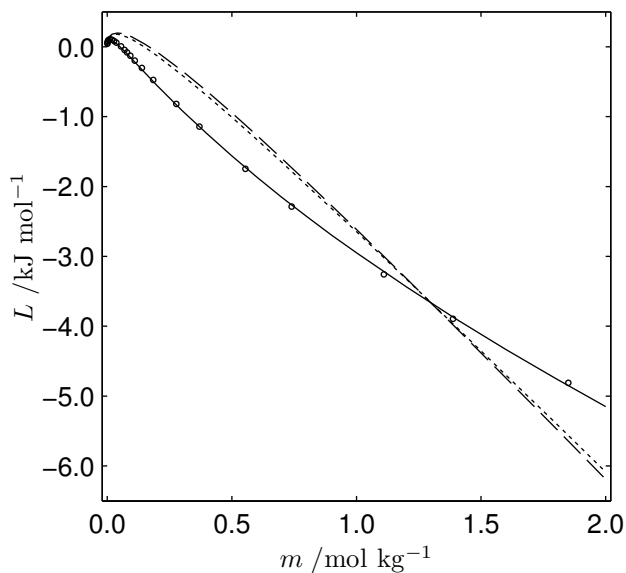


Figure 7: Apparent molar relative enthalpies for $\text{KNO}_3(\text{aq})$ at $t = 25\text{ }^\circ\text{C}$ from the literature,⁵⁵ the Hückel equation (solid line), the model with a independent of temperature and pressure (dashed line) and the best-fitting SIT equation (dotted line) calculated from this work.

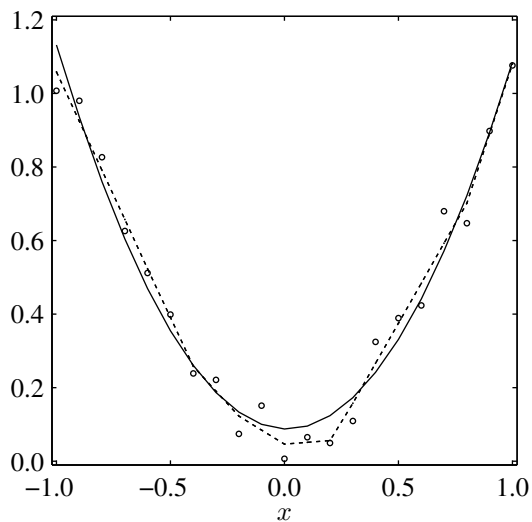


Figure 8: Example of approximating a noisy dataset (\circ) with a constrained linear spline (dotted line). The best-fitting second-degree polynomial is also shown (solid line).

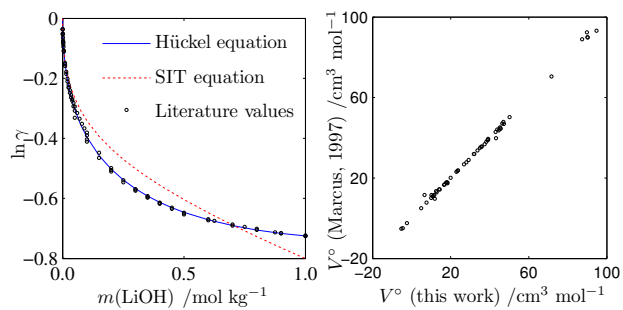


Figure 9: For Table of Contents use only.

Thermodynamics of strong aqueous electrolyte solutions at $t = 25 \text{ }^\circ\text{C}$ described by the Hückel equations

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