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Predictive models for the phase behaviour and solution properties of weak electrolytes: nitric, sulphuric, and carbonic acids

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The distribution of ionic species in electrolyte systems is important in many fields of science and engineering, ranging from the study of degradation mechanisms to the design of systems for electrochemical energy storage. Often, other phenomena closely related to ionic speciation, such as ion pairing, clustering and hydrogen bonding, which are difficult to investigate experimentally, are also of interest. Here, we develop an accurate molecular approach, accounting for reactions as well as association and ion pairing, to deliver a predictive framework that helps validate experiment and guides future modelling of speciation phenomena of weak electrolytes. We extend the SAFT-VRE Mie equation of state [D. K. Eriksen *et al.*, *Mol. Phys.*, 2016, **114**, 2724–2749] to study aqueous solutions of nitric, sulphuric, and carbonic acids, considering complete and partially dissociated models. In order to incorporate the dissociation equilibria, correlations to experimental data for the relevant thermodynamic equilibrium constants of the dissociation reactions are taken from the literature and are imposed as a boundary condition in the calculations. The models for water, the hydronium ion, and carbon dioxide are treated as transferable and are taken from our previous work. We present new molecular models for nitric acid, and the nitrate, bisulfate, sulfate, and bicarbonate anions. The resulting framework is used to predict a range of phase behaviour and solution properties of the aqueous acids over wide ranges of concentration and temperature, including the degree of dissociation, as well as the activity coefficients of the ionic species, and the activity of water and osmotic coefficient, density, and vapour pressure of the solutions. The SAFT-VRE Mie models obtained in this manner provide a means of elucidating the mechanisms of association and ion pairing in the systems studied, complementing the experimental observations reported in the literature.

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1 Introduction

Many applications involving liquid solutions relate to degradation, the reaction between compounds and, in general, to the formation of new species. In such systems the thermodynamic description of equilibrium, which necessarily requires the complete characterisation of the existing substances and their interactions also means accounting for any occurring speciation. In relation to electrolyte solutions, thermodynamic modelling with equations of state has been performed extensively for

strong electrolytes, yet remains rather more limited for solutions of partially dissociated electrolytes. The intermolecular interactions pertinent to charged species involve complex long- and short-ranged forces, which are further compounded in weak electrolyte solutions by the consideration of dissociation equilibria as well as the higher likelihood of ion pairing. The characterisation of mixtures containing weak electrolytes is not trivial, requiring an explicit treatment of chemical reaction equilibria alongside the physical model. A general framework to model solutions of weak electrolytes is essentially that of a reactive system, although the calculation of the activities of the species present requires methods that incorporate a treatment of Coulombic (and often polar) interactions. Two challenges need to be addressed in order to model weak electrolytes: the first is to account for the reactive nature of the system alongside phase equilibrium; the second to achieve an appropriate description of the range of intermolecular interactions participating in the system.

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The development of methodologies to treat chemical equilibria has received much attention, since, as well as describing the formation of new chemical species, the concepts of chemical equilibria have been found to be useful in mimicking physical associations such as those in hydrogen-bonding fluids.¹ Moreover, a number of approaches have been presented that describe the hydration of ions as chemical equilibria.^{2–5} Some of the interrelations and differences between the degree of physical or chemical association are discussed in an early paper by Guggenheim⁶ in 1960 through what he referred to as “sociation” and association, respectively. In the terrain of electrolytes, Guggenheim defined a degree of supersociation to characterise the association between ions through a modified equilibrium constant that establishes an infinitely dilute system as the reference to describe the fraction of ion pairs. In this way he aimed to avoid ambiguities in the definition of the limit demarcating associated ion pairs from free ions.⁶

The most widely used thermodynamic models for electrolyte solutions are activity coefficient models and consequently much of the modelling of weak electrolytes has been presented with this type of approaches.⁷ Typically, the thermodynamic equilibrium constant determined experimentally is employed in order to solve the required electrolyte dissociation equilibria in parallel with the phase equilibria. Much of the earlier work on weak electrolytes^{8–11} was performed using the electrolyte activity coefficient model of Pitzer,¹² while subsequent approaches tended towards extending activity coefficient models for non-electrolytes with the Debye–Hückel¹³ theory. For example, the e-NRTL model presented by Chen *et al.*¹⁴ combines the NRTL activity coefficient model of Renon and Prausnitz¹⁵ with the Debye–Hückel theory, and was applied to weak electrolytes by Austgen *et al.*¹⁶ and by Que and Chen.¹⁷ Similarly, the e-UNIFAC model presented by Achard *et al.*¹⁸ is based on the UNIFAC group-contribution approach of Fredenslund *et al.*¹⁹ By supplementing e-UNIFAC with a numerical procedure to predict partial dissociation phenomena, Achard *et al.*²⁰ effectively modelled solutions of weak acids and bases. Wang *et al.*²¹ later applied the electrolyte-UNIQUAC model – which was first presented by Christensen *et al.*²² – to model weak electrolytes in mixed solvents, and an interesting application of the electrolyte-UNIQUAC model was presented by Thomsen and co-workers,^{23,24} who modelled ternary mixtures containing mixed weak electrolytes by employing the electrolyte-UNIQUAC model for the liquid phase and the Soave–Redlich–Kwong equation of state²⁵ for the vapour phase.

Although activity coefficient models have proven to be highly effective in reproducing the thermodynamic behaviour of electrolyte solutions, including multi-solvent and mixed-electrolyte mixtures containing weak electrolytes, an important drawback of these methods is that they require a large number of adjustable parameters. In this respect, equations of state have an advantage as thermodynamic modelling tools. Equations of state based on perturbation theories such as the perturbed hard-chain theory of Beret and Prausnitz²⁶ and the perturbed-anisotropic-chain theory of Vimalchand and Donohue²⁷ were directly adapted to model electrolytes in the 1980s, with application to weak electrolytes presented by Daumn *et al.*²⁸ and

by Jin and Donohue,²⁹ respectively. In the context of perturbation-based equation of state approaches, the statistical associating fluid theory (SAFT)^{30,31} has been extensively applied to model electrolytes. In particular, the perturbed-chain SAFT for electrolytes (ePC-SAFT) of Cameretti *et al.*³² has been most broadly applied to weak electrolytes.^{33–37} The method is based on the PC-SAFT equation of state^{38,39} with the addition of a Debye–Hückel term to account for the electrostatic interactions. In the first application of ePC-SAFT to weak electrolytes Held and Sadowski³³ considered (among other weak electrolytes) weak acids that form ion pairs. A chemical model for ion pairing was employed, and the ion pairs were modelled as distinct species with no net charge. Reschke *et al.*³⁴ later used ePC-SAFT to model the stepwise dissociation of multiprotic weak acids, while Cassens *et al.*³⁵ implemented ePC-SAFT to study the aqueous solubility of weak bases in response to a pH-changing agent.

The SAFT equation of state for square-well potentials of variable range (SAFT-VR SW)^{40,41} was extended to treat electrolyte solutions early on^{42,43} and was shown to be useful for the prediction of salting out in mixtures of water and alkanes.⁴⁴ The implementation of this SAFT-VRE SW equation of state to weak electrolytes has thus far been limited to the work of Paricaud *et al.*,⁴⁵ in which the phase equilibrium of aqueous hydrogen iodide was modelled in parallel with the dissociation and reaction equilibria of the system. The SAFT-VRE SW approach has been revised recently⁴⁶ to incorporate a Born⁴⁷ solvation energy contribution to deliver solvation free energies which are physically relevant and to allow for salt partitioning in liquid–liquid equilibria. In a similar vein, Coulombic and Born terms have been included in the SAFT-VRE Mie equation of state⁴⁸ (an extension of the SAFT-VR Mie equation of state⁴⁹ to model electrolyte solutions). Taking an ion-specific modelling approach and requiring only one adjustable parameter per ion, the SAFT-VRE Mie approach was applied to model a wide range of thermophysical properties of aqueous solutions of strong electrolytes, including hydration free energies, mean-ionic coefficients, osmotic coefficients and solubility limits for a range of strong electrolytes. In our current paper we use the SAFT-VRE Mie equation of state to model weak electrolytes. A similar framework can be applied with the SAFT- γ Mie group contribution approach,^{50–52} following appropriate mappings to incorporate the ionic free energy contributions.

The focus of our current work is on aqueous solutions of three inorganic acids of fundamental importance in industrial applications, namely sulphuric, nitric, and carbonic acids. Their dissociation equilibria have been well characterised experimentally. We couple the experimental data for the equilibrium constant of the dissociation reaction with the SAFT-VRE Mie approach⁵⁰ to obtain a reliable equation-of-state-based model for these acids. Experimental data of the degree of dissociation of the three acids in aqueous solution are readily available and are used to determine the adjustable parameters in our model. In contrast, only limited quantitative information regarding the nature of ion–ion association or ion pairing and ion–water hydrogen bonding interactions can be found in the literature. The SAFT-VRE Mie approach provides an opportunity to test

different association schemes and to thereby elucidate which types of interactions have a governing impact on the thermodynamic behaviour of these systems.

We first provide a concise review on the thermodynamics of (weak) electrolytes (Section 2), including the treatment of the dissociation equilibrium. This is followed by an overview of the SAFT-VRE Mie theory in Section 3 and a description of the molecular models employed therein. We first consider the case of aqueous sulphuric acid and present our proposed model (Section 4), which is developed in light of experimental information for ion hydration and ion association phenomena. Aqueous nitric acid is studied in Section 5. We consider modelling approaches treating the acid as both a strong and a weak electrolyte, as a means of evaluating the relative benefit of the latter approach for electrolytes which dissociate appreciably albeit not completely. In Section 6, results for aqueous carbonic acid are presented. Conclusions are provided in Section 7.

2 Thermodynamics of weak electrolytes

2.1 Dissociation, true and overall composition

Consider the (possibly incomplete) dissociation of a salt $A_{\nu_A}B_{\nu_B}$ into its constituent ions A^{z_A+} and B^{z_B-} in a solvent W :

For ease of notation, the stoichiometric coefficient indices ν_A and ν_B in the salt $A_{\nu_A}B_{\nu_B}$ are dropped in the following analysis, and only + and – are written as exponents of the ions instead of the charge numbers z_{A+} and z_{B-} .

Suppose a solution of AB is prepared by mixing $\tilde{n}_{AB}$ moles AB with $\tilde{n}_W$ moles of solvent. These two numbers of moles represent the ‘overall’ composition of the solution; always indicated by a tilde ($\sim$) in this work. By virtue of the dissociation reaction however, the ‘true’ composition of the solution at any given temperature T and pressure p is specified by the numbers of moles of the undissociated salt n_{AB} , solvent n_W , cation n_{A+} and anion n_{B-} . (This distinction of ‘overall’ and ‘true’ values pertains also other thermodynamic properties, especially the chemical potential and related properties, cf. Section 2.3.) The ‘overall’ and ‘true’ compositions are related through the material balances. Here,

$$n_{A+} = \nu_A \xi \quad (2)$$

$$n_{B-} = \nu_B \xi \quad (3)$$

$$n_{AB} = \tilde{n}_{AB} - \xi, \quad (4)$$

where ξ is the molar extent of reaction. Instead of the molar extent of reaction, the degree of dissociation α is often used:

$$\alpha = \frac{\xi}{\tilde{n}_{AB}}, \quad (5)$$

where ξ , or α , respectively, are computed from the condition of chemical equilibrium.

2.2 Dissociation equilibrium

At specified temperature T and pressure p the total Gibbs free energy of a mixture is given by

$$G(T, p, \mathbf{n}) = \sum_{i=1}^N n_i \mu_i, \quad (6)$$

where N is the number of components, $\mathbf{n}$ is the vector of mole numbers of these components, μ_i is the chemical potential of component i in the mixture, and a single phase is assumed. As discussed earlier, a reaction will lead to changes in the mole numbers, and

$$dG(T, p, \mathbf{n}) = \sum_{i=1}^N (\nu_i d\xi) \mu_i, \quad (7)$$

where, $\nu_i < 0$ for reactants and $\nu_i > 0$ for products. The necessary condition for equilibrium in a closed system specifies the derivative of the Gibbs free energy be zero with respect to the extent of reaction ξ , resulting in

$$\sum_{i=1}^N \nu_i \mu_i = 0, \quad (8)$$

which when applied to the dissociation presented in the previous section leads to

$$\nu_A \mu_{A+} + \nu_B \mu_{B-} - \mu_{AB} = 0. \quad (9)$$

In general, the chemical potential μ_i is written as the sum of a reference term and a term capturing the deviation from the chosen reference, *i.e.*,

$$\mu_i = \mu_i^{\text{ref}} + RT \ln a_i, \quad (10)$$

noting that depending on the component of interest, different standard states μ_i^{ref} and corresponding activities a_i are often used.⁵³ Using eqn (10) in eqn (9) and rearranging yields

$$\exp\left(-\frac{\nu_A \mu_{A+}^{\text{ref}} + \nu_B \mu_{B-}^{\text{ref}} - \mu_{AB}^{\text{ref}}}{RT}\right) = \frac{a_{A+} a_{B-}}{a_{AB}}, \quad (11)$$

where the left-hand side is referred to as the thermodynamic equilibrium constant K_a of the reaction:

$$K_a = \exp\left(-\frac{\nu_A \mu_{A+}^{\text{ref}} + \nu_B \mu_{B-}^{\text{ref}} - \mu_{AB}^{\text{ref}}}{RT}\right). \quad (12)$$

The values of K_a found for different solutions of weak electrolytes can differ by several orders of magnitude and for easier comparison, a logarithmic scale,

$$pK_a = -\log_{10}(K_a), \quad (13)$$

is introduced.

In the present work, we use correlations of experimental data for the temperature dependence of pK_a of the systems of interest reported in the literature, and couple them with the thermodynamic modelling carried out with the SAFT-VRE Mie equation of state.

2.3 Chemical potential scales

2.3.1 Ionic species. Two measures of concentration are typically employed when studying electrolyte solutions. The molality m_i is defined as

$$m_i = \frac{n_i}{\bar{m}_W}, \quad (14)$$

where n_i is the number of moles of component i in solution and $\bar{m}_W$ is the mass of pure solvent W. The molarity c_i is defined as

$$c_i = \frac{n_i}{V}, \quad (15)$$

where V is the volume of the solution. For the chemical potential of a given ionic species i in solution, a Henry-like normalization to infinite dilution is often used. Using a molality scale this leads to

$$\begin{aligned} \mu_i &= \mu_i^{\text{ref } m}(T, p, \mathbf{x}^*) + RT \ln a_i^{*m}(T, p, \mathbf{x}) \\ &= \mu_i^{\text{ref } m}(T, p, \mathbf{x}^*) + RT \ln \left(\frac{m_i}{m^0} \gamma_i^{*m}(T, p, \mathbf{x}) \right), \end{aligned} \quad (16)$$

where $\mathbf{x}$ denotes the solution composition, $\mu_i^{\text{ref } m}(T, p, \mathbf{x}^*)$ is the reference chemical potential, $\gamma_i^{*m}(T, p, \mathbf{x})$ is the activity coefficient in the molality scale, and the unit molality $m^0 = 1 \text{ mol kg}^{-1}$ is introduced to render the last term dimensionless. The asterisk $*$ denotes that the normalization is carried out with respect to component i at infinite dilution in the solvent W, with $\mathbf{x}^*$ the corresponding reference solution composition. Similarly, in the molarity scale, the chemical potential of the ionic species can be obtained as

$$\begin{aligned} \mu_i &= \mu_i^{\text{ref } c}(T, p, \mathbf{x}^*) + RT \ln a_i^{*c}(T, p, \mathbf{x}) \\ &= \mu_i^{\text{ref } c}(T, p, \mathbf{x}^*) + RT \ln \left(\frac{c_i}{c^0} \gamma_i^{*c}(T, p, \mathbf{x}) \right), \end{aligned} \quad (17)$$

where each of the terms has an analogous meaning as for the molality scale.

Inserting each of the two chemical potential scales presented in eqn (16) and (17) leads to two possible formulations for the dissociation equilibrium condition. The molality-based description yields

$$K_a^m(T, p) = \exp \left(-\frac{\nu_A \mu_{A^+}^{\text{ref } m} + \nu_B \mu_{B^-}^{\text{ref } m} - \mu_{AB}^{\text{ref } m}}{RT} \right), \quad (18)$$

where

$$K_a^m(T, p) = \frac{m_{A^+} m_{B^-} \gamma_{A^+}^{*m} \gamma_{B^-}^{*m}}{m_{AB} m^0 \gamma_{AB}^{*m}} \quad (19)$$

is the equilibrium constant of the dissociation reaction in the molality scale, and the molarity scale leads to

$$K_a^c(T, p) = \exp \left(-\frac{\nu_A \mu_{A^+}^{\text{ref } c} + \nu_B \mu_{B^-}^{\text{ref } c} - \mu_{AB}^{\text{ref } c}}{RT} \right), \quad (20)$$

where

$$K_a^c(T, p) = \frac{c_{A^+} c_{B^-} \gamma_{A^+}^{*c} \gamma_{B^-}^{*c}}{c_{AB} c^0 \gamma_{AB}^{*c}} \quad (21)$$

is the equilibrium constant on the molarity scale. Note that K_a^m and K_a^c depend on both T and p and, by virtue of the

normalization employed, also on the choice of solvent W. Here, we consider aqueous solutions at low pressures, so that only the temperature dependence needs to be considered explicitly. The molality scale m_i is generally preferred over the molarity c_i as no knowledge of the density of the solution is required. Thus, our discussion is limited to properties on the molality scale and we drop the superscript 'm' hereafter.

2.3.2 Neutral compound. First, we note that at chemical equilibrium, the chemical potential of the neutral compound viewed from the 'true' and 'overall' perspective must be equal:

$$\mu_{AB}(T, p, \mathbf{x}) = \tilde{\mu}_{AB}(T, p, \mathbf{x}). \quad (22)$$

This equality, also known as Prigogine's theorem,⁵⁴ is derived in Appendix A.

At chemical equilibrium, according to eqn (9) the chemical potential of the neutral compound AB is

$$\mu_{AB}(T, p, \mathbf{x}) = \nu_A \mu_{A^+}(T, p, \mathbf{x}) + \nu_B \mu_{B^-}(T, p, \mathbf{x}), \quad (23)$$

so that using the molality scale (eqn (16)) together with Prigogine's theorem yields

$$\begin{aligned} \tilde{\mu}_{AB}(T, p, \mathbf{x}) &= \tilde{\mu}_{AB}^{\text{ref } m}(T, p, \mathbf{x}^*) + RT \ln \left[\left(\frac{m_{A^+}}{m^0} \right)^{\nu_A} \left(\frac{m_{B^-}}{m^0} \right)^{\nu_B} \right] \\ &\quad + RT \ln \left[\left(\gamma_{AB}^{*m}(T, p, \mathbf{x}) \right)^{\nu_A + \nu_B} \right], \end{aligned} \quad (24)$$

where

$$\tilde{\mu}_{AB}^{\text{ref } m}(T, p, \mathbf{x}^*) = \nu_A \mu_{A^+}^{\text{ref } m}(T, p, \mathbf{x}^*) + \nu_B \mu_{B^-}^{\text{ref } m}(T, p, \mathbf{x}^*), \quad (25)$$

and

$$\tilde{\gamma}_{AB}^{*m}(T, p, \mathbf{x}) = \left[\left(\gamma_{A^+}^{*m}(T, p, \mathbf{x}) \right)^{\nu_A} \left(\gamma_{B^-}^{*m}(T, p, \mathbf{x}) \right)^{\nu_B} \right]^{\frac{1}{\nu_A + \nu_B}}, \quad (26)$$

is the mean-ionic activity coefficient.

From the definition of γ_i^{*m} given in eqn (16) it is clear that $\tilde{\gamma}_{AB}^{*m}$ depends on the true solution composition. Evaluating this composition when measuring the properties of weak electrolyte solutions is, however, a cumbersome task, so that instead of $\tilde{\gamma}_{AB}^{*m}$ its so-called 'stoichiometric' counterpart $\tilde{\gamma}_{AB}^{*m, \text{stoich}}$ is often used. In principle, $\tilde{\gamma}_{AB}^{*m, \text{stoich}}$ gives the value for the mean-ionic activity coefficient if AB were dissociated completely at a certain molality $\tilde{m}_{AB}$. It can be shown (cf. Appendix B) that $\tilde{\gamma}_{AB}^{*m, \text{stoich}}$ can be related to the ionic activity coefficients through

$$\tilde{\gamma}_{AB}^{*m, \text{stoich}} = \left[\frac{1}{\nu_A^{\nu_A} \nu_B^{\nu_B}} \frac{\left(\frac{m_{A^+}}{m^0} \right)^{\nu_A} \left(\frac{m_{B^-}}{m^0} \right)^{\nu_B}}{\left(\frac{\tilde{m}_{AB}}{m^0} \right)^{\nu_A + \nu_B}} \left(\gamma_{A^+}^{*m} \right)^{\nu_A} \left(\gamma_{B^-}^{*m} \right)^{\nu_B} \right]^{\frac{1}{\nu_A + \nu_B}}. \quad (27)$$

2.3.3 Solvent. As for the neutral compound, at equilibrium the 'true' and 'overall' chemical potentials of the solvent are equal (cf. Appendix A), i.e.,

$$\mu_W(T, p, \mathbf{x}) = \tilde{\mu}_W(T, p, \mathbf{x}). \quad (28)$$

The chemical potential of solvent W is normalized with respect to the pure liquid at the solution's T and p ,

$$\mu_{\text{W}}(T, p, \mathbf{x}) = \mu_{\text{W}}^{\text{pure liq}}(T, p) + RT \ln a_{\text{W}}(T, p, \mathbf{x}), \quad (29)$$

and the solvent activity is often rescaled to the osmotic coefficient, which is defined as

$$\Phi(T, p, \mathbf{x}) = -\frac{\ln a_{\text{W}}(T, p, \mathbf{x})}{M_{\text{W}} \sum_{i=1, i \neq \text{W}}^N m_i}, \quad (30)$$

where M_{W} is the molar mass of the solvent (in kg mol^{-1}). As evaluating this equation requires knowledge of the true composition of the solution, the stoichiometric osmotic coefficient, defined as,

$$\Phi^{\text{stoich}}(T, p, \mathbf{x}) = -\frac{\ln a_{\text{W}}(T, p, \mathbf{x})}{M_{\text{W}}(\nu_{\text{A}} + \nu_{\text{B}})\tilde{m}_{\text{AB}}}, \quad (31)$$

evaluated assuming that the compound AB is fully dissociated at molality $\tilde{m}_{\text{AB}}$, is used instead.

2.4 Combined dissociation and phase equilibria

The calculation of vapour-liquid equilibria (VLE) involving weak electrolytes requires that the condition for chemical equilibrium, *cf.* eqn (9), is satisfied simultaneously with the phase equilibrium condition at fixed T and p , *i.e.*,

$$\mu_i' = \mu_i'', \quad (32)$$

where the primes indicate the two phases, for all components i present in both phases. Due to the low dielectric permittivity of the vapour phase, the ions remain principally in the liquid phase and hence the phase equilibrium condition (eqn (32)) for ionic species i does not need to be solved explicitly. This drastically simplifies the numerical solution of the resulting system of equations. Moreover, it has been shown in previous work⁴⁶ that if condition (32) is also considered explicitly for the ions, the SAFT-VRE Mie modelling would yield very low values for the mole fractions of the ions in the vapour phase.

3 SAFT-VRE Mie

3.1 Equation of state

The treatment of electrolytes with the SAFT-VRE Mie equation of state (EOS) was presented by Eriksen *et al.*⁴⁸ The total Helmholtz free energy of the mixture is expressed as a sum of residual terms:

$$A = A^{\text{Ideal}} + A^{\text{Mono}} + A^{\text{Chain}} + A^{\text{Assoc}} + A^{\text{Ion}} + A^{\text{Born}}. \quad (33)$$

The first four terms constitute the SAFT-VR Mie EOS presented by Lafitte *et al.*⁴⁹ and correspond to: the ideal gas free energy (A^{Ideal}); the contribution accounting for monomeric spherical segments interacting through Mie potentials of variable range (A^{Mono}); the contribution of these monomers bonding to form chain molecules (A^{Chain}); and the effect of molecular association through short-ranged directional forces (A^{Assoc}). The electrostatic interactions arising from the presence of charged species are

treated within the primitive model formalism, where the electrostatic properties of the solvent is described by a uniform dielectric medium. A model for the relative permittivity of the dielectric medium was presented by Schreckenber *et al.*,⁴⁶ and is adopted here. As the description of the relative permittivity is found to be important for the solutions of weak electrolytes studied here, this model is addressed in more detail in Section 3.4. The Coulombic interactions between charged species in a solvent medium are accounted for in A^{Ion} , using the primitive unrestricted mean spherical approximation (MSA-PM) model of Blum.^{55,56} Instead of an explicit treatment of ion-polar interactions, these are accounted for in A^{Born} , which takes into account the change in free energy associated with charging the ions in a solvent.

We employ two distinct ion size parameters for the two terms: in A^{Ion} , we use the crystal radius, whereas we use larger values of the size parameter for the Born contribution A^{Born} to effectively account for the solvation-effects of the ions. It has been shown by molecular-dynamics simulation^{57,58} and in a recent generalisation of the Born model⁵⁹ that it would be more accurate to interpret the solvation free-energy change associated with ion-solvent interactions as related to the effect of the ion on the orientation of solvent dipoles in the first and second solvation shells, which leads to a reduced local permittivity rather than to an increase in the ion size. We follow here the original picture of Born as we use a primitive model for the electrostatics, in which the solvent is regarded as a continuum and in order that the models proposed here are consistent with those of our previous work relating to strong electrolytes.

Details of the expressions for each of the Helmholtz energy contributions are not repeated here; the reader is instead referred to the original publications.^{48,49}

3.2 Calculation of activity coefficients with SAFT-VRE Mie

The activity coefficient is usually defined at a certain state point determined by T , p , and $\mathbf{x}$. However, molecular equations of state, written in terms of the Helmholtz free energy, such as SAFT-VRE Mie, are expressed with T , V , and $\mathbf{x}$ as the independent variables. As a result the volume V_p at a certain pressure of interest p needs to be evaluated from the equation of state. The fugacity coefficients may then be calculated according to

$$\phi_i(T, p, \mathbf{x}) \equiv \phi_i(T, V_p, \mathbf{x}) = \frac{nRT}{pV_p} \exp\left(\frac{\mu_i^{\text{res}}(T, V_p, \mathbf{x})}{RT}\right), \quad (34)$$

where μ_i^{res} is the residual chemical potential obtained as

$$\mu_i^{\text{res}} = \left(\frac{\partial(A - A^{\text{Ideal}})}{\partial n_i}\right)_{T, V, n_j \neq i}, \quad (35)$$

and where A is given by eqn (33). The activity coefficient in the molality scale (*cf.* (16)) can be obtained as

$$\gamma_i^{\text{m}}(T, p, \mathbf{x}) = \left(\frac{1}{1 + M_{\text{W}} \sum_{i=1, i \neq \text{W}}^N m_i}\right) \frac{\phi_i(T, p, \mathbf{x})}{\phi_i^{\infty}(T, p)}, \quad (36)$$

where the fugacity coefficients ϕ_i are in the mole fraction scale, and the term in brackets takes care of the conversion to the molality scale. The fugacity coefficient of component i at infinite dilution in the solvent,

$$\phi_i^\infty(T, p) = \lim_{x_i \rightarrow 0} \phi_i(T, p, \mathbf{x}), \quad (37)$$

is calculated here by considering a mixture in which the mole fraction of component i is $x_i = 10^{-10}$.

3.3 Species models

3.3.1 Neutral compounds. In the SAFT-VRE Mie EOS, molecules are considered as associating homonuclear chains composed of m spherical segments interacting *via* Mie intermolecular potentials u^{Mie} of variable range. The interaction between components i and j in the mixture is given by:

$$u^{\text{Mie}} = C \varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{\lambda_{r,ij}} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^{\lambda_{a,ij}} \right], \quad (38)$$

with

$$C = \frac{\lambda_{r,ij}}{\lambda_{r,ij} - \lambda_{a,ij}} \left(\frac{\lambda_{r,ij}}{\lambda_{a,ij}} \right)^{\frac{\lambda_{a,ij}}{\lambda_{r,ij} - \lambda_{a,ij}}}, \quad (39)$$

where r_{ij} is the centre–centre distance between segments i and j of the respective components, σ_{ij} is the segment diameter, ε_{ij} is the depth of the potential, and $\lambda_{a,ij}$ and $\lambda_{r,ij}$ are the attractive and repulsive exponents of the intersegment interaction. In the case of associating molecules, the number $N_{\text{ST},i}$ of site types, the number of sites $n_{y,i}$ of each type y , together with the energy $\varepsilon_{ij,ab}^{\text{HB}}$ and the corresponding bonding volume $K_{ij,ab}^{\text{HB}}$ of association between sites must also be specified. All parameters are characterised following the minimisation of an objective function by comparison with experimental data for the system of interest.

3.3.2 Ionic species. In addition to the Mie and association contributions, ionic species possess additional coulombic contributions to the Helmholtz free energy, incorporated *via* A^{ion} and A^{Born} . The ionic contribution is completely defined by the charge of the ion and the parameters introduced earlier; for the Born contribution an additional parameter $\sigma_{ii}^{\text{Born}}$ is introduced. In the present work, all ions i are assumed to be spherical ($m_i = 1$) and are taken to interact *via* the Lennard-Jones potential ($\lambda_{r,ii} = 12$ and $\lambda_{a,ij} = 6$). The segment diameter σ_{ii} of a given ion i , and the Born diameter $\sigma_{ii}^{\text{Born}}$ are taken from the literature. The like and unlike ion–ion dispersion energy parameters ε_{ii} and ε_{ij} , respectively, are calculated using a combining rule,^{48,60} based on the work of Hudson and McCoubrey,⁶¹ which takes into account the polarisability α_0 and ionisation potential I of the interacting species:

$$\varepsilon_{ij} = \frac{(\lambda_{r,ij} - 3)(\lambda_{a,ij} - 3)}{2C(\lambda_{r,ij} - \lambda_{a,ij})} \frac{\alpha_{0,i}\alpha_{0,j}}{(4\pi\epsilon_0)^2\sigma_{ij}^6} \frac{I_i I_j}{I_i + I_j}, \quad (40)$$

where ϵ_0 is the permittivity of vacuum. A number of the ionic species studied here are modelled including unlike association

interactions with other species; self-association of ionic species is however not considered.

3.3.3 Unlike interactions. The interactions between a given pair of unlike components i and j can be estimated through appropriate combining rules, provided that the parameters of the individual segments in the models have been characterised. In the present work, the unlike segment diameter is always obtained as a simple arithmetic mean,⁶²

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2}. \quad (41)$$

Furthermore, the combining rule derived from applying the geometric-mean criterion to the van der Waals attractive energy^{49,50} is applied throughout the present work to obtain all of the unlike attractive and repulsive Mie exponents:

$$\lambda_{z,ij} = 3 + \sqrt{(\lambda_{z,ii} - 3)(\lambda_{z,jj} - 3)}, \quad z \in \{a, r\}. \quad (42)$$

In the case of interactions between two neutral compounds i and j , the unlike dispersion energy can be obtained using an augmented geometric mean which accounts for the size asymmetry of the segments,⁶²

$$\varepsilon_{ij} = \frac{\sqrt{\sigma_{ii}^3 \sigma_{jj}^3}}{\sigma_{ij}^3} \sqrt{\varepsilon_{ii} \varepsilon_{jj}}. \quad (43)$$

The value obtained from this combining rule is, however, typically used only as an initial estimate to guide further refinement of this parameter with respect to experimental data. In the case of interactions between unlike ions i and j , the unlike dispersion energy parameter is always obtained from the Hudson–McCoubrey combining rule, *cf.* eqn (40).

Combining rules can also be used to determine the parameters of the association interaction between an unlike pair of molecules associating *via* site a on molecule i and site b on molecule j . A simple geometric combining rule is used for the unlike association energy,^{51,63}

$$\varepsilon_{ij,ab}^{\text{HB}} = \sqrt{\varepsilon_{ii,aa}^{\text{HB}} \varepsilon_{jj,bb}^{\text{HB}}}, \quad (44)$$

and the unlike bonding volume is obtained by an arithmetic combining rule averaging the volumes of the like interactions:^{51,63}

$$K_{ij,ab}^{\text{HB}} = \left(\frac{\sqrt[3]{K_{ii,aa}^{\text{HB}}} + \sqrt[3]{K_{jj,bb}^{\text{HB}}}}{2} \right)^3. \quad (45)$$

However, as for the unlike dispersion energy, the unlike association parameters resulting from the expressions above are often used only as initial estimates for further refinement of the model with respect to experimental data.

3.4 Relative permittivity model

The relative permittivity D is a key property of electrolyte systems. In the present work, it is required for the evaluation of the A^{ion} and A^{Born} contributions of the Helmholtz free energy. In addition to the dependence of D on the state conditions, the so-called dielectric decrement, *i.e.* the decrease in the relative

permittivity with increasing concentration of the ions, is well-known. By using an electrostatic field-theory^{64,65} and Monte Carlo simulations⁶⁶ the origin of the dielectric decrement has recently been identified to be the saturation of solvent dipoles in close proximity to an ion. In the context of our work it is also of interest to highlight the work of Maribo-Mogensen *et al.*⁶⁷ who have proposed a model for the relative permittivity over wide ranges of temperature, pressure and composition to be used in equation of state models, which can account for the decrement in the values of D as the ion concentration increases. Moreover, a further consideration arises from the fact that the relative permittivity must be formulated in a way such that the resulting equation of state is thermodynamically consistent.⁴⁶

A simple model for the relative permittivity that fulfills the requirements has been presented:⁴⁶ it accounts (to some extent) for the dielectric decrement as the ion concentration increases, and satisfies the Gibbs–Duhem thermodynamic relation. In our model the relative permittivity D of the solution is given by

$$D = 1 + \rho_{\text{solv}} d, \quad (46)$$

where d is a solvent-dependent parameter given by

$$d = d_{\text{v}} \left(\frac{d_{\text{T}}}{T} - 1 \right), \quad (47)$$

and where it is important to note that since the density of the solvent in the mixture ρ_{solv} appears in eqn (46), the model intrinsically accounts for the dielectric decrement effect. In case of mixed solvents, the following combining rules are applied:⁴⁶

$$d(\hat{x}_i) = \sum_{i=1}^{N_{\text{solv}}} \sum_{j=1}^{N_{\text{solv}}} \hat{x}_i \hat{x}_j d_{ij}, \quad (48)$$

where the hat is used to indicate true ion-free mole fractions, *i.e.*,

$$\hat{x}_i = \frac{n_i}{\sum_{j=1, j \neq \text{ion}}^N n_j}, \quad (49)$$

where the sum runs over all non-charged species, and the parameter d_{ij} is given by

$$d_{ij} = \frac{d_{ii} + d_{jj}}{2}. \quad (50)$$

In these systems, all neutral molecular species must be treated as ‘additional solvents’, especially at high concentrations of such species. Thus, they need to be assigned d_{v} and d_{T} parameters in the model, as they would otherwise contribute an unphysical dielectric decrement effect akin to that of the ions. This is especially important when modelling aqueous solutions of nitric acid, for which the entire concentration range from pure water to pure nitric acid is studied. At high concentrations of nitric acid in water, the equilibrium is such that almost all of the nitric acid remains in its molecular (neutral) form, *cf.* Section 5.3.1. The relative permittivity of undissociated nitric acid is needed to model this region. Unfortunately, to the best of our knowledge, no experimental data on the relative permittivity of pure nitric acid are available. We propose the use of an analogy: nitric acid and methanol have similar molar densities

and dipole moments of similar order of magnitude. In the model given by eqn (46), the parameter d provides a measure of ‘polarity per volume’. Thus, if two substances have the same molar density and a similar polarity, they can be expected to be characterised by a similar d parameter. We therefore adopt the d_{v} and d_{T} parameters for methanol presented in earlier work.⁴⁶ and use them to obtain an estimate of the relative permittivity of nitric acid. In the carbonic acid system, carbon dioxide is the only additional molecular species, for which the parameters d_{v} and d_{T} have been provided.⁴⁶ In the solutions of sulphuric acid, water is the only molecular species.

3.5 Parameter estimation strategy

In the present work, we develop new SAFT-VRE Mie models for the ions needed to model aqueous solutions of sulphuric, nitric, and carbonic acid, as well as a model for molecular nitric acid. Models for water and the hydronium ion are taken from previous work.^{48,51} All parameters of the model of pure nitric acid are determined by comparison to experimental vapour–liquid equilibrium data. As outlined above, in order to model the mixtures of interest, the only parameters that are estimated from the experimental data are the unlike energy parameters ε_{ij} (where either i or j , or both, is a neutral compound or solvent) and the association parameters $\varepsilon_{ij}^{\text{HB}}$ and K_{ij}^{HB} (where i and j may be a neutral or ionic species). These parameters are obtained by minimising an objective function F_{obj} , containing the sum of squares of the relative deviations between experimental data and calculated values of several objectives Z_k :

$$\min F_{\text{obj}} = \sum_{k=1}^{N_{\text{Prop}}} \frac{1}{N_{p,k}} \sum_{l=1}^{N_{p,k}} \left(\frac{Z_{k,l}^{\text{exp}} - Z_{k,l}^{\text{calc}}}{Z_{k,l}^{\text{exp}}} \right)^2 \quad (51)$$

where N_{Prop} is the number of properties considered, $N_{p,k}$ is the number of evaluated state points for property Z_k , and $Z_{k,l}^{\text{exp}}$ and $Z_{k,l}^{\text{calc}}$ denote the experimental and calculated values of property Z_k at state point l . Details of the parameter estimation procedure, *i.e.*, the choice of properties and parameters to adjust for each of the weak electrolytes considered, are given in the corresponding section.

The parameters of the SAFT-VRE Mie models developed in the present work are compiled in Tables 1–3, and the ionisation potentials and polarisabilities used for determining the ion–ion dispersion energy parameters are compiled in Table 4.

4 Sulphuric acid

Sulphuric acid (H_2SO_4) is a highly polar substance, which is in the liquid state at ambient conditions. It undergoes autoprotolysis and is highly hygroscopic. In aqueous solution, sulphuric acid is generally regarded as a ‘strong’ acid due to its 2:1 stoichiometry, forming the bisulfate (HSO_4^-) and sulfate (SO_4^{2-}) ions. Although it can also be considered a weak electrolyte, in that the dissociation of the second proton is typically incomplete, except at very high dilution. Nevertheless, aqueous solutions of sulphuric acid are highly acidic and are used as oxidizing and dehydrating agents.

Table 1 SAFT-VRE Mie model parameters for the species present in aqueous solutions of sulphuric acid, nitric acid, and carbonic acid. The models for H₂O, H₃O⁺, and CO₂ are taken from previous work (ref. 48, 51 and 68 respectively). All other models are developed in this work. For a species *i*, *m_i* is the chain length, *σ_{ii}* the segment diameter, *σ_{ii}^{Born}* is the Born diameter (applicable to ions only), *λ_{r,ii}* and *λ_{a,ii}* are the repulsive and attractive exponents of the Mie potential, respectively, *ε_{ij}* is the dispersion energy, *n_{H,i}* and *n_{e,i}* are the numbers of 'H' (hydrogen-bond donor) and 'e' (hydrogen-bond acceptor) type association sites, respectively, *ε_{ii,ab}^{HB}* is the association strength of the interaction of two sites *a* and *b*, and *K_{ii,ab}^{HB}* is the corresponding bonding volume

Species <i>i</i>	<i>m_i</i>	<i>σ_{ii}/Å</i>	<i>σ_{ii}^{Born}/Å</i>	<i>λ_{r,ii}</i>	<i>λ_{a,ii}</i>	<i>(ε_{ii}/k_B)/K</i>	<i>n_{H,i}</i>	<i>n_{e,i}</i>	<i>(ε_{ii,ab}^{HB}/k_B)/K</i>	<i>K_{ii,ab}^{HB}/Å³</i>
H ₂ O	1.0000	3.0063	—	17.020	6.0000	266.68	2	2	1985.4	101.69
H ₃ O ⁺	1.0000	3.0063	3.0063	17.020	6.0000	68.190	3	—	—	—
HSO ₄ [−]	1.0000	4.1200	4.4084	12.000	6.0000	82.086	—	—	—	—
SO ₄ ^{2−}	1.0000	4.6000	5.1600	12.000	6.0000	70.322	—	4	—	—
HNO ₃	1.3452	3.6190	—	16.347	6.0000	496.33	1	3	1300.0	8.9978
NO ₃ [−]	1.0000	3.5800	4.0000	12.000	6.0000	97.853	—	3	—	—
CO ₂	1.6936	3.0500	—	26.408	5.0550	207.89	—	1	—	—
HCO ₃ [−]	1.0000	3.1200	4.3000	12.000	6.0000	378.24	—	4	—	—

Table 2 SAFT-VRE Mie unlike-interaction parameters for the species present in aqueous solutions of sulphuric acid, nitric acid, and carbonic acid. The unlike-interaction parameters *σ_{ij}*, *λ_{r,ji}*, and *λ_{a,ji}* are omitted from this table as they are obtained with combining rules, eqn (41) and (42), respectively. The interaction parameters for H₂O–H₃O⁺ and H₂O–CO₂ are taken from ref. 48 and 68, respectively. All other unlike interaction parameters are developed in this work. All unlike ion–ion dispersion energies are calculated using the Hudson–McCoubrey rule.⁶¹ The procedures for the determination of the remaining parameters are detailed in the text

Species		Site		<i>(ε_{ij,ab}^{HB}/k_B)/K</i>	<i>K_{ij,ab}^{HB}/Å³</i>	<i>(ε_{ij}/k_B)/K</i>
<i>i</i>	<i>j</i>	<i>i,a</i>	<i>j,b</i>			
H ₂ O	H ₃ O ⁺	e	H	1985.4	101.69	391.04
H ₂ O	HSO ₄ [−]	—	—	—	—	142.57
H ₂ O	SO ₄ ^{2−}	—	—	—	—	128.03
HSO ₄ [−]	H ₃ O ⁺	—	—	—	—	60.476
HSO ₄ [−]	SO ₄ ^{2−}	—	—	—	—	75.239
H ₃ O ⁺	SO ₄ ^{2−}	H	e	2266.0	43.700	53.609
H ₂ O	HNO ₃	H	e	2900.0	38.401	270.00
H ₂ O	HNO ₃	e	H	1606.6	38.401	270.00
H ₂ O	NO ₃ [−]	H	e	2350.0	97.014	161.55
HNO ₃	H ₃ O ⁺	—	—	—	—	181.61
HNO ₃	NO ₃ [−]	—	—	—	—	220.37
H ₃ O ⁺	NO ₃ [−]	H	e	2900.0	38.401	61.788
H ₂ O	CO ₂	H	e	1398.1	91.419	226.38
H ₂ O	HCO ₃ [−]	H	e	1398.1	91.419	317.43
CO ₂	H ₃ O ⁺	—	—	—	—	189.86
CO ₂	HCO ₃ [−]	—	—	—	—	371.59
H ₃ O ⁺	HCO ₃ [−]	H	e	1398.1	91.419	130.28

Table 3 Parameters for the dielectric constant correlation, taken from ref. 46

Species	<i>d_v/dm³ mol^{−1}</i>	<i>d_T/K</i>
H ₂ O	0.3777	1403.0
HNO ₃	0.5484	1011.0
CO ₂	−0.0250	0

4.1 Dissociation equilibrium

In aqueous solution, sulphuric acid undergoes two sequential dissociation steps,⁷⁴ both of which entail a proton-transfer reaction with water:

Table 4 Values for the polarisability and electron affinity of the ions relevant to this work. Data for HSO₄[−] and SO₄^{2−} are taken from ref. 69–71, data for NO₃[−] are taken from ref. 69 and 72, and data for CO₂ and HCO₃[−] are taken from ref. 69 and 73

Species	<i>α₀/(10^{−24} cm³)</i>	<i>I/eV</i>
HSO ₄ [−]	5.0890	4.7500
SO ₄ ^{2−}	6.3270	5.1000
NO ₃ [−]	4.4800	3.1450
CO ₂	2.9100	13.780
HCO ₃ [−]	5.3900	3.6800

and

The thermodynamic equilibrium constants *K_{a1}* and *K_{a2}* corresponding to the first and second dissociation steps, respectively, characterise the thermodynamic equilibrium for these reactions. Using the molality scale, they are given by (cf. eqn (19))

$$K_{a1}(T) = \frac{m_{\text{H}_3\text{O}^+} m_{\text{HSO}_4^-} \gamma_{\text{H}_3\text{O}^+}^{\text{sm}} \gamma_{\text{HSO}_4^-}^{\text{sm}}}{m_{\text{H}_2\text{SO}_4} m^0 \gamma_{\text{H}_2\text{SO}_4}^{\text{sm}}}, \quad (54)$$

and

$$K_{a2}(T) = \frac{m_{\text{H}_3\text{O}^+} m_{\text{SO}_4^{2-}} \gamma_{\text{H}_3\text{O}^+}^{\text{sm}} \gamma_{\text{SO}_4^{2-}}^{\text{sm}}}{m_{\text{HSO}_4^-} m^0 \gamma_{\text{HSO}_4^-}^{\text{sm}}}. \quad (55)$$

There is consensus in the literature that *K_{a1}*(*T*) → ∞, so that the first dissociation step is essentially complete, except at very high acid concentrations *c_{H₂SO₄}* > 14 mol l^{−1}.^{74–76} By contrast, the second dissociation step is comparatively weak, with *K_{a2}*(298 K) = 0.0105,⁷⁷ i.e., p*K_{a2}* ≈ 1.98. A variety of reaction mechanisms have been suggested, with investigators proposing a range of intermediate proton transfer steps, hydrogen-bonded ion–solvent complexes, and ion-association equilibria.^{78–81} For the purpose of equation-of-state modelling, the intermediate reaction steps need not be explicitly considered; nevertheless, these propositions can provide valuable insight into association interactions that may be incorporated in a SAFT-type modelling (cf. Section 4.2).

Within the composition range (*m* ≤ 10 mol kg^{−1}) where the SAFT-VRE Mie EOS is applicable to electrolyte solutions,⁴⁶ the first dissociation step of sulphuric acid can be considered to be

complete, and therefore the reaction equilibrium for the first dissociation step does not need to be taken into account explicitly. The second (weak) dissociation step is solved by imposing the thermodynamic equilibrium constant K_{a2} at the temperature of interest in the SAFT-VRE Mie calculations.

Significant research effort has been expended into determining the second thermodynamic equilibrium constant of sulphuric acid. Dickson *et al.*⁸² employed electrochemical-cell measurements to determine K_{a2} and proposed an empirical equation applicable in the temperature range 283–523 K. Holmes and Mesmer⁸³ used their correlation together with new and previously published⁸⁴ isopiestic data to propose a new correlation for K_{a2} . A thorough examination of the thermodynamic data (osmotic coefficient, vapour pressure, electromotive force, enthalpy of dilution, heat capacity, and degree of dissociation) available at the time was performed by Clegg *et al.*,⁷⁷ on the basis of which a value of 0.0105 was recommended for K_{a2} at 298 K. Using this benchmark, Clegg *et al.* evaluated various correlations for K_{a2} based on their reproduction of critically assessed experimental data in the ranges of $\tilde{m}_{\text{H}_2\text{SO}_4} = 0\text{--}6.1 \text{ mol kg}^{-1}$ and $T = 273\text{--}328 \text{ K}$ using an extended Pitzer model. They recommended a truncated version of Dickson's equation, given as

$$\begin{aligned} \log_{10} K_{a2} = & 562.69486 - 102.5154 \ln(T/\text{K}) \\ & - 1.117033 \times 10^{-4} ((T/\text{K})^2) \\ & + 0.2477538(T/\text{K}) - \frac{13273.75}{(T/\text{K})}. \end{aligned} \quad (56)$$

More recently, Sippola^{85,86} examined six equations for the thermodynamic equilibrium constant, including those of Pitzer *et al.*,⁸⁴ Matsushima and Okuwaki,⁸⁷ Dickson *et al.*,⁸² Hovey and Hepler,⁸⁸ Clegg *et al.*,⁷⁷ and Knopf *et al.*⁸⁹ The equations of Matsushima, Dickson, Hovey, and Clegg *et al.* were found to give the most reliable values for K_{a2} overall, although the equation of Knopf *et al.* was found to be more suitable for use at high temperatures. Sippola concludes that the choice of correlation ultimately depends on the temperature range of the intended application. For the purpose of this work, we choose to apply the correlation given by eqn (56). This equation has been developed so as to give an accurate K_{a2} value at 298 K, which is the temperature at which most of the thermodynamic data are available for sulphuric acid.

4.2 Association scheme

The appropriate speciation behaviour in this complex system is still the subject of much debate. Edward and Wang⁷⁸ measured the ultraviolet absorption of aqueous sulphuric acid solutions and used the Raman spectrum data of Young *et al.*⁹⁰ to propose the existence of sulfate–hydronium ion pairs $[\text{H}_3\text{O}^+ \cdot \text{SO}_4^{2-}]$ and ion triplets $[\text{H}_3\text{O}^+ \cdot \text{SO}_4^{2-} \cdot \text{H}_3\text{O}^+]$, predominantly at high concentrations of $\tilde{c}_{\text{H}_2\text{SO}_4} > 7 \text{ mol l}^{-1}$. The authors argue that these ion pairs are the result of abundant hydrogen bonding between the hydronium ions and water molecules, which limits the amount of water available to hydrate other ions, thus promoting ion-association of the unhydrated sulfate ions. A similar conclusion

was reached by Irish and Chen,⁸¹ who examined Raman spectra of aqueous sulphuric acid and suggested that the second dissociation step of sulphuric acid is driven by a proton transfer equilibrium between the hydrated bisulfate ion $(\text{H}_2\text{O})\text{HSO}_4^-$ and the sulfate–hydronium ion-pair $[\text{H}_3\text{O}^+ \cdot \text{SO}_4^{2-}]$, *i.e.*,

In subsequent work, Chen and Irish⁷⁹ extended this argument by proposing the formation of the bisulfate–hydronium ion pair $[\text{H}_3\text{O}^+ \cdot \text{HSO}_4^-]$ through a further proton-transfer reaction equilibrium:

Cox *et al.*⁸⁰ also analysed Raman spectra and put forward a dissociation sequence for sulphuric acid involving three equilibrium steps. In this scheme, the first acid dissociation reaction given by eqn (52) is replaced by two equilibrium steps: first the formation of a hydrated bisulfate–hydronium ion pair,

followed by equilibrium of this ion pair with the free bisulfate and hydronium ions. The existence of the $[(\text{H}_2\text{O})\text{HSO}_4^- \cdot \text{H}_3\text{O}^+]$ ion pair at high concentrations was first proposed by Irish and Chen⁸¹ as an alternative interpretation of the $[\text{H}_3\text{O}^+ \cdot \text{H}_2\text{SO}_4]$ species suggested by Wyatt.⁹¹ Cox *et al.*,⁸⁰ however, argued that the hydronium–bisulfate ion-pair is formed in the initial dissociation step and is present at all acid concentrations, including dilute solutions.

Admittedly, the presence of these various ion pairs has not been verified and the true composition of the aqueous sulphuric acid solution is still under debate.⁹² In addition, the hydration state of the sulfate and bisulfate ions also remains unresolved. Both ions would be expected to form multiple hydrogen bonds with water and studies have suggested that both sulfate and bisulfate ions form complex hydrogen-bonded clusters with water in solution. Yacovitch *et al.*⁹³ studied the hydration of the bisulfate ion using infrared spectroscopy, observing $\text{HSO}_4^-(\text{H}_2\text{O})_n$ clusters involving up to 16 water molecules with inter-water bonding within the clusters, starting at $n \geq 2$. In a study using photoelectron spectroscopy to study the hydration of the sulfate ion, Wang *et al.*⁹⁴ identified $\text{SO}_4^{2-}(\text{H}_2\text{O})_n$ clusters involving up to 10 water molecules. A minimum of three water molecules were found necessary to stabilise the SO_4^{2-} ion, and inter-water bonding within the cluster was proposed to start at $n \geq 5$.

Despite doubt over the longevity of the hydration clusters and inconclusive evidence of ion association, hydrogen bonding of HSO_4^- and SO_4^{2-} with water and with the hydronium ion are considered in our SAFT-VRE Mie modelling approach, the latter interaction intended to mimic the ion pairing effects. Several different association schemes are tested here. When studying the sensitivity of the thermodynamic properties with respect to the association parameters, we observe that only one of the many possible association interactions has a noticeable impact on the resulting agreement between our model and the experimental data: the association between SO_4^{2-} and H_3O^+ . Thus, only this

association is introduced in the final SAFT-VRE Mie model for aqueous sulphuric acid. Four 'e' type sites are placed on SO_4^{2-} which only interact with the 'H' type sites on H_3O^+ .

4.3 Model development

4.3.1 Objectives. Two target properties are considered in the adjustment of the model parameters (*cf.* eqn (51)): the degree of dissociation of the bisulfate ion $\alpha_{\text{HSO}_4^-}$, defined as

$$\alpha_{\text{HSO}_4^-} = \frac{m_{\text{SO}_4^{2-}}}{m_{\text{HSO}_4^-} + m_{\text{SO}_4^{2-}}} = \frac{m_{\text{SO}_4^{2-}}}{\tilde{m}_{\text{H}_2\text{SO}_4}}, \quad (60)$$

and the water activity $a_{\text{H}_2\text{O}}$ (eqn (29)), both at 298.15 K and 1 bar. The experimental data for the degree of dissociation^{78,79,95} are considered up to $\tilde{c}_{\text{H}_2\text{SO}_4} \approx 5 \text{ mol l}^{-1}$ and the water activity data^{96–98} are considered up to $\tilde{m}_{\text{H}_2\text{SO}_4} \approx 3 \text{ mol kg}^{-1}$ in the parameter determination step.

4.3.2 Like parameters. The ionic diameters σ_{ii} assigned to the ions must reflect the size and charge density of the species relative to each other. The more negative charge and hence stronger repulsions in the SO_4^{2-} ion lead to a larger diameter compared to HSO_4^- , in which the gain of a proton leads to more tightly held electrons. The sizes of these ions are reported in the literature, most commonly as the radius of the ions in a crystal lattice. The thermochemical ionic sizes given by Krestov⁹⁹ are selected for both ions in this work; using a single internally consistent source for these parameters also satisfies the requirement of relative size mentioned above.

The Born diameter for the SO_4^{2-} model is obtained from the extensive study of Babu and Lim,⁵⁷ in which the Born cavity size of the ions was identified using molecular-dynamics simulations. The bisulfate ion was not considered in their study, therefore the Born cavity diameter of HSO_4^- is determined by implementing the method proposed by Rashin and Honig,¹⁰⁰ namely that a reasonable measure of the cavity size of anions can be obtained by applying a 7% increase to the ionic diameters of the ions. The diameter that Babu and Lim⁵⁷ recommend for the sulfate ion is 12% larger than the crystal ionic diameter assigned to this ion. This is comparable to the 7% increase recommended

by Rashin and Honig, hence the two sources are considered compatible.

The dispersion energy ε_{ii} corresponding to the attractive interaction between two ions of the same type i is determined by applying the ion–ion combining rule given in eqn (40). The polarisabilities of HSO_4^- and SO_4^{2-} are obtained from Pyper *et al.*⁶⁹ and Hou *et al.*,⁷⁰ respectively, and the ionisation potentials of both ions are obtained from Wang *et al.*,⁷¹ these values are collected in Table 4.

4.3.3 Unlike parameters. The parameters $\lambda_{a,ij}$, $\lambda_{r,ij}$, and σ_{ij} between any two unlike species, as well as the dispersion energy parameter ε_{ij} between any two ions are determined from combining rules as detailed in Section 3.3.3. The remaining interaction parameters that need to be determined are the dispersion energies $\varepsilon_{\text{H}_2\text{O},\text{HSO}_4^-}$ and $\varepsilon_{\text{H}_2\text{O},\text{SO}_4^{2-}}$ as well as the parameters of the association interaction between SO_4^{2-} and H_3O^+ .

When estimating these parameters by comparison to experimental data, it is found that the degree of dissociation and water activity rather insensitive to the unlike energy parameters $\varepsilon_{\text{H}_2\text{O},\text{SO}_4^{2-}}$ and $\varepsilon_{\text{H}_2\text{O},\text{HSO}_4^-}$, and the values obtained from the combining rule, *cf.* eqn (43), are used directly. By contrast, the association parameters between SO_4^{2-} and H_3O^+ have a great influence on both objectives. Optimizing the description of the experimental data by varying the two association parameters $\varepsilon_{\text{H}_3\text{O}^+,\text{SO}_4^{2-}}^{\text{HB}}$ and $K_{\text{H}_3\text{O}^+,\text{SO}_4^{2-}}^{\text{HB}}$ leads to parameters indicating a strong association interaction, *cf.* Table 2. This supports the hypothesis of strongly associated $[\text{H}_3\text{O}^+\cdot\text{SO}_4^{2-}]$ ion pairs, discussed in Section 4.2.

4.4 Description of thermodynamic properties

4.4.1 Degree of dissociation and solution composition. In Fig. 1, experimental data for the degree of dissociation of the bisulfate ion and the individual ion molarities are shown as a function of the overall sulphuric acid molarity and compared with the results of our model. In order to calculate the molarity, we use the density of the solution as calculated by the model for the given thermodynamic conditions.

Fig. 1 Degree of dissociation of the bisulfate ion (left) and individual ion molarities (right) as functions of the overall molarity of sulphuric acid in aqueous solution at 298.15 K. Continuous curves: SAFT-VRE Mie calculations, symbols: experimental data from the literature (circles,⁷⁹ squares,⁷⁸ triangles,¹⁰¹ diamonds⁹⁵).

The degree of dissociation data of Hood and Reilly¹⁰¹ show considerable scatter and are therefore disregarded in the parameter estimation of the SAFT-VRE Mie model. The other three experimental data sets for $\alpha_{\text{HSO}_4^-}$ ^{78,79,95} are in mutual agreement. It can be seen that an infinitely dilute solution of sulphuric acid contains a negligible fraction of bisulfate ions, with $\alpha_{\text{HSO}_4^-}$ approaching unity. With increasing concentration of the acid, the degree of dissociation quickly falls to a minimum of ≈ 0.17 , indicating that the majority of HSO_4^- ions do not dissociate, then rises to a maximum of ≈ 0.37 before again decreasing steadily with increasing acid concentration. The SAFT-VRE Mie model is in excellent agreement with these data. This of course translates to a good representation of the individual ion molarities.

4.4.2 Water activity and mean-ionic activity coefficient. As outlined in Section 2.3.3, using the osmotic coefficient in model development can be misleading when studying weak electrolytes. This is especially the case for aqueous solutions of sulphuric acid which has more than one dissociation step. Instead, the water activity (*cf.* eqn (29)) is studied here. The water activity and the stoichiometric mean-ionic activity coefficient of sulphuric acid, defined as (*cf.* eqn (27))

$$\gamma_{\text{H}_2\text{SO}_4}^{\text{m,stoich}} = \left[\frac{1}{4} \frac{(m_{\text{H}_3\text{O}^+})^2 m_{\text{SO}_4^{2-}}}{(\tilde{m}_{\text{H}_2\text{SO}_4})^3} (\gamma_{\text{H}_3\text{O}^+}^{\text{m}})^2 \gamma_{\text{SO}_4^{2-}}^{\text{m}} \right]^{1/3}, \quad (61)$$

are presented as a function of the overall sulphuric acid molality in Fig. 2.

The water activity is included in the estimation of the model parameters for molalities up to $\tilde{m}_{\text{H}_2\text{SO}_4} \approx 3 \text{ mol kg}^{-1}$. The SAFT-VRE Mie model provides a good description of these data and moreover, the water activities at much higher acid concentrations are also predicted to be in good agreement with the experimental data.

The stoichiometric mean-ionic activity coefficient is not included in the fit and is thus described predictively with the present SAFT-VRE Mie model (*cf.* Fig. 2, right panel). Despite not considering this property in the model development, the SAFT-VRE Mie predictions are found to be in excellent agreement

with the experimental data. The accurate prediction of this property at high temperatures not only highlights the predictive capability of our modelling approach, but also further validates the chosen association scheme.

4.4.3 Vapour pressure and solution density. We now examine two further properties which can be predicted with the SAFT-VRE Mie model: the vapour pressure and the liquid density of aqueous solutions of sulphuric acid. These are presented as a function of the overall sulphuric acid molarity at different temperatures in Fig. 3.

The vapour pressure is significantly affected by the value of the solvent-solute dispersion interaction. The predictions obtained using our SAFT-VRE Mie model for the vapour pressure of aqueous solutions of sulphuric acid are in excellent agreement with the experimental data across a wide temperature range and up to high acid concentrations, indicating that the dispersion interactions are modelled accurately.

The liquid density is another key property for assessing the performance of our sulphuric acid model since most of the SAFT-VRE Mie parameters with the greatest influence on the density, namely the size and energy parameters of the Mie potential, are either assigned experimental values or set by combining rules. In Fig. 3 a good agreement between the SAFT-VRE Mie predictions and the experimental data for the solution density at different temperatures and concentrations is seen, indicating that suitable ionic diameters have been assigned to the HSO_4^- and SO_4^{2-} ions, and that the choice of implementing combining rules is appropriate for assigning the dispersion interactions in this system.

5 Nitric acid

5.1 Pure nitric acid model

Nitric acid (HNO_3) is a challenging compound to work with, as it undergoes spontaneous decomposition as well as self-ionic dissociation. This unstable chemical behaviour makes the pure acid difficult to obtain and maintain for experimental purposes. In practice the true composition of a quantity of

Fig. 2 Activity of water at 298.15 K (left) and stoichiometric mean-ionic activity coefficient of sulphuric acid at different temperatures (right) as functions of the overall molality of sulphuric acid in aqueous solution. Continuous curves: SAFT-VRE Mie predictions, symbols: experimental data from the literature (left: circles,⁹⁶ squares,⁹⁷ triangles,⁹⁸ right: circles,¹⁰² squares¹⁰³).

Fig. 3 Vapour pressure (left) and liquid density (right) as functions of the overall molality of sulphuric acid in aqueous solution at different temperatures. Continuous curves: SAFT-VRE Mie prediction, symbols: experimental data from the literature (left:¹⁰⁴ right: circles,⁸⁸ squares¹⁰⁵).

'pure' nitric acid also contains nitrate, nitronium, and hydronium ions, as well as water and nitrogen dioxide.¹⁰⁶ However, experimental data for nitric acid are not accompanied by any such information regarding the degree to which HNO_3 decomposes or ionises, hence it is not possible to take this into account for the purpose of model development. The assumption adopted here is that these reactions may be considered negligible such that experimental data may be taken to correspond to pure nitric acid.

5.1.1 Association scheme. A distinctive characteristic of the HNO_3 molecule is its strong affinity to hydrogen bonding. A spectroscopic study by Guillory and Bernstein¹⁰⁷ has suggested that nitric acid self-associates *via* intermolecular hydrogen bonding, forming doubly hydrogen bonded cyclic dimers – a structure that Odutola and Dyke¹⁰⁸ later confirmed. Nitric acid dimerisation is mediated in the SAFT-VRE Mie model *via* association sites on the HNO_3 model. In principle, the dimerisation can be achieved with one donor ('H'-type) site and one acceptor ('e'-type) site (self-association of the donor and acceptor sites is forbidden). However, since the HNO_3 model will also be used in aqueous solutions, it is prudent to design the association scheme in such a way as to facilitate its association with water. McCurdy *et al.*¹⁰⁹ have concluded through spectroscopic observation and theoretical calculations that HNO_3 molecules form stable clusters with up to four water molecules, although they agree with previous work by Canagaratna *et al.*¹¹⁰ that in any given cluster no more than two water molecules are directly bonded to the nitric acid molecule. In order to take into account the thermodynamic influence of these clusters in an effective manner, we implement an association scheme that includes one donor ('H'-type) site and three acceptor ('e'-type) sites on HNO_3 .

5.1.2 Model development. The SAFT-VRE Mie model for the HNO_3 molecule is developed by estimating the model parameters from the vapour pressure and the saturated-liquid density, making use of the whole range of temperatures for which data are available. Experimental data at temperatures higher than $T > 373$ K are not available, possibly due to the aforementioned difficulties associated with nitric acid stability. A prediction of the critical properties exists,¹¹¹ but is excluded

from the present analysis and discussion as the resulting estimate for the critical temperature is so high that it is likely that the acid would decompose to a large extent at those conditions.

Our optimal model for nitric acid is presented in Table 1. In the development of the model, the attractive Mie exponent is fixed to $\lambda_a = 6$ and the number of association sites is assigned as $n_H = 1$ and $n_e = 3$; all other parameters are characterised by minimisation of the objective function (*cf.* (51)). We find a value for the parameter m which corresponds to a non-spherical geometry, a finding which is in accordance with the planar structure of the HNO_3 molecule.¹⁰⁶ Taking into account the optimised segment diameter σ , the overall size of the HNO_3 molecule is $\sim 26\%$ larger than the size experimentally determined for the NO_3^- ion (see Section 5.2.3), which is physically reasonable. In terms of the energetic parameters, the strong self-association energy at short range parallels the expected dimerisation behaviour. The performance of the model is illustrated in Fig. 4 in terms of the vapour pressure and saturated-liquid density of pure nitric acid, in comparison to experimental data.

The SAFT-VRE Mie model calculations are in good agreement with the available experimental data. For both properties, the temperature range for which experimental data are available roughly matches the temperature range for which the corresponding data are available for aqueous solutions of nitric acid, so that altogether, this model provides a good starting point for modelling the aqueous solutions.

5.2 Aqueous nitric acid

In aqueous solution, nitric acid dissociates incompletely, yet appreciably, producing a solution containing solvated nitrate ions (NO_3^-), hydronium ions (H_3O^+), and the molecular acid (HNO_3). Nitric acid is generally regarded as a 'strong' acid due to its high degree of dissociation at low concentrations, *e.g.* at room temperature, $\alpha_{\text{HNO}_3} \geq 95\%$ for $m_{\text{HNO}_3} \leq 2 \text{ mol kg}^{-1}$. Within this range of solution compositions nitric acid could be reasonably approximated as a strong electrolyte. However, in order to model nitric acid across a wide range of compositions it is useful to develop a general model that incorporates speciation.

Fig. 4 Vapour pressure (left) and saturated-liquid density (right) of pure nitric acid as functions of the temperature. Only the temperature range in which experimental data are available is shown. No data are available for the saturated-vapour density of nitric acid. Curves: SAFT-VRE Mie predictions, symbols: experimental data from the literature (left: circles,¹¹² squares,¹¹³ triangles,¹¹⁴ diamonds,¹¹⁵ right: circles,¹¹⁶ squares,¹¹⁷ triangles¹¹⁸).

Both approaches are pursued here as a means of demonstrating the benefit of modelling the weak electrolyte explicitly. We use the terms ‘strong electrolyte model’ and ‘weak electrolyte model’ to distinguish both approaches in the following discussion.

5.2.1 Dissociation equilibrium. In aqueous solution, nitric acid partially dissociates according to the following proton-transfer reaction with water:

In the molality scale, the thermodynamic equilibrium constant K_a of this reaction is given by (cf. eqn (19))

$$K_a(T) = \frac{m_{\text{H}_3\text{O}^+} m_{\text{NO}_3^-} \gamma_{\text{H}_3\text{O}^+}^{\text{m}} \gamma_{\text{NO}_3^-}^{\text{m}}}{m_{\text{HNO}_3} m^0 \gamma_{\text{HNO}_3}^{\text{m}}}, \quad (63)$$

and at room temperature $\text{p}K_a \approx -1.40$. This thermodynamic equilibrium constant has been studied over a wide temperature range, employing a range of experimental techniques. In an early investigation, Hood and Reilly¹¹⁹ determined the thermodynamic equilibrium constant for aqueous nitric acid at three temperatures between 273–343 K by using proton magnetic resonance to obtain the dissociation quotient of the reaction and then combining this with activity coefficient measurements from previous studies to calculate K_a . Using flow calorimetry, Oscarson *et al.*¹²⁰ obtained K_a for three temperatures between 523–592 K, and later Chlistunoff *et al.*¹²¹ measured K_a for nitric acid at 653 K and 673 K using UV-vis spectroscopy. Taking an indirect approach, Marshall and Slusher¹²² determined the thermodynamic equilibrium constant of nitric acid in water by measuring the solubility of calcium sulphate in aqueous nitric acid solutions. The measured solubility product for the salt and the known thermodynamic equilibrium constant of the second dissociation step of sulphuric acid were used to deduce K_a for nitric acid by extrapolation. Marshall and Slusher¹²³ also used the same approach to obtain K_a for nitric acid from solubility measurements of magnesium sulphate in aqueous nitric acid, with comparable results. In each study the authors proposed a correlation to calculate K_a as a function of temperature; the two correlations provide similar predictions for the thermodynamic equilibrium constant of nitric acid.

In the former publication, the authors included also data from other studies in the regression, thus obtaining a correlation which is applicable for temperatures between 273–623 K:

$$\log_{10} K_a = 5.424 - \frac{134.37}{(T/\text{K})} - 0.01199(T/\text{K}). \quad (64)$$

Eqn (64) is chosen as the best means for calculating the thermodynamic equilibrium constant of nitric acid in the present work.

5.2.2 Association scheme. The hydration number for nitrate ions in aqueous solution has been reported over the range of 1.3–17.7 based on diffraction measurements in the bulk solution,^{124,125} leading to conflicting interpretations of the ion being either unhydrated or weakly hydrogen bonded to water. By contrast, *ab initio* theoretical calculations by Howell *et al.*¹²⁶ suggested that NO_3^- forms stable clusters with three water molecules, each of which hydrogen bonds to the oxygen atoms on the NO_3^- ion such that all six lone electron pairs on the ion are occupied. In a subsequent study Wang *et al.*¹²⁷ demonstrated using photoelectron spectroscopy that the first solvation shell of the nitrate ion consists of three water molecules, and also confirmed Howell’s aforementioned hydrogen-bonding scheme between NO_3^- and H_2O *via* density functional theory (DFT) calculations.

Spectroscopic and theoretical studies of hydrogen bonding between molecular nitric acid and water have suggested that HNO_3 associates with up to four H_2O molecules, with the acid ionising upon associating with the fourth water molecule. McCurdy *et al.*¹⁰⁹ identified $\text{HNO}_3(\text{H}_2\text{O})_n$ clusters with $n = 1$ –3 using Fourier transform infrared spectroscopy. Using first principles electronic structure calculations, the authors obtained the structures for clusters with $n = 1$ –4 and showed that for $n = 4$ two stable hydrogen bonded clusters are feasible: $\text{HNO}_3(\text{H}_2\text{O})_4$ as a global minimum and the solvated ion pair $[\text{NO}_3^-(\text{H}_2\text{O})_3 \cdot \text{H}_3\text{O}^+]$ as a local minimum. Shortly afterwards, Scott and Wright¹²⁸ studied the same $\text{HNO}_3(\text{H}_2\text{O})_n$ clusters using *ab initio* and DFT molecular orbital calculations. Although these authors proposed a different geometry for the nitrate–hydronium ion pair, the existence of both $\text{HNO}_3(\text{H}_2\text{O})_4$

and $[\text{NO}_3^-(\text{H}_2\text{O})_3\cdot\text{H}_3\text{O}^+]$ species was supported, corresponding to the equilibrium

However, the species $[\text{NO}_3^-(\text{H}_2\text{O})_3\cdot\text{H}_3\text{O}^+]$ has not been experimentally observed and, since it is calculated to be less stable than the $\text{HNO}_3(\text{H}_2\text{O})_4$ cluster, it is likely to be an intermediate product of the acid's dissociation. Indeed, Marinkovic *et al.*¹²⁹ have demonstrated that nitrate ions form contact ion pairs with hydronium ions, in a study using *in situ* infrared reflection spectroscopy to examine the electric double layer on gold electrodes in nitric acid solutions. Whether the contact ion pairs observed in the double layer would also form in bulk solution remains undetermined.

These studies are taken into consideration to inform the association interactions that may be accounted for in a SAFT-VRE Mie model of aqueous solutions of nitric acid. The hydrogen-bonding interactions are straightforwardly assigned following the experimental evidence: three 'e'-type sites are assigned to the NO_3^- ion. They can in principle interact with the 'H' type sites on H_2O and H_3O^+ . While the importance of the NO_3^- - H_2O association is apparent from the studies mentioned earlier, the SAFT-VRE Mie framework allows one to investigate the impact of the NO_3^- - H_3O^+ association on the thermodynamic properties of the mixture, thereby probing the existence of the $[\text{NO}_3^-(\text{H}_2\text{O})_3\cdot\text{H}_3\text{O}^+]$ cluster. The association between molecular HNO_3 and H_2O is determined by the interactions of the 'e' and 'H' type sites on HNO_3 with the 'H' and 'e' type sites on H_2O , respectively.

5.2.3 Model development

5.2.3.1 Objectives. Three target properties are considered in the adjustment of the model parameters (*cf.* eqn (51)): the first objective is the degree of dissociation of nitric acid, defined as

$$\alpha_{\text{HNO}_3} = \frac{m_{\text{NO}_3^-}}{m_{\text{HNO}_3} + m_{\text{NO}_3^-}} = \frac{\tilde{m}_{\text{NO}_3^-}}{\tilde{m}_{\text{HNO}_3}}, \quad (66)$$

at 298.15 K and 1 bar. All available experimental data on the degree of dissociation are considered.^{76,130–133} These data span the entire composition range from pure water to pure nitric acid. As the second objective, vapour-liquid equilibrium data in the nitric-acid-rich region of the phase diagram, *i.e.*, where the overall mole fraction of nitric acid in the liquid phase is $\tilde{x}_{\text{HNO}_3} \geq 0.5 \text{ mol mol}^{-1}$, is used in the parameter estimation.^{134–137} At these high concentrations, nitric acid remains almost completely in its molecular form (*cf.* Section 5.3.1), so that these data should be especially sensitive to the parameters characterising the HNO_3 - H_2O interaction. As the third objective, the stoichiometric osmotic coefficient of aqueous solutions of nitric acid for concentration up to 6 molal is employed.¹³⁸ At these relatively low concentrations, nitric acid dissociates almost completely, so that these data should be especially sensitive to the parameters characterising the NO_3^- - H_2O interaction.

5.2.3.2 Like parameters. The diameter $\sigma_{\text{NO}_3^-}$ is assigned according to the value corresponding to the ion's diameter in a crystal lattice, as reported by Marcus.¹³⁹ The corresponding Born diameter $\sigma_{\text{NO}_3^-}^{\text{Born}}$ is obtained from the molecular-dynamics

simulation study of Babu and Lim,⁵⁷ in which the Born cavity diameter of NO_3^- was calculated to be 10.5% larger than the ionic diameter chosen here. This relative magnitude of the two sizes for the NO_3^- ion is in line with the 7% increase recommended by Rashin and Honig,¹⁰⁰ hence the value proposed by Babu and Lim is considered to be reasonable. The like-ion dispersion energy $\epsilon_{\text{NO}_3^-}$ is obtained by applying the combining rule given by eqn (40). The polarisability⁶⁹ and ionisation potential (negative electron affinity)⁷² of NO_3^- are reported in Table 4.

5.2.3.3 Unlike parameters. The unlike dispersion energy $\epsilon_{\text{NO}_3^-, \text{H}_3\text{O}^+}$ between the nitrate and hydronium ions is calculated with eqn (40), and the unlike energy parameters involving one of the ions and either water or nitric acid ($\epsilon_{\text{H}_2\text{O}, \text{NO}_3^-}$, $\epsilon_{\text{HNO}_3, \text{H}_3\text{O}^+}$ and $\epsilon_{\text{HNO}_3, \text{NO}_3^-}$) using eqn (43), using the parameters given in Tables 1 and 4. The remaining unlike dispersion energy $\epsilon_{\text{H}_2\text{O}, \text{HNO}_3}$ between water and nitric acid is estimated by comparison to experimental data (*cf.* eqn (51)). The reason for this procedure is that the entire composition range from pure water to pure nitric acid is investigated here. The degree of dissociation depends largely on the concentration of nitric acid, which results in different interactions dominating the thermodynamic behaviour of the solution at different compositions.

Additionally, association interactions between HNO_3 - H_2O , NO_3^- - H_2O and NO_3^- - H_3O^+ are considered during the model development. Two types of interactions are relevant for the association between the molecular species HNO_3 and H_2O , corresponding to the two types of e-H site-site interactions: one involves the e-type sites of the oxygen atom of water with the H-type sites of the hydrogen atom in nitric acid; the second involves the e-site types of the oxygen atoms of nitric acid interacting with the H-type sites of the hydrogen atoms of water. Thus, four parameters (two association energy and two bonding volume parameters) need to be determined. As an initial estimate, they are computed from the appropriate combining rules, *cf.* eqn (44) and (45). A sensitivity analysis reveals that the description mainly depends on the strength of the interaction of the e-type sites present in nitric acid and the nitrate ion and the H-type sites preset in water and the hydronium ion. Adjusting the parameters $\epsilon_{\text{H}_2\text{O}, \text{H-HNO}_3, \text{e}}^{\text{HB}}$ and $\epsilon_{\text{H}_3\text{O}^+, \text{H-NO}_3^-, \text{e}}^{\text{HB}}$ results in an increased strength of these association interactions. The H_2O - HNO_3 association is thus treated as asymmetric, which reflects the proposition that the water molecule associating with the electron site on the nitric acid molecule leads to the ionisation of the acid. The parameters for the NO_3^- - H_2O association interaction are also included in the parameter estimation. The values found for $\epsilon_{\text{NO}_3^-, \text{H}_2\text{O}}^{\text{HB}}$ and $K_{\text{NO}_3^-, \text{H}_2\text{O}}^{\text{HB}}$ are characteristic of hydrogen bonding, hence substantiating the proposed hydration of the nitrate ion. Interestingly, including a NO_3^- - H_3O^+ association in the optimisation always yields non-negligible values for both the association energy $\epsilon_{\text{NO}_3^-, \text{H}_3\text{O}^+}^{\text{HB}}$ and the bonding volume $K_{\text{NO}_3^-, \text{H}_3\text{O}^+}^{\text{HB}}$. This would suggest that this association interaction plays an important role the thermodynamic behaviour of the system. In the final model proposed here this interaction has been set to be equal to the

Fig. 5 Degree of dissociation of nitric acid (left) and vapour-liquid equilibrium (right) as functions of the overall mole fraction of nitric acid in aqueous solution at 298.15 K. Curves: SAFT-VRE Mie description, symbols: experimental data from the literature (left: circles,¹³⁰ squares,¹³¹ triangles,¹³² diamonds,¹³³ crosses,⁷⁶ right: circles,¹⁴⁰ squares,¹³⁴ triangles,¹³⁵ diamonds,¹³⁶ crosses¹³⁷).

water-nitric acid association interaction. This result supports the proposition of the existence of the $[\text{NO}_3^-(\text{H}_2\text{O})_3\cdot\text{H}_3\text{O}^+]$ species and the proposed equilibrium (65).

5.3 Description of thermodynamic properties

5.3.1 Degree of dissociation and vapour-liquid equilibrium.

The degree of dissociation of nitric acid and the vapour-liquid equilibrium of water and nitric acid at 298 K are shown in Fig. 5. It is noted here that both properties are plotted over the overall mole fraction of nitric acid, thereby covering the entire composition range from pure water to pure nitric acid.

The experimental data for α_{HNO_3} are characterised by a steady decrease with increasing concentration of nitric acid; it is seen that HNO_3 completely dissociates at high dilution, whereas it completely remains in its molecular form from about an equimolar composition onwards. This behaviour highlights the need to include most of the unlike dispersion energy parameters in the estimation: depending on the concentration, different interactions are dominant. The final SAFT-VRE Mie model captures the experimental data well, with slightly larger deviations for concentrations in the range $\tilde{x}_{\text{HNO}_3} \geq 0.3 \text{ mol mol}^{-1}$. Nevertheless, the model is found to provide an excellent description of the experimental vapour-liquid equilibrium of the mixture, of which only the data points with $\tilde{x}_{\text{HNO}_3} \geq 0.5 \text{ mol mol}^{-1}$ are used in the model development. The model is able to capture the low-boiling azeotropic behaviour of the system, which is typical of aqueous acids, in excellent agreement with the experimental data. The water-rich side of the phase diagram is described very accurately, with both the azeotropic composition and azeotropic pressure predicted accurately. To the best of our knowledge, this is the first instance of an equation of state model with explicit treatment of the partial dissociation of a weak electrolyte used to describe the entire phase diagram. It would be interesting to assess the performance of the model at other temperatures, however, possibly due to the aforementioned difficulties in handling solutions of HNO_3 in the laboratory, such data are scarce and only available at temperatures very close to the one investigated here.

The degree of dissociation and the vapour-liquid equilibrium thus far presented, can only be considered when the partial dissociation is treated explicitly, and molecular nitric acid is incorporated in the model. In the following two sections, we investigate properties that can in principle also be modelled if nitric acid is assumed to be a strong electrolyte that completely dissociates into H_3O^+ and NO_3^- ions; *i.e.*, a model that does not account for the presence of nitric acid in the solution. Comparing the results of the two approaches will reveal the benefits of treating the acid as a weak electrolyte.

5.3.2 Stoichiometric osmotic coefficient and mean-ionic activity coefficient. The stoichiometric osmotic coefficient and mean-ionic activity coefficient of nitric acid are defined as (*cf.* eqns (26) and (31))

$$\phi^{\text{stoich}} = -\frac{\ln a_{\text{W}}}{M_{\text{W}} 2\tilde{m}_{\text{HNO}_3}}, \quad (67)$$

and

$$\tilde{\gamma}_{\text{HNO}_3}^{\text{m}} = \sqrt{\gamma_{\text{H}_3\text{O}^+}^{\text{m}} \gamma_{\text{NO}_3^-}^{\text{m}}}. \quad (68)$$

Both properties can be calculated assuming the complete ('strong electrolyte') and the partial ('weak electrolyte') dissociation models. The comparison is presented in Fig. 6, where ϕ^{stoich} and $\tilde{\gamma}_{\text{HNO}_3}^{\text{m}}$ are shown as functions of the overall nitric acid molality.

The experimental data on the stoichiometric osmotic coefficient for concentrations up to 6 molal are used in the parameter estimation (the $\text{H}_2\text{O}-\text{NO}_3^-$ hydrogen bonding interaction). As can be seen, the weak electrolyte model clearly outperforms the strong electrolyte model, both in the case of the stoichiometric coefficient, used in the parameter estimation, and in the case of the predicted mean-ionic activity coefficient as a function of concentration.

5.3.3 Vapour pressure and solution density. The advantage of treating the partial dissociation of the acid explicitly is also evident when studying the vapour pressure and the liquid density of aqueous solutions of nitric acid, which are shown in Fig. 7 as functions of the overall molality of nitric acid. Both

Fig. 6 Stoichiometric osmotic coefficient (left) and mean-ionic activity coefficient (right) as functions of the overall molality of nitric acid in aqueous solution at 298.15 K. Continuous curves: SAFT-VRE Mie description with partial dissociation, dashed curves: SAFT-VRE Mie description with complete dissociation, circles: experimental data from the literature.¹³⁸

properties are predictions obtained with the present model. Note that the concentration range investigated here is rather 'dilute' when compared to the full composition range shown in Section 5.3.1, so the vapour is essentially pure water. This feature enables the calculation of the vapour pressure in the 'strong electrolyte' model.

In Fig. 7 it is evident that the vapour pressure is predicted very accurately when the 'weak electrolyte' model is considered. At low concentrations, the strong electrolyte model performs equally well but increasing deviations become apparent with increasing concentration of nitric acid. Of course, as for the properties presented in the previous section, the refinement of the parameters of the strong electrolyte model would be possible and might lead to a better overall representation; the complete vapour–liquid equilibrium presented in Section 5.3.1 could not, however, be computed with such a model. In terms of the liquid densities, both approaches perform similarly, with some slight differences at higher concentrations. As might have been expected, the partial dissociation only has a minor impact on the density. The good agreement with the experimental data confirms that the diameters assigned for HNO_3 (obtained in the parameter estimation of pure HNO_3 , based on VLE data) and

NO_3^- (assigned from a literature value of the crystal diameter) are reasonable.

6 Carbonic acid

Carbonic acid (H_2CO_3) differs from our two earlier examples in that the molecular acid is unstable. The stable form is carbon dioxide (CO_2), which is of particular topical interest for its role as a greenhouse gas. In this context, the dissolution and speciation reaction of carbon dioxide in water, which results in the formation of bicarbonate (HCO_3^-) ions, is of relevance in ocean acidification. This slightly acidic character also facilitates capturing carbon dioxide, *e.g.* in absorption processes using amine solutions. In contrast to the bisulfate ion, the bicarbonate ion is a base, *i.e.*, it donates its proton only in basic solutions.

6.1 Dissociation equilibrium

In aqueous solution, carbon dioxide undergoes the following reaction with water:

Fig. 7 Vapour pressure (left) and liquid density (right) as functions of the overall molality of nitric acid in aqueous solution at different temperatures. Continuous curves: SAFT-VRE Mie description with partial dissociation, dashed curves: SAFT-VRE Mie description with complete dissociation, symbols: experimental data from the literature (left: circles,¹⁴¹ squares,¹⁴² triangles,¹⁴³ right: circles¹⁴⁴).

Subsequently, the bicarbonate anion HCO_3^- can donate one more proton to form the carbonate anion CO_3^{2-} , *i.e.*,

The corresponding conditions for chemical equilibrium are, *cf.* eqn (19),

$$K_{a1}(T) = \frac{m_{\text{H}_3\text{O}^+} m_{\text{HCO}_3^-} \gamma_{\text{H}_3\text{O}^+}^{\text{m}} \gamma_{\text{HCO}_3^-}^{\text{m}}}{m_{\text{CO}_2} m^0 \gamma_{\text{CO}_2}^{\text{m}}}, \quad (71)$$

and

$$K_{a2}(T) = \frac{m_{\text{H}_3\text{O}^+} m_{\text{CO}_3^{2-}} \gamma_{\text{H}_3\text{O}^+}^{\text{m}} \gamma_{\text{CO}_3^{2-}}^{\text{m}}}{m_{\text{HCO}_3^-} m^0 \gamma_{\text{HCO}_3^-}^{\text{m}}}. \quad (72)$$

We note in passing that K_{a1} refers to $\text{CO}_2(\text{aq})$ here; in the literature, sometimes an equilibrium constant with respect to $\text{CO}_2(\text{gas})$ is presented in which the Henry's law constant of CO_2 in H_2O is included to account for the necessary dissolution of CO_2 . However, as we use the SAFT-VRE Mie equation of state here and take the phase equilibrium into account explicitly, this is not necessary.

At ambient temperature, $\text{p}K_{a1} \approx 6.35$ and $\text{p}K_{a2} \approx 10.32$,¹⁴⁵ so that compared to the acids studied in the previous sections CO_2 is a 'truly weak' electrolyte. More importantly, with the present approach, the second dissociation step cannot be treated. As $\text{p}K_{a2} > 7$, a basic solution is required for the carbonate formation, so that data on additional species, other than H_2O and CO_2 , would be needed. Thus, only the formation of bicarbonate, *i.e.*, the first dissociation step, is considered here, and a new model for HCO_3^- is developed.

The thermodynamic equilibrium constant of the bicarbonate formation has been studied over a wide temperature range. Harned and Davis,¹⁴⁶ Harned and Bonner,¹⁴⁷ and Curry and Hazelton¹⁴⁸ carried out electromotive force measurements of aqueous solutions of sodium bicarbonate and extrapolated their results to zero ionic strength to obtain the thermodynamic equilibrium constant in the range $273 \leq T/\text{K} \leq 323$. Over the same temperature range, Näsänen¹⁴⁹ and Näsänen *et al.*¹⁵⁰ measured the pH of the solution and combined these data with titration determinations. At higher temperatures ($373 \leq T/\text{K} \leq 523$), Ryzhenko¹⁵¹ and Read¹⁵² determined the K_{a1} from conductivity measurements. The aforementioned data sets were employed by Plummer and Busenberg¹⁴⁵ to obtain an empirical correlation for K_{a1} :

$$\begin{aligned} \log_{10} K_{a1} = & -356.3094 - 0.06091964(T/\text{K}) + 21834.37(\text{K}/T) \\ & + 126.8339 \log_{10}(T/\text{K}) - 1\,684\,915(\text{K}/T)^2. \end{aligned} \quad (73)$$

This correlation, which is appropriate in the temperature range $273 \leq T/\text{K} \leq 523$, is used here.

6.2 Association scheme

The association and hydration of the HCO_3^- anion in aqueous solutions have recently been studied, mainly employing quantum-chemical methods. Using Car-Parrinello molecular dynamics (MD) simulations, Kumar *et al.*¹⁵³ showed that on average HCO_3^- forms four hydrogen bonds with H_2O . Garand *et al.*¹⁵⁴

conducted infrared spectroscopic measurements and analysed them together with electronic structure calculations. They confirmed the hydration number of four and also found that water molecules interact directly with the CO_2 moiety of the bicarbonate anion, while binding of water to the hydroxyl group is particularly disfavoured. Dopieralski *et al.*¹⁵⁵ used a combination of *ab initio* MD calculations and acoustic experiments. They evaluated the hydration numbers of HCO_3^- in the range 5.3–5.6 and also disproved the existence of HCO_3^- self-association, as only minor amounts of HCO_3^- dimers were found in solution. From their MD simulations, England *et al.*¹⁵⁶ have reported a coordination number of 4.26 for H_2O around HCO_3^- . Later, Stefansson *et al.*¹⁵⁷ found excellent agreement for the $\text{HCO}_3^- \cdot n\text{H}_2\text{O}$ clusters with the work of Garand *et al.*,¹⁵⁴ and Wen *et al.*¹⁵⁸ confirmed with DFT calculations that the first four water molecules prefer to interact with the CO_2 moiety of the HCO_3^- anion. Very recently, Kong *et al.*¹⁵⁹ studied the vibration of HCO_3^- in $\text{HCO}_3^- \cdot n\text{H}_2\text{O}$ clusters with *ab initio* MD simulations and found water libration for $n \geq 6$.

We use these findings to inform the choice of bonding schemes in our SAFT-VRE Mie approach. As H_2O is found to associate exclusively with the CO_2 moiety of the HCO_3^- anion, we propose to follow the type of association and the parameters obtained by Papaioannou *et al.*⁶⁸ for the system $\text{H}_2\text{O} + \text{CO}_2$ to model the association of $\text{H}_2\text{O} + \text{HCO}_3^-$. To this end, four e-type sites are placed on the HCO_3^- anion that can only associate with the H-type sites on H_2O , as at most four water molecules are found to associate with one HCO_3^- anion. The same association interaction is also introduced between the three H-type sites on H_3O^+ and the HCO_3^- ion.

6.3 Model development

6.3.1 Objectives. The models for sulphuric and nitric acids presented in the previous sections were mainly developed from speciation data. However, as CO_2 is a much weaker electrolyte, speciation data are difficult to determine experimentally. Instead, for optimisation we employ a single objective (*cf.* eqn (51)) closely related to speciation: the pH of saturated aqueous solutions of CO_2 , which is defined as

$$\text{pH} = -\log_{10} a_{\text{H}_3\text{O}^+}^{\text{m}}. \quad (74)$$

We estimate the model interaction parameters from the experimental pH data at $T = 323\text{ K}$.¹⁶⁰

6.3.2 Like parameters. For the HCO_3^- anion, both the diameter $\sigma_{\text{HCO}_3^-}$ and the Born diameter $\sigma_{\text{HCO}_3^-}^{\text{Born}}$ are taken from the work of Marcus.^{139,161} The dispersion energy parameter $\epsilon_{\text{HCO}_3^-}$ is calculated with the Hudson-McCoubrey rule, *cf.* eqn (40). The ionisation potential of HCO_3^- is estimated as its adiabatic electron detachment energy taken from Wang and Xantheas,⁷³ and the polarisability is approximated as that of the CO_3^{2-} ion from Pyper *et al.*,⁶⁹ *cf.* Table 4.

6.3.3 Unlike parameters. The unlike dispersion energies $\epsilon_{\text{CO}_2, \text{H}_3\text{O}^+}$, $\epsilon_{\text{CO}_2, \text{HCO}_3^-}$ and $\epsilon_{\text{H}_3\text{O}^+, \text{HCO}_3^-}$ are all calculated using the Hudson-McCoubrey rule, *cf.* eqn (40). As discussed earlier, we adopt the association scheme and the corresponding

Fig. 8 pH as a function of the total pressure of carbon dioxide in aqueous solution at different temperatures. Continuous curves: SAFT-VRE Mie calculations, circles: experimental data from the literature.¹⁶⁰

parameters for the $\text{H}_2\text{O}-\text{HCO}_3^-$ and $\text{H}_3\text{O}^+-\text{HCO}_3^-$ association from the $\text{CO}_2-\text{H}_2\text{O}$ interaction parameterised by Papaioannou *et al.*⁶⁸ The only parameter employed in the parameter estimation here is the unlike dispersion energy $\varepsilon_{\text{H}_2\text{O},\text{HCO}_3^-}$, determined from the experimental pH of aqueous solutions of CO_2 at $T = 323$ K.

6.4 Description of thermodynamic properties

6.4.1 pH. We start our discussion with the property used in the determination of parameters, namely the pH of saturated aqueous solutions of CO_2 . This property is shown at several temperatures as a function of the total pressure in Fig. 8.

As can be seen in Fig. 8, the present model, using only one adjustable parameter, is capable of accurately representing the pH at the temperature considered in the fit ($T = 323$ K). The same parameter can be used to predict the temperature dependence of the pH in very good agreement with the experimental data.

6.4.2 Gas solubility. In Fig. 9, the VLE of the $\text{H}_2\text{O} + \text{CO}_2$ mixture, including the dissociation of CO_2 modelled as described in the previous section, is shown. The total pressure of the system is plotted as a function of the overall CO_2 mole fraction in the liquid and vapour phases, respectively, for various temperatures.

The SAFT-VRE Mie model represents both the liquid and vapour phase compositions as a function of the pressure in good agreement with the experimental data. It should be noted that the agreement is mostly due to the original parameterisation of the $\text{H}_2\text{O}-\text{CO}_2$ interaction carried out by Papaioannou *et al.*⁶⁸ Nevertheless, it is remarkable that the SAFT-VRE Mie model is able to represent the maximum in the vapour-phase composition $\tilde{y}_{\text{CO}_2}$ as a function of pressure.

The model developed here for solutions of carbon dioxide in water, including the speciation of the acid, demonstrates the strong physical basis of our SAFT-VRE Mie approach. The association scheme, and corresponding parameters, have been obtained considering the interactions of carbon dioxide and bicarbonate with water. Using only one adjustable parameter, an excellent description of the pH of the solution is obtained over a broad temperature range. The model developed here for the bicarbonate ion will be of great use in applications involving systems with additional reacting components in future work.

7 Conclusions

The SAFT-VRE Mie equation of state has been applied to aqueous solutions of three important inorganic acids: sulphuric acid, nitric acid, and carbonic acid. Building on experimental information for the thermodynamic equilibrium constant of the dissociation reaction, we demonstrate that SAFT-VRE Mie is a valuable tool for the description of the thermodynamic properties of aqueous solutions of weak electrolytes. As found previously for solutions of strong electrolytes, experimental values can be used to estimate the parameters of the ions. Only few unlike interaction parameters need to be adjusted with respect to experimental data for the speciation and activity or phase equilibrium data, at a single temperature. The SAFT-VRE Mie models obtained in this manner reproduce these training data accurately, and the predictive capability of the approach is highlighted by the quality of description that can be achieved for other properties over a wide temperature range, such as osmotic coefficients, mean-ionic activity coefficients and vapour pressures.

Fig. 9 Pressure as function of the overall mole fraction of carbon dioxide in the liquid phase (left) and the vapour phase (right) for aqueous solutions of carbon dioxide at different temperatures. Continuous curves: SAFT-VRE Mie calculations, circles: experimental data from the literature.¹⁶²

The sound physical basis of the SAFT-VRE Mie approach also enables elaborating on ambiguities regarding association interactions in the solutions studied, including hydrogen bonding and ion pairing. In aqueous solutions of sulphuric acid, the SAFT-VRE Mie model reveals that the thermodynamic properties are mainly governed by a strong association of the hydronium ion with the sulfate ion, indicative of the formation of an ion pair. In aqueous solutions of nitric acid, we observe a strong, asymmetric association between water and nitric acid; a strong solvation of the nitrate anion is also found. Finally, aqueous solutions of carbon dioxide can be modelled accurately by assuming that water associates mainly with the CO₂ moiety of the bicarbonate anion, confirming quantum mechanical studies from the literature.

In future work, we plan to incorporate this approach in the SAFT- γ Mie group-contribution equation of state to develop models of complex organic ions as heteronuclear chains containing charged and uncharged segments, extending our recent work in this area.¹⁶³

Data statement

Data underlying this article can be accessed on Zenodo at <http://doi.org/10.5281/zenodo.3894279>, and used under the Creative Commons Attribution license.

Conflicts of interest

There are no conflicts to declare.

Appendix A: derivation of Prigogine's theorem

Consider the Gibbs free energy of the solution of an electrolyte AB in a solvent W. The 'overall' composition point of view leads to

$$G = \tilde{n}_{AB}\tilde{\mu}_{AB} + \tilde{n}_W\tilde{\mu}_W \quad (75)$$

and the 'true' composition point of view leads to

$$G = n_{AB}\mu_{AB} + n_W\mu_W + n_{A^+}\mu_{A^+} + n_{B^-}\mu_{B^-}. \quad (76)$$

Inserting the material balances (eqns (2)–(4)) into eqn (76) and rearranging yields

$$G = \tilde{n}_{AB}\mu_{AB} + \tilde{n}_W\mu_W + (\nu_{A^+}\mu_{A^+} + \nu_{B^-}\mu_{B^-} - \mu_{AB})\zeta. \quad (77)$$

In chemical equilibrium, *cf.* eqn (9), the expression in brackets vanishes, so that

$$G = \tilde{n}_{AB}\mu_{AB} + \tilde{n}_W\mu_W \quad (78)$$

The Gibbs free energy is of course independent of the point of view, so that the 'true' and 'overall' perspective must yield the same value for G . Thus, comparing eqn (75) and (78) yields:

$$\mu_{AB} = \tilde{\mu}_{AB} \quad (79)$$

$$\mu_W = \tilde{\mu}_W \quad (80)$$

Appendix B: derivation of the definition of the stoichiometric mean-ionic activity coefficient

Consider the dissociation of a weak electrolyte AB in two ways. In general, one can write for the chemical potential of the electrolyte as

$$\tilde{\mu}_{AB} = \tilde{\mu}_{AB}^{\text{ref m}} + RT \ln \left[\left(\frac{m_{A^+}}{m^0} \right)^{\nu_A} \left(\frac{m_{B^-}}{m^0} \right)^{\nu_B} \right] + RT \ln \left[(\tilde{\gamma}_{AB}^{*m})^{\nu_A + \nu_B} \right], \quad (81)$$

which is simply eqn (24). If the electrolyte is formally assumed to dissociate completely (*i.e.*, to stoichiometric composition), the material balances (eqns (2)–(4)) can be inserted into eqn (81) to yield

$$\begin{aligned} \tilde{\mu}_{AB} = \tilde{\mu}_{AB}^{\text{ref m}} + RT \ln \left[\nu_A^{\nu_A} \nu_B^{\nu_B} \left(\frac{\tilde{m}_{AB}}{m^0} \right)^{\nu_A + \nu_B} \right] \\ + RT \ln \left[(\tilde{\gamma}_{AB}^{*m, \text{stoich}})^{\nu_A + \nu_B} \right], \end{aligned} \quad (82)$$

where the exponent 'stoich' is introduced in the mean-ionic activity coefficient to avoid confusion with the corresponding property in eqn (81). The chemical potential of the electrolyte AB as such must of course be independent of the way the solution is treated formally, so that eqn (81) and (82) have to be equal. The reference terms then cancel to give

$$\begin{aligned} \nu_A^{\nu_A} \nu_B^{\nu_B} \left(\frac{\tilde{m}_{AB}}{m^0} \right)^{\nu_A + \nu_B} (\tilde{\gamma}_{AB}^{*m, \text{stoich}})^{\nu_A + \nu_B} \\ = \left(\frac{m_{A^+}}{m^0} \right)^{\nu_A} \left(\frac{m_{B^-}}{m^0} \right)^{\nu_B} (\tilde{\gamma}_{AB}^{*m})^{\nu_A + \nu_B}. \end{aligned} \quad (83)$$

Inserting the definition of the mean-ionic activity coefficient, *cf.* eqn (26), finally yields the desired relation:

$$\tilde{\gamma}_{AB}^{*m, \text{stoich}} = \left[\frac{1}{\nu_A^{\nu_A} \nu_B^{\nu_B}} \left(\frac{m_{A^+}}{m^0} \right)^{\nu_A} \left(\frac{m_{B^-}}{m^0} \right)^{\nu_B} \left(\frac{\tilde{m}_{AB}}{m^0} \right)^{\nu_A + \nu_B} (\tilde{\gamma}_{A^+}^{*m})^{\nu_A} (\tilde{\gamma}_{B^-}^{*m})^{\nu_B} \right]^{\frac{1}{\nu_A + \nu_B}}. \quad (84)$$

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