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Contributions to ionic activity coefficients: A review and comparison of equations of state with molecular simulations

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ABSTRACT

Advanced Equations of State for electrolyte solutions (e-EoS) consist of many contributions stemming from different intermolecular forces, e.g. repulsion, dispersion, hydrogen bonding, as well as ionic interactions between ions, ion solvation and possibly others. It is difficult to establish a priori which is the correct balance of the various contributions, and different parameter estimation strategies may result in similar performance of models having entirely different trends with respect to the contribution of the various terms. The first part of this work is a literature review on the balance of forces exhibited by existing electrolyte models, both activity coefficient models and e-EoS. In the second part of this work, the activity coefficients and the contributions of the various terms calculated by molecular simulation (MS) based on the recent studies by Saravi and Panagiotopoulos are analyzed and compared to their e-EoS counterparts at 25 °C and 1 bar. We have considered three e-EoS from literature, namely the eSAFT-VR Mie, ePPC-SAFT and e-CPA. MS studies have been presented in literature both using the so-called implicit and explicit simulations, but only the latter are considered here where water is treated as a molecule, as these are in closer agreement to experimental data. Although correspondence between MS contributions and e-EoS terms is not fully established, some conclusions related to the performance of e-EoS are obtained.

1. Introduction and motivation

It has been a popular but difficult topic in thermodynamics to “divide” models in various terms and try to analyze and understand their behavior from that point of view. However difficult this task it, it is highly valuable. A case where this type of analysis has led to the clarification and ultimately, the improvement of a whole generation of thermodynamic models for non-electrolytes, that of EoS/ g^E models (EoS stands for Equations of State, g^E stands for excess Gibbs free energy

models), will be briefly discussed to showcase the importance and possible extensions of the current work.

The motivation behind the development of EoS/ g^E models about 40 years ago, was to derive new mixing rules for EoS, that would extend the robust predictive ability of g^E models to higher pressures via incorporating them to cubic EoS. Both EoS and activity coefficient (g^E) models consist of two types of terms corresponding to two types of contributions, one related to size/shape of molecules, sometimes called entropic or entropic-free-volume or combinatorial term and the second related to

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energy, sometimes referred to as energetic or residual term. Over the years, the terminology “entropic” and “energetic” contributions has led to various misconceptions [1–5], the reason being that, although the combinatorial-free volume term is referred to as an entropic term, it is **not** identical to s^E , and neither is the residual term identical to u^E or h^E for EoS nor for g^E models. For example, in the Wilson model, the combinatorial and excess entropy terms become equal only if all the energy differences in the residual term are equal to zero [6] and NRTL does not have a combinatorial term, but it does have a s^E term and is thus not purely an excess enthalpy model (h^E), as is sometimes stated in the literature [7]. On the other hand, in the well-known van der Waals (vdW) cubic equation the combinatorial-free-volume, excess volume and residual term are exactly equivalent to excess entropy, volume and internal energy only if the energy parameter is temperature independent (which is the case in the vdW EoS, but it is a highly unrealistic assumption that has not been used in any engineering cubic EoS) [1].

Despite these difficulties and complications in identifying the separate size/entropic and energetic/residual contributions, this analysis and discussion has led to understanding of the various contributions to EoS and the role of the underlying mixing and combining rules, either vdW one fluid (vdW1f) [5] or EoS/ g^E mixing rules [1–3,8,9]. More specifically, the use of EoS/ g^E methodology at infinite pressure (Huron-Vidal [10] and Wong-Sandler [11] approaches) at its initial stages utilized the complete g^E model. However, after a careful analysis of the derivation and separation of the combinatorial and residual terms in EoS, it was found that the mixing rule at infinite pressure should only involve the residual excess Gibbs energy (and not the complete g^E model), because, at infinite pressure, the combinatorial/free volume term of EoS disappears. Equally unclear was the fact that such mixing rules using the zero-reference pressure assumption suffer from the presence of the so-called “double combinatorial difference” [12], making these models unsuccessful for size-asymmetric systems. Such a problem has been identified by carefully analyzing the contributions of various terms into the activity coefficient models and EoS and have been resolved in mixing rules employed today in modern engineering models like the VTPR EoS [13].

Returning now to electrolytes, it is of equal interest to find ways to assess the relative importance of the terms in electrolyte models. Such models, include more terms than their non-electrolyte counterparts, as shown in Fig. 1, they are therefore more complex. Both e-EoS and e- g^E models typically have both terms for non-electrolyte contributions (a cubic or Statistical Associating Fluid Theory (SAFT) [14] type EoS or a model like UNIQUAC in case of [15] or NRTL in case of [16]) and additional terms for the electrolyte contributions. The latter include, as minimum, a term for ion-ion interactions, e.g. as obtained from the Mean Spherical Approximation (MSA) [17] or Debye-Hückel (DH) [18] theories and often also an ion-charging or Born-type term [19], which accounts for solvation or hydration phenomena. However, more terms

can be present, such as a Bjerrum term for ion-pairing [20].

The literature is rich in investigations of the balance between contributions of different terms of electrolyte models to MIAC, in order to identify which of these terms dominate. This work follows this path and has two objectives, a) to compare and analyse the balance of forces exhibited by different models found in the literature and b) to compare the balance of forces of three popular e-EoS against molecular simulation results, both of which we consider highly important and novel. Furthermore, we have evaluated the balance of forces also for IIAC, and not just for MIAC. Although IIAC measurements [21–23] are not accepted by everyone due to possible fundamental issues [24–26], we consider the fact that the trends shown from experimental measurements are confirmed by molecular simulations in ref [27] a positive step towards their wide acceptance, therefore we have included them in this study.

All the discussion of this manuscript is based on results for 25 °C and 1 bar, as these are the only conditions with available contribution plots in the literature and molecular simulations. The literature review presented in Section 2 is complemented with an analysis of the contributions of various literature e-EoS and e- g^E models along with some conclusions obtained from it. Section 2 serves as a way to prove that models with completely different approaches have similar accuracy, confirming the complexity of electrolyte modelling and re-enforcing the need for guidelines towards more physically sound model development and parameterization strategies. The second part of this work is a comparison between contributions of forces obtained via molecular simulation and three e-EoS. Section 3 reports an analysis of recent molecular simulation data and how they can be decomposed in various contributions (Lennard-Jones and Coulombic), Section 4 presents the results for three e-EoS and Section 5 offers a unified discussion on the topic of balance of forces and our final conclusions are presented in Section 6.

2. Literature review and analysis of the contributions of forces in electrolyte models

An important question in multi-term (and multi-parameter) models for electrolytes, like e-EoS and e- g^E models, is to determine the correct relative magnitude of the various terms for electrolyte systems and how this changes with concentration, temperature and pressure. Here “relative magnitude” refers to the qualitative behavior of the different terms, e.g. which terms should be larger or smaller and how this changes with the diverse conditions. We do not mean the exact values as these would depend on each model and its parameters. Such knowledge may help in model development and validation and, ultimately, in the selection of the most suitable approach for model development and parameterization. Much has been said and written on this topic, but there is no consensus, not even about the relative magnitude of the contributions in the electrolyte part of the models, as shown in the rest of

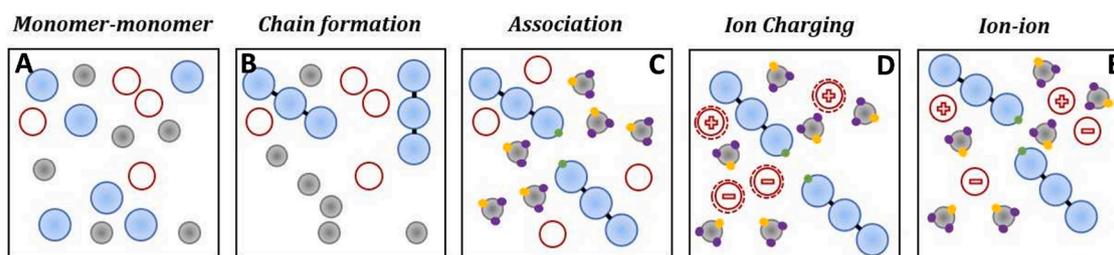


Fig. 1. eSAFT-VR Mie schematic explanation showing the terms of this equation of state.

Section 2. Two main types of models are discussed in this section, those that comprise only electrolyte terms (ion-ion + Born) and those that are “complete” models that also include physical interactions (physical term + ion-ion + Born). The effect of the composition dependency of the Relative Static Permittivity (RSP) is crucial in these discussions, especially with respect to the Born term.

2.1. Activity coefficient models of the type of ion-ion + Born interactions

Many studies showcasing the importance of the various terms have been carried out for “simpler” activity coefficient models for electrolytes, which only contain ion-ion terms (e.g. from DH or MSA) and the Born term for solvation effects. Such models have been presented by Shilov-Lyaschenko (SL) [28,29], Validsko-Boda (VB) [30,31] and others e.g. Khomutov [32]. These models do not contain any terms for non-electrolyte interactions, and typically use default ion-size parameters from some literature experimental source (e.g. Pauling and Marcus values) and salt-composition-dependent RSP in both ion-ion and Born terms. A salt composition dependent RSP will affect both the ion-ion and Born contributions to the activity coefficient, and the magnitude of the two terms appears to be comparable (similar order of magnitude) and in opposite directions (positive for Born and negative for ion-ion). However, if the RSP is constant, the Born term has no contribution to the activity coefficient. The actual results will depend a lot on the choice of the expressions for the RSP and especially the values and methods for estimating the ion-size parameters. The effect of the exact theory used for ion-ion effects (DH, MSA or something else) appears to be less crucial compared to all other factors mentioned, especially the RSP salt-concentration dependency.

Another model in the same category is the famous Hückel model from 1925 [33], Eq. (1), along with the Bromley model [34] which is based on Hückel’s equation, according to which:

$$\ln \gamma_i^{el} = -z_i^2 \frac{A\sqrt{I}}{1+B\sqrt{I}} + CI \quad (1)$$

Hückel [33] commented extensively in his manuscript on the need to account for the concentration dependency of the RSP and on the importance of the solvation effects. He also mentioned that the extended Debye-Hückel form which included the finite size of ions, although an improvement over the limiting law, could not account for the increase of ion activity coefficient at high concentration due to the repulsive solvation forces, therefore the need for the Born term was apparent. Indeed, as Silva et al. showed in a recent publication [35], the Hückel model is a combined DH + Born equation using a linear salt-concentration-dependent RSP in both terms. The equation shown above is a simplified form of the actual Hückel equation and more detailed forms can be found in the 1925 publication [33] and in the recent analysis by Silva et al. [35]. Both in the work of Silva et al. [35] and others (e.g. Helgeson et al. [36]), it is clearly demonstrated that the Hückel equation corrects the DH equation, via the Born term and a concentration dependent RSP, for some important omissions, notably the ion solvation effects. As implied from these discussions, and verified from results in literature, a proper inclusion of all effects in the DH equation renders the model suitable even for highly concentrated solutions.

Sun et al. [37] and Liang and co-workers [38,39] have also evaluated such ion-ion + ion-water (DH or MSA + Born) models for their performance to predict individual ion activity coefficients (IIAC). The main

conclusion from this analysis is that the correct balance between DH and Born is important for obtaining qualitatively correct results for IIAC and this highly depends on the ion diameter used in the DH and Born terms. It has been also concluded that, in order to get qualitatively correct results for IIAC (for almost all systems), we should employ an average ion size parameter in the ion-ion term (and not an individual ion size diameter), while it is entirely fine to use an ion-dependent Born radius in the Born term. Thus, although the original full DH theory is derived without considering the average ion size assumption, it seems that a mean ionic diameter value performs “better”, at least judging from the analysis of IIAC. The average ion size is “more accepted” (than the use of DH with individual ion size parameters) in literature; Guggenheim considered the use of average ion diameter value in the DH theory to be the correct approach [40].

Another interesting approach is that of Fawcett and Tikanen [41,42], who applied the MSA theory for ion-ion interactions together with a hard-sphere (HS) term. They did not use a Born term, but they employed a concentration dependent RSP. They noticed that a very significant improvement in MSA description of electrolyte solutions was obtained when the concentration dependency of the solvent RSP was included in the model. They commented that “the success of the theory is remarkable considering the fact that the two contributions to the activity coefficient, the electrostatic and hard-sphere increase in opposite directions with increase in electrolyte concentration” using RSP as function of composition. Thus, they observed the same “balancing terms” between MSA and HS as we previously discussed between DH and Born.

Silva et al. [43,44] have recently studied the DH + Born model using both a constant and a concentration dependent RSP, with the concentration dependency included either after the charging process (most of the literature approaches) or before the charging process (as SL did, but in a more general way). The results of the DH + Born when the RSP dependency is introduced before the charging process are overall better (regardless whether the Silva et al. [43,44] or SL [28,29] methods are used).

There is a very significant difference between the ion-ion + Born models mentioned above and the more complete e-g^E and e-EoS we discuss in subsequent sections. In these simpler activity coefficient models, despite being entirely predictive with literature values for their ion-size parameters, all ion-ion interactions are obtained directly from the Debye-Hückel or some other ion-ion theory without the use of any energy interactions between ions. The energy parameter is a “must” parameter not only in all e-EoS, but also in “complete” e-g^E models like extended UNIQUAC [15] or e-NRTL [16].

2.2. Activity coefficient models containing both physical and electrolyte terms

Two activity coefficient models with both physical and electrolyte terms will be discussed here. Fig. 2 shows a typical example of the magnitude of the contributions of short-range and long-range terms in extended UNIQUAC [15] for the mean ionic activity coefficients. Extended UNIQUAC has no Born term and no composition dependent RSP. It is well-established that the model represents the experimental data very well and that the DH (ion-ion) term is more significant at lower concentrations, while the “physical interactions” term (UNIQUAC part) becomes increasingly more important at higher concentrations. So, in this case the physical interactions “counterbalance” the ion-ion term.

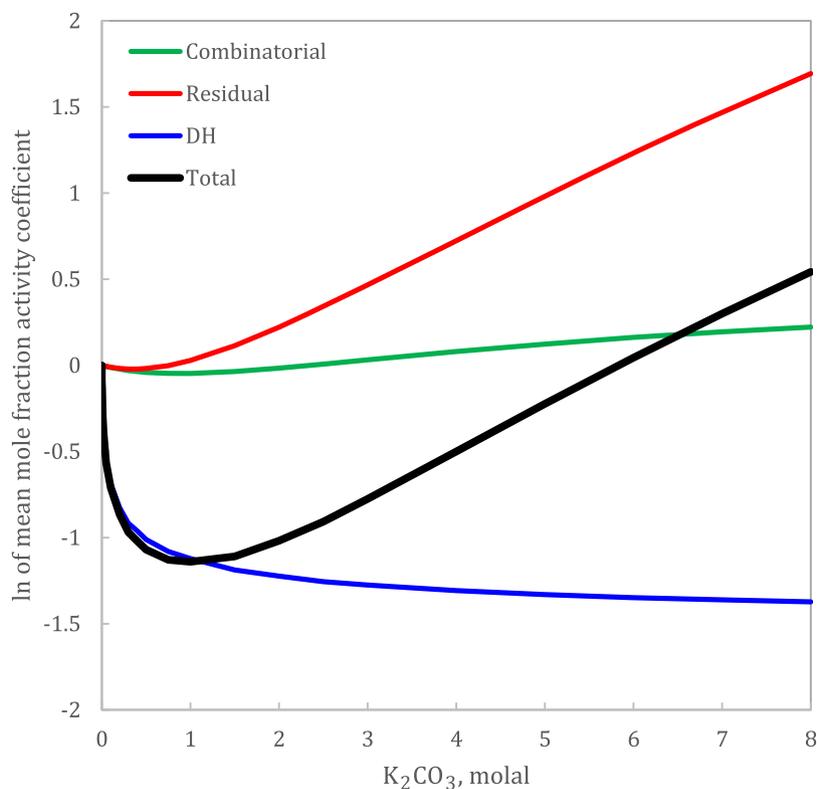


Fig. 2. Contributions to the mean ionic activity coefficient of K_2CO_3 in water at 298.15 K with extended UNIQUAC comprising short-range (Combinatorial and Residual) and long-range (Debye-Hückel) terms. Red line: residual, green line: combinatorial, blue line: Debye-Hückel, black line: total value. The figure is courtesy of Professor Kaj Thomsen and has not been previously published.

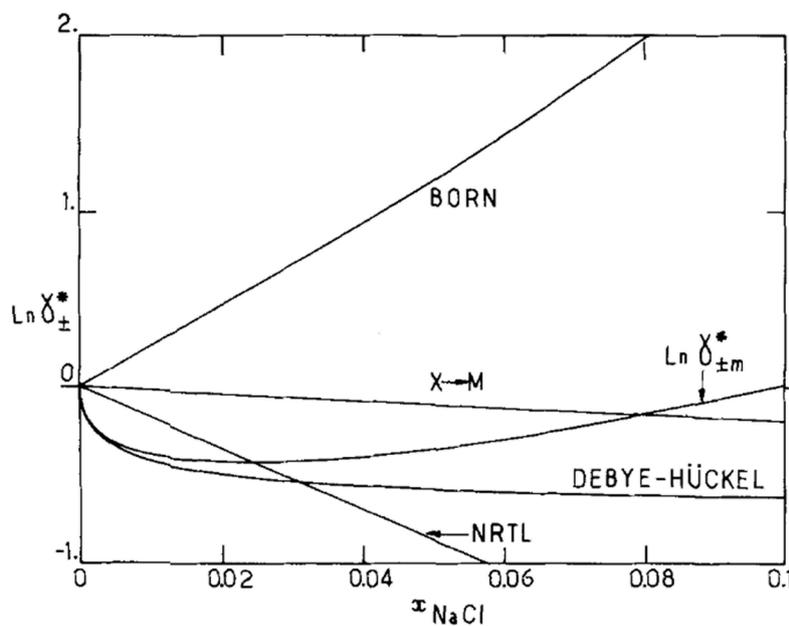


Fig. 3. Contributions to the mean ionic activity coefficient of NaCl in water at 298.15 K with eNRTL comprising of three different terms, NRTL + Debye-Hückel + Born and composition-dependent RSP. Reproduced from Cruz and Renon [16] with permission of John Wiley and Sons. Original caption: Contributions to the mean ionic activity coefficient in the H_2O -NaCl mixture. In this plot, γ_{\pm}^* is the asymmetric activity coefficient in the mole fraction scale, x_{NaCl} is the mole fraction of salt in solution, $\gamma_{\pm m}^*$ is the asymmetric activity coefficient in the molality scale, $X \rightarrow M$ corresponds to the conversion from mole fraction to molality scale.

Another trend is shown for e-NRTL [16] in Fig. 3. This model has both Born term and composition dependent RSP. In this case, the Born term increases with concentration and is of the opposite sign compared

to the combined “physical” (NRTL) and ion-ion (DH) terms. We can see that the “dominant” terms for the two models shown in Figs. 2 and 3 are different, although both of them are known to represent the

experimental activity coefficient data well.

2.3. The electrolyte equation of state of Simon et al. [45] and the e-CPA of the IFPEN group [46]

The Simon and Prausnitz EoS from 1991 [45] combines the SRK model for physical interactions with the Pitzer-Debye-Hückel (PDH) term for ion-ion, ion-dipole and dipole-dipole effects as well as a Born-type term for solvation. The RSP of solvent mixtures is calculated from the Buckingham model and then corrected for and extended to include ions. For NaCl-water an interesting term analysis is shown (see Fig. 4), with the Born and Debye-Hückel terms exhibiting large and opposite results (positive and negative, respectively) to the activity

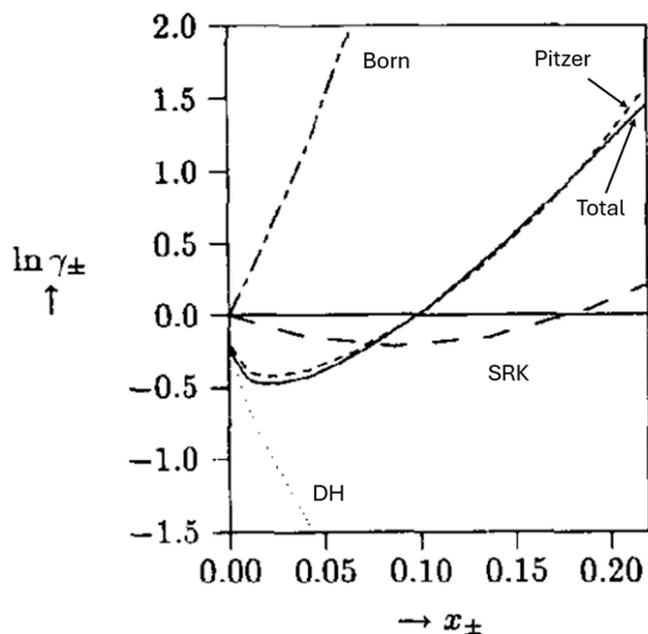


Fig. 4. Contributions to the mean ionic activity coefficient of NaCl in water at 298.15 K with using the Simon et al. [45] EoS (solid line) and Pitzer (short-dash line). Contribution to this model: SRK (long-dash line), Born (dash-dot line), DH + residual (dotted line). Reproduced from Simon et al. [45] with permission of Elsevier. Original caption: Contributions to the activity coefficient for NaCl in H₂O at 298.15 K and ambient pressure. In this plot, γ_{\pm} is the asymmetric activity coefficient in the mole fraction, x_{\pm} is the mean mole fraction of salt in solution, for definition refer to [45].

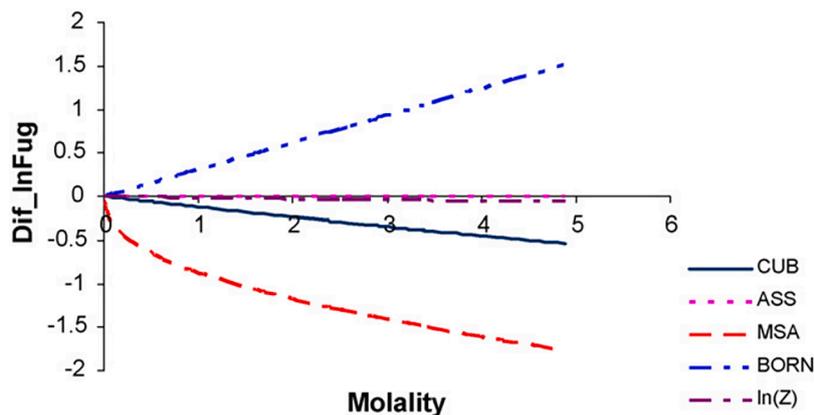


Fig. 5. Contributions to the mean ionic activity coefficient of NaCl in water at 298.15 K with the e-CPA from IFPEN group [46]. There is a contribution from the Born term because the RSP used depends on salt concentration. CUB stands for the contribution of the cubic without association and ASS stands for the contribution due to association, $\ln(Z)$ originates from change of variables from T, V, n to T, P, n . Reproduced from Inchekel et al. [46] with permission of Elsevier. Original caption: Decomposition of the different contributions to the NaCl activity coefficient.

coefficients. This early discovery was later verified for many other models, as shown in literature (see later in this section) when the Born term is included with a composition-dependent RSP. The SRK contribution is rather small over the whole concentration range. We also observe that the behavior shown in Figs. 3 and 4 is quite similar. We can thus conclude that some e-EoS and e- g^E models behave similarly under the “same conditions” (type of terms and RSP salt-concentration effect).

The e-CPA by IFPEN [46] combines an SRK-based CPA with the simplified implicit form of MSA (non-restrictive to same ion diameter), the Born term, and an additional term, the so-called SR2. The latter is identical to the term used by Fürst and Renon in their e-EoS [47] and is used to represent the short-range ionic interactions. Water is modelled as a 4-site molecule in the CPA part (4C-scheme), but there are no sites on ions and no water-ion association. Thus, the association term is only used for water.

The IFPEN e-CPA contains two ionic parameters (SRK’s energy parameter and the ionic diameter) as well as binary interaction parameters (k_{ij}) between water-ions or the W_{ij} interaction parameters of the SR2 term. The correlation results are satisfactory, and it is concluded in [46] that the preferred approach is to use the Born term with the Simonin RSP expression, which includes an additional adjustable parameter. Excellent results are obtained by using the same ionic diameter values in all expressions where the diameter enters (MSA, SR2, Born), although this is somewhat in contradiction with the physical meaning of the diameter in these expressions. Also, these authors carried out a relative analysis of the various electrolyte terms, which is shown in Fig. 5.

It can be seen that the Born contribution is positive and nearly counterbalances the (negative) MSA contribution, while there is hardly any contribution from the association term.

These conclusions are like those obtained by Simon et al. [45]. According to Inchekel et al. [46], if the composition dependency of the RSP is ignored (and thus the Born term does not contribute to the activity coefficients), then the other terms of the EoS counterbalance the MSA effect in order to obtain the correct activity coefficient slope at high salt concentrations.

3. Conclusions so far

Both e-EoS and e- g^E models have a similar behavior in terms of the various contributions. There is no debate that an ion-ion term is needed in electrolyte models, whether it is DH or MSA and both terms behave in a similar way, with negative contributions to the activity coefficients. The ion-ion term can be “counterbalanced” either by physical forces or a Born term, which dominate at higher salt concentrations. The

concentration dependency of the RSP has a significant effect on both electrolyte terms (ion-ion and Born), but especially for the Born contribution to the activity coefficient, which vanishes when the RSP is constant.

The first category of successful models has ion-ion and self-energy (Born-type) terms with a concentration dependent RSP. These models might have a physical term as well, but this is not necessary. Some research groups consider this to be the only correct approach and even in the context of e-EoS, it has been sometimes stated that failing to include the composition dependency of the RSP (in the Born term) may put “too much pressure” on the fitting parameters of e-EoS whose only electrolyte contribution is the DH or MSA term. The second category of successful models has an ion-ion + physical part, where the Born term and/or composition dependency of the RSP have been ignored and still successful results are obtained, as seen with extended UNIQUAC [15]. In this case, the physical terms of these e-EoS carry the effect otherwise assumed by the Born term (when the RSP depends on salt concentration).

As reported, the effect of the RSP is significant, but there are numerous discussions and speculations on this topic. For example, it has been stated that the salt concentration dependent RSP expressions used in e-EoS and activity coefficient models are rather empirical [48,49], raising potential issues in their compositional derivatives required by the models. Moreover, it is typically assumed that in thermodynamic models we can use the total reduction of the RSP with respect to salt concentration. This is convenient but not necessarily correct, as the measured values of the RSP consist of a static (thermodynamic) and a kinetic depolarization term [50] and it is unclear whether the latter should be included in thermodynamic models.

Based on this analysis, we conclude that there is no consensus either on the “correct” terms that should be used in e-EoS nor in e- g^E models, nor on the use of composition-dependent RSP and of the Born term, while an ion-ion term (DH or MSA) is necessary. The next section will go deeper into the topics of RSP and its concentration dependency, as well as the balance of ion-ion and Born terms as compared to the other

contributions of e-EoS. This will be done in the context of recent results with the electrolyte versions of the CPA and various SAFT EoS.

3.1. Further insights from modern e-EoS terms (e-CPA, ePPC-SAFT, and eSAFT-VR Mie)

Modern e-EoS usually comprise physical terms, an ion-ion term and a Born term, with different approaches for the RSP. We notice that, in this discussion, the RSP is of special importance, as some models use a constant value, equal to that of the solvent (usually water), and others use a functional form producing decreasing RSP values with increasing salt concentration. Without a salt-concentration-dependency of the RSP, the Born term does not contribute to the activity coefficient.

The first type of models comprise a physical term, an ion-ion term (DH or MSA) and a Born term with a salt concentration dependent RSP, e.g. the e-EoS from Simon et al. [45] and the e-CPA from IFPEN group [46]. Various versions of e-PC-SAFT exist such as the ePPC-SAFT from IFPEN [51,53–59] and the e-PC-SAFT advanced from Bülow et al. [52], both of which include a Born term but different RSP.

Furthermore, Sun et al. [37] have performed an analysis of the performance of e-CPA (using a weak RSP concentration dependency) to predict IIAC. While the e-CPA results are accurate for MIAC (the model parameters are fitted to such data), the results for IIAC are quantitatively not satisfactory and often also qualitatively wrong. It is unclear, in the case of e-CPA, whether the failure to obtain better IIAC is due to the overall parameter estimation and the physical terms or due to the use of ion-specific parameters in the DH term (which, as mentioned above, perform worse compared to average DH diameters).

In all these e-EoS, the ion-ion term and the Born term are dominant, while other terms e.g. physical and association contribute less. For the latter this is the case when ion-ion association is neglected. One could argue that, since this approach produced satisfactory results, it is also the correct one. However, the situation is more complex. As seen for e-CPA, Fig. 6, it is possible to obtain good MIAC for NaCl-water using either the Born term with concentration dependent RSP or a constant

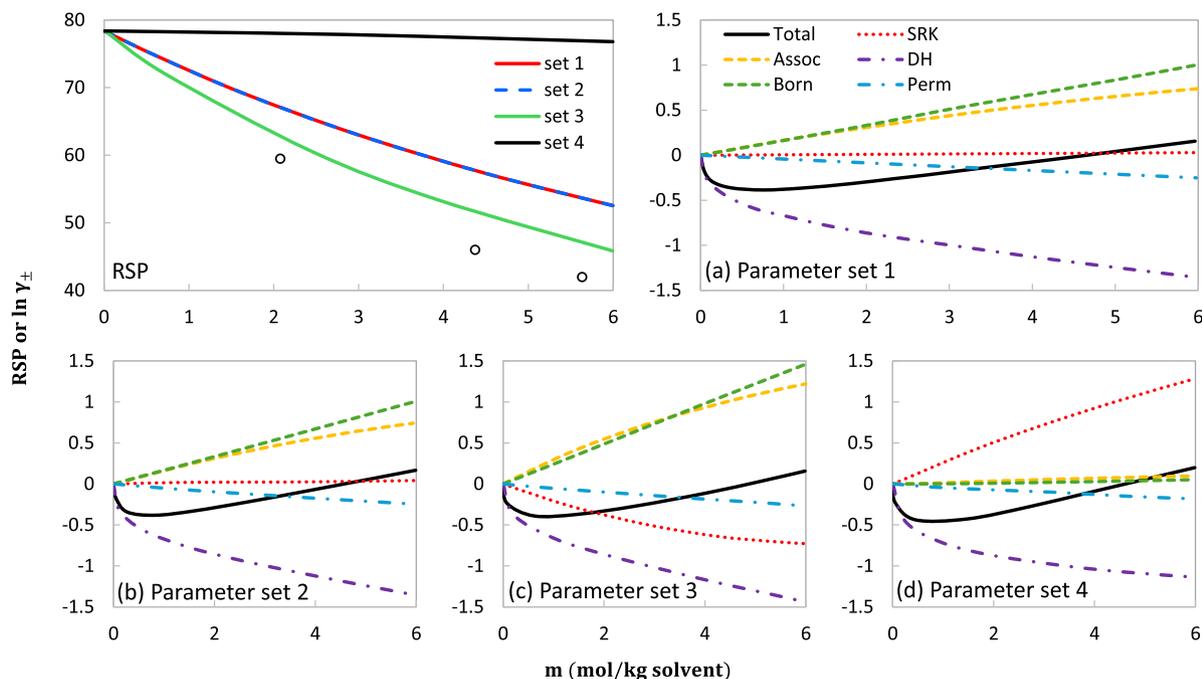


Fig. 6. The RSP and contributions of the different terms of e-CPA to the mean ionic activity coefficients for the water–NaCl system at 298.15 K for some of the parameterizations. eCPA results from Olsen et al. 2021 [69]. When a salt-concentration-dependent RSP is used (sets 1–3 have RSP that depends on salt molality, see first figure), the Born term contributes to the activity coefficient and counterbalances the DH term. When a salt-concentration-independent RSP is used (e.g. the water RSP, set 4 RSP of water, see first figure), the Born term does not contribute to the activity coefficient and the SRK term counterbalances the DH term.

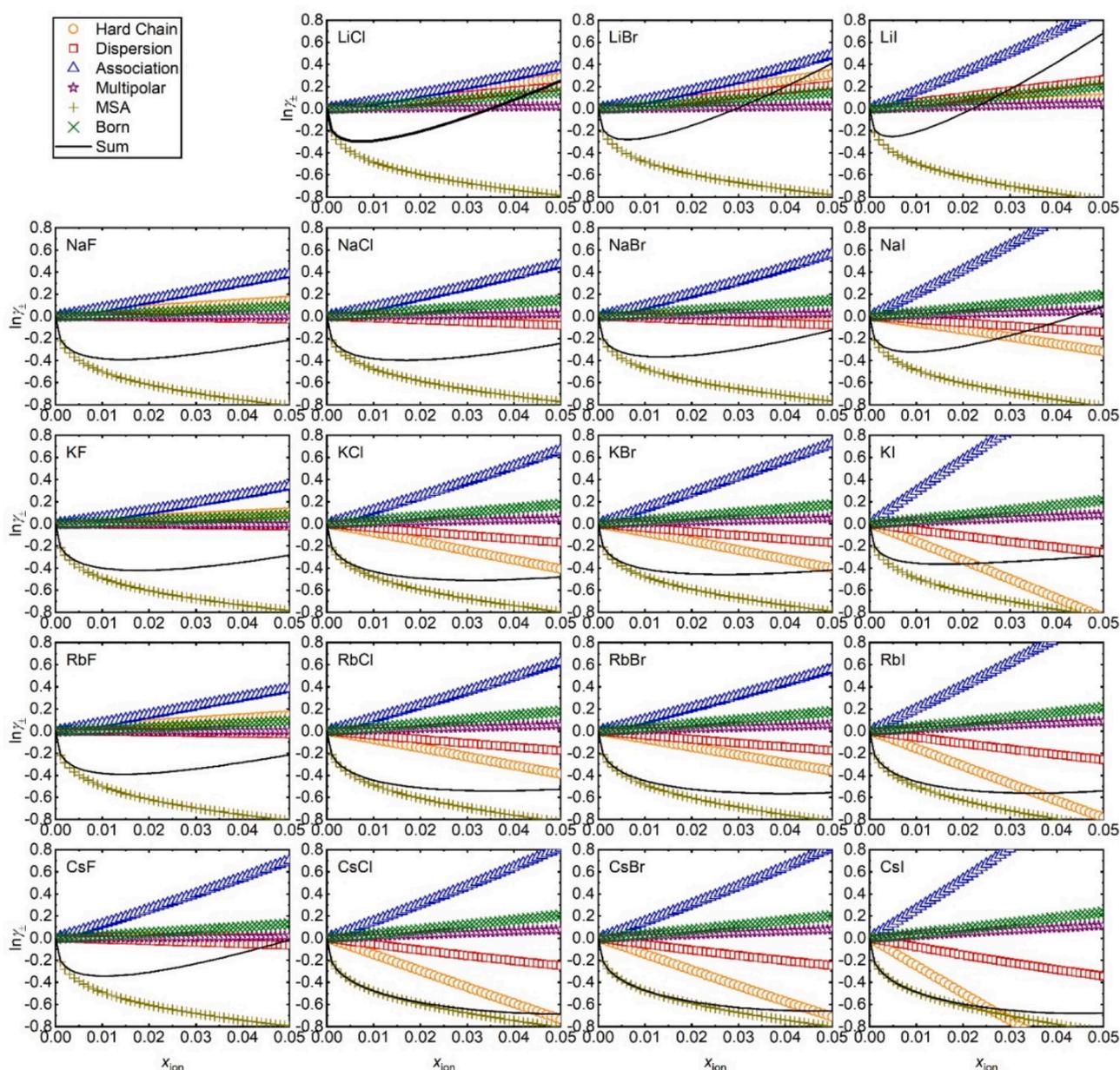


Fig. 7. Contributions to $\ln \gamma_{\pm}$ of the terms of the recommended parameter set for the aqueous alkali halide solutions at 298.15 K and 0.1 MPa with ePPC-SAFT. Reproduced from Yang et al. [55] with permission of Elsevier.

RSP equal to that of water (where the Born term has no contribution to MIAC). In the latter case, the SRK term is the one which “counterbalances” the large negative ion-ion (DH in this case) contribution.

The behavior is similar with ePPC-SAFT [51,53–59]. This model consists of hard chain, dispersion, association, polar, non-additive hard sphere, MSA, and Born terms. Roa Pinto et al. [59] investigated the short-range interactions and RSP models in ePPC-SAFT [60–62]. It was found that adding salt-composition dependence on top of the Schreckenberg et al. [60] model, in which salt-composition dependency is accounted for only implicitly through the density of the solution, is not needed.

Yang et al. [54,55] carried out a systematic ion-specific parameterization for the ePPC-SAFT model based on critically evaluated experimental databases [63,64]. In order to describe ion-ion and ion-solvent interactions, they compared different approaches: using only dispersion, only association, or both dispersion and association in addition to the MSA and Born terms. The association approach was recommended for

all ions except for Li^+ , while both dispersion and association terms were needed for accurately extending this ion-specific parameterization approach to Li^+ salts. For aqueous solutions of NaCl and KCl, the association approach correctly predicted the relative magnitudes of the cation and anion IAC for aqueous NaCl and KCl solutions. Contributions of the ePPC-SAFT (the association approach) terms are shown in Fig. 7 for all alkali halide salts. Compared to e-CPA, the association is larger in magnitude, as ion-ion and ion-solvent association are included.

A similar plot is shown in Fig. 8 with the eSAFT-VR Mie model. This model (as published by Novak et al. [65] and Selam et al. [66]) have used water’s RSP and the Born term (which is included) does not contribute to MIAC. When all electrolyte terms are added (Born+DH), their sum is comparable in magnitude to the “physical” term (as the Born term is zero and the ion-ion term is negative for the ion activity coefficients).

A detailed parametric analysis of eSAFT-VR Mie has been carried out by Walker et al. [67] using the Born term (with constant RSP, and RSP

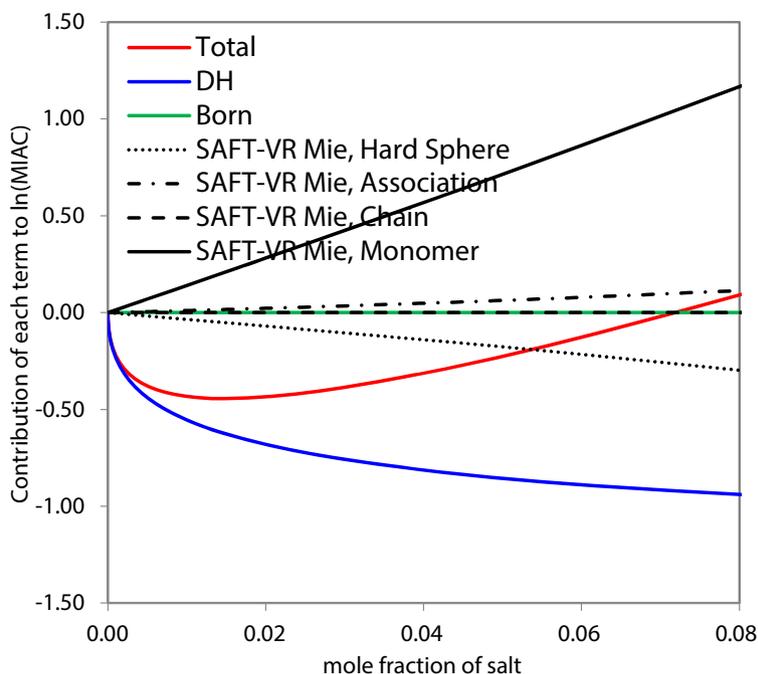


Fig. 8. Effect of the various terms of eSAFT-VR Mie (using the version by Selam et al. [66]) on the logarithm of the mean ionic activity coefficient for NaCl at 298.15 K and atmospheric pressure. The RSP is independent of composition and is equal to that of water.

from various theories) and both DH and MSA as ion-ion theories. They have found that the difference between the full DH and MSA is almost insignificant no matter the RSP value. However, the RSP has a huge effect overall in both theories. When the “real” salt-concentration-dependent RSP is used, the two theories predict larger absolute values of MIAC compared to using a constant RSP, equal to that of the solvent. When the “real” RSP is used, the “physical” SAFT-VR Mie contribution is much smaller compared to either the Born or any of the ion-ion terms (DH or MSA).

Moreover, Walker et al. [67] found that when all electrolyte terms are added (Born+ion-ion), their sum is comparable in magnitude to the “physical” term (as the Born term is positive and the ion-ion term is negative for the ion activity coefficients). Thus, it does look that all forces have a rather delicate balance. It seems that the sum of the ion-ion+Born contribution only with “real” RSP (maybe together with “physical” term also) has the trend of the experimental activity coefficients (the expected curvature), although the values of the activity coefficients are overestimated. The ion-ion+Born contribution with “constant” RSP appears to be very flat and asymptotic even at high concentration and twice as large compared to the physical part even at high concentrations (surprising, as with increasing concentration electrostatic effects should somewhat diminish and physical effects should become more dominant). These results appear to confirm the need for “real” salt-concentration-dependent RSP in e-EoS models, at least from a qualitative point of view. Novak et al. [68] showed that with eSAFT-VR Mie, a mild salt-concentration dependency of the RSP is best for quantitative results.

From this part of the work, in addition to the conclusions presented in the previous section, we can add the following observations. If the RSP does not depend on salt concentration and is that of pure solvent, then the Born term does not contribute to the activity coefficient and there is usually a balance of ion-ion and physical terms (Fig. 2, Fig. 6 and Fig. 8). In the opposite case, that of a salt-composition-dependent RSP in the Born and in the ion-ion (DH or MSA) terms, both terms are equally important (similar order of magnitude), the ion-ion interactions are negative and counterbalance the large positive solvation (Born) effects (Fig. 3, Fig. 7). Water association has no significant effect, but if ion-

water and ion-ion association also exists, this term becomes important.

It is possible, as shown in recent studies [52,68,70] that a difference in these two approaches (ion-ion counterbalancing Born with small effect of physical forces and ion-ion counterbalancing physical forces when Born term is zero) can be identified when the models are extended to non-aqueous or mixed solvents. Typically, e-models do not extrapolate well in non-aqueous or mixed solvent solutions, therefore new adjustable parameters between the non-aqueous solvent and the ions are needed. For ePC-SAFT [52] and eSAFT-VR Mie [68], it was found that a predictive approach to extending to non-aqueous solvents without new-adjustable parameters required the use of a Born term with a salt-concentration-dependent RSP.

4. Activity coefficients from explicit molecular simulation studies

Saravi and Panagiotopoulos [27] calculated IIAC and MIAC for NaCl, KCl, NaF, and KF from molecular dynamics simulations that treat water as molecules, referred to as explicit molecular simulations (EMS). Furthermore, IIAC and MIAC are reported by the same authors [71] for NaCl and KCl from molecular dynamics simulations where water is a dielectric continuum (not a distinct molecule), referred to as implicit molecular simulations (IMS). In these studies, quoting the original article: “the activity coefficients of the individual ions can be calculated from the difference between the chemical potential at a finite concentration from that at the infinite dilution reference state”. These works also report Lennard-Jones (LJ) and Coulombic (Cb) contributions of the chemical potential. In this section, the LJ and Cb contributions to the chemical potential values are converted to activity coefficients, in order to compare them with their EoS counterparts. The procedure is described in this section and the comparison with EoS will be presented in the next sections. We will only present in this work conversions, comparisons and discussions against the explicit molecular simulation studies.

In the work of Saravi and Panagiotopoulos [27], the values of IIAC and MIAC for the four salts (NaCl, KCl, NaF, and KF), as well as ionic chemical potentials from EMS were reported. For details on these

simulations, the reader is referred to the original article [27]. The activity coefficient is directly linked to the values of the chemical potential of ion i , μ_i , at fixed temperature and pressure:

$$\mu_i = \mu_i^{\infty,m} + RT \ln m_i \gamma_i^m \quad (2)$$

$$\mu_i = \mu_i^{\infty,*} + RT \ln x_i \gamma_i^* \quad (3)$$

where m_i is the molality, x_i is the mole fraction of ion i , γ_i^m is the molal activity coefficient, γ_i^* is the mole fraction activity coefficient. The reference chemical potentials in the two scales are $\mu_i^{\infty,m}$ and $\mu_i^{\infty,*}$, respectively, which are connected via $\mu_i^{\infty,m} = \mu_i^{\infty,*} + RT \ln M_w$, where M_w is the molecular weight of water. The reference state used for the calculation of activity coefficient in this work are asymmetric and they become unity in the infinite dilution limit. Activity coefficients from two different scales are connected via Eq. (4).

$$\ln \gamma_i^* = \ln \gamma_i^m - \ln x_w \quad (4)$$

To arrive at activity coefficients, the value of the reference chemical potential ($\mu_i^{\infty,m}$ or $\mu_i^{\infty,*}$) must first be determined. The value of the total chemical potential, μ_i , is the sum of the ideal gas (IG) chemical potential, μ_i^{IG} , and the residual contribution, μ_i^r , (called excess in the original paper) at fixed temperature and pressure. The residual contribution, as shown in Eq. (5), is the sum of the LJ and Cb terms, values for which were reported in the supplementary material of [27].

$$\mu_i = \mu_i^r + \mu_i^{IG} = \mu_i^{LJ} + \mu_i^{Cb} + \mu_i^{IG} \quad (5)$$

Since an ideal gas is also an ideal solution, its chemical potential at constant temperature and pressure can be calculated using Eq. (6):

$$\mu_i^{IG} = \mu_i^{IG,\infty,*} + RT \ln x_i \quad (6)$$

If we replace the mole fraction of the ions with molality $x_i = m_i x_w M_w$

Eq. (6) becomes Eq. (7)

$$\mu_i^{IG} = \mu_i^{IG,\infty,m} + RT \ln(m_i x_w) \quad (7)$$

with $\mu_i^{IG,\infty,m} = \mu_i^{IG,\infty,*} + RT \ln M_w$.

Now all that is required is to obtain the value of residual reference state chemical potential, $\mu_i^{r,\infty} = \mu_i^{\infty} - \mu_i^{IG,\infty,*}$, which will be calculated using the double extrapolation method (DE), as described by Saravi and Panagiotopoulos [27]. Residual reference state chemical potential values were not provided in the original publication [27], apart from those of Na^+ and Cl^- , which will be used for validation of the calculation that we repeat here. The DE method enforces the DH limiting law at low salt molality for the three lowest concentrations from EMS. The DH limiting law at the infinite dilution limit, dictates that:

$$\ln \gamma_i^m = \ln x_w - A \sqrt{m_i} \quad (8)$$

where A is the Debye-Hückel parameter.

The DH limiting law in Eq. (8) is introduced into Eq. (2), resulting in Eq. (9), valid at infinite dilution:

$$\mu_i = \mu_i^{\infty,m} + RT \ln m_i + RT \ln x_w - ART \sqrt{m_i} \quad (9)$$

If the Eq. (7) for the ideal gas chemical potential is introduced into Eq. (9), the following equation is obtained:

$$\mu_i - \mu_i^{IG} = \mu_i^{\infty,m} - ART \sqrt{m_i} - \mu_i^{IG,\infty,m}$$

which can be written as

$$\mu_i^{r,\infty} = \mu_i^r + ART \sqrt{m_i} \quad (10)$$

with $\mu_i^{\infty,m} - \mu_i^{IG,\infty,m} = \mu_i^{\infty,*} - \mu_i^{IG,\infty,*} = \mu_i^{r,\infty}$ and $\mu_i^r = \mu_i - \mu_i^{IG}$. The residual reference state chemical potential, $\mu_i^{r,\infty}$, is determined as the intercept of the linear fit of the three lowest concentrations, as shown in

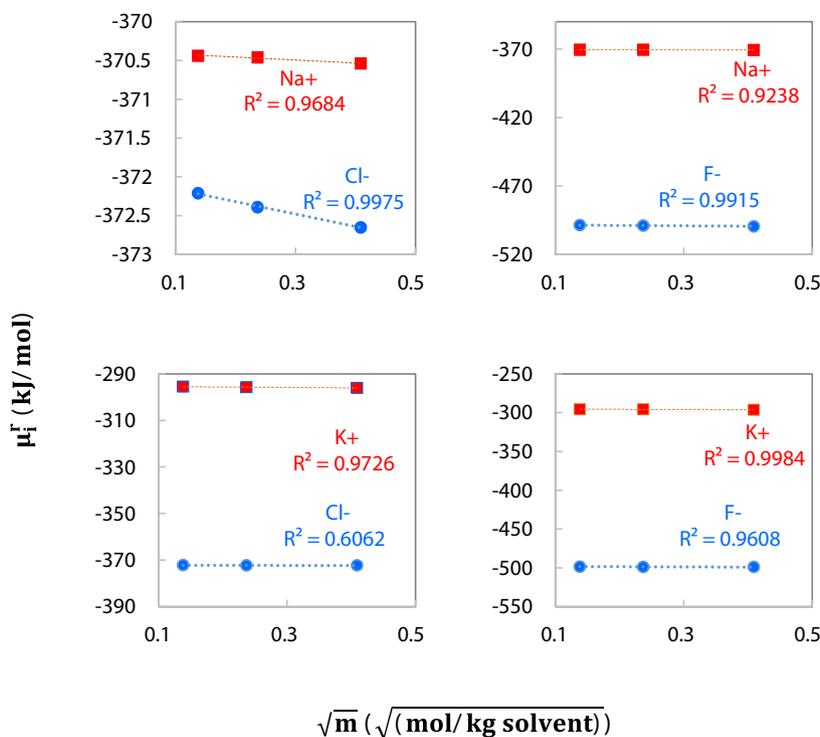


Fig. 9. Determination of residual reference state chemical potential, $\mu_i^{r,\infty}$, with the double extrapolation method for NaCl, NaF, KCl, KF at 298.15 K. Red is cation, blue is anion.

Fig. 9.

In the original publication [27], the residual chemical potentials were calculated at different system sizes, and then extrapolated to infinite system size for the residual and total chemical potentials but not for the LJ and Cb contributions separately. The procedure for obtaining the infinite system size values for the LJ and Cb contributions was not described by Saravi and Panagiotopoulos [27]. When the infinite system size residual chemical potential is used, R^2 of the DE extrapolation is very small. This could possibly be because of the errors introduced when extrapolating the system size to infinity. Therefore, the procedure is applied on the maximum system size values with good R^2 . Then, the obtained reference state of the residual chemical potential is scaled using the sum of the infinite system size and maximum system size values.

EMS calculations in [27] were performed in a stepwise manner, enabling the determination of the different contributions to the chemical potential. To quote Saravi and Panagiotopoulos [27]: “The μ_i values are calculated from the Helmholtz free energy difference for insertion of a single ion into an aqueous salt solution. Such an insertion is carried out slowly by first placing a ghost particle into the solution followed by turning on its Lennard-Jones (LJ) and Coulombic interactions (Cb) in a stepwise manner.”

The different contributions to the activity coefficient are calculated using Eqs. (11) and (12):

$$\ln \gamma_i^{LJ,*} = \frac{\mu_i^{LJ} - \mu_i^{LJ,\infty}}{RT} \tag{11}$$

$$\ln \gamma_i^{Cb,*} = \frac{\mu_i^{Cb} - \mu_i^{Cb,\infty}}{RT} \tag{12}$$

The reference state chemical potentials of the two contributions ($\mu_i^{LJ,\infty}$ and $\mu_i^{Cb,\infty}$) should be determined.

The LJ term is practically linear with molality, as shown in Fig. 10. This allows us to determine the $\mu_i^{LJ,\infty}$ by linear extrapolation. The LJ chemical potentials are scaled using the infinite system size and maximum system size residual chemical potential values.

The Cb contribution is then calculated using Eq. (13):

Table 1

Reference state chemical potential in kJ/mol for the various terms from EMS at 298.15 K. $\mu_i^{r,\infty}$ is calculated using the double extrapolation method (Eq. (10)), $\mu_i^{LJ,\infty}$ using linear fitting, $\mu_i^{Cb,\infty}$ from Eq. (13). In the parenthesis the values provided by Saravi and Panagiotopoulos [27] are shown, when available, to validate our results.

NaCl	Na ⁺	Cl ⁻
$\mu_i^{r,\infty}$	-369.90 (-369.69)	-371.49 (-371.66)
$\mu_i^{LJ,\infty}$	2.18	27.73
$\mu_i^{Cb,\infty}$	-372.08	-399.22
KCl	K ⁺	Cl ⁻
$\mu_i^{r,\infty}$	-294.65	-371.53
$\mu_i^{LJ,\infty}$	3.12	27.70
$\mu_i^{Cb,\infty}$	-297.76	-399.23
NaF	Na ⁺	F ⁻
$\mu_i^{r,\infty}$	-369.93	-497.60
$\mu_i^{LJ,\infty}$	2.15	19.46
$\mu_i^{Cb,\infty}$	-372.08	-517.06
KF	K ⁺	F ⁻
$\mu_i^{r,\infty}$	-294.67	-497.63
$\mu_i^{LJ,\infty}$	3.03	19.46
$\mu_i^{Cb,\infty}$	-297.70	-517.09

$$\mu_i^{Cb,\infty} = \mu_i^{r,\infty} - \mu_i^{LJ,\infty} \tag{13}$$

In Table 1 the infinite dilution chemical potentials for the various terms as calculated in this work from EMS are shown. The values have been scaled using the infinite and maximum system size values of the residual chemical potential. It is assumed that the LJ and Cb contributions are proportional to the total residual chemical potential when scaled to the infinite system size.

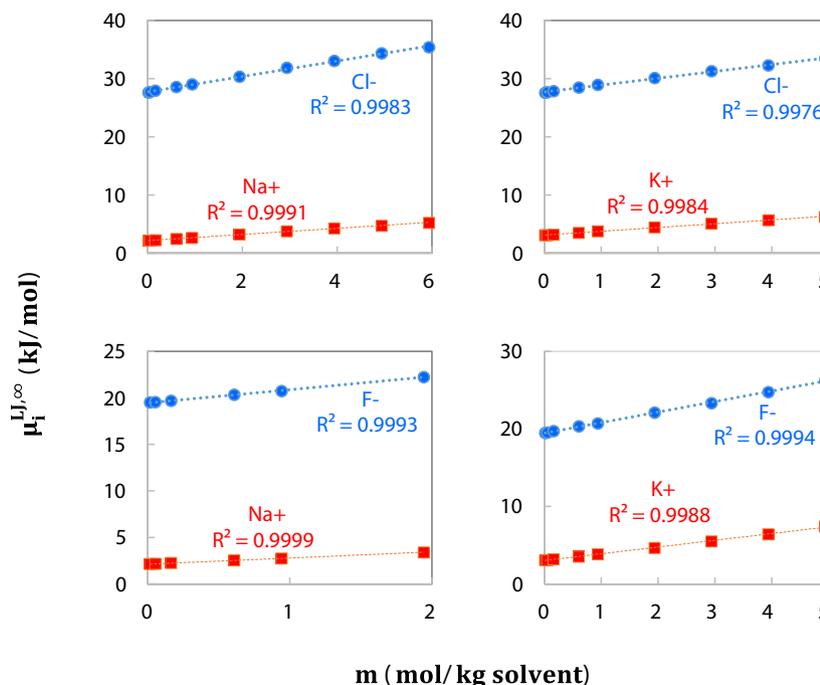


Fig. 10. Determination of infinite dilution LJ chemical potential by linear extrapolation for NaCl, NaF, KCl, KF at 298.15 K. Red is cation, blue is anion.

5. Comparison between contributions from molecular simulation and electrolyte equations of state

5.1. Correspondence between molecular simulation and EoS contributions

The purpose of this work is to compare the Cb/LJ contributions from molecular simulations to the “corresponding” EoS terms, it is therefore crucial to identify the appropriate correspondence between the MS and EoS contributions.

The three models considered in this work are the ePPC-SAFT, eSAFT-VR Mie, and e-CPA EoS with parameters from the original publications (for more details see Yang et al. [54–57], Novak et al. [68,72] and Olsen et al. [69,73,74]). The models can be represented in their simplified forms as shown in Eqs. (14a), (14b) and (14c).

$$A_{ePPC-SAFT}^{res} = A^{hc} + A^{disp} + A^{assoc} + A^{polar} + A^{MSA} + A^{Born} \quad (14a)$$

$$A_{eSAFT-VR\ Mie}^{res} = A^{hs} + A^{disp} + A^{ch} + A^{assoc} + A^{Debye-Hückel} + A^{Born} \quad (14b)$$

$$A_{e-CPA}^{res} = A^{SRK} + A^{assoc} + A^{Debye-Hückel} + A^{Born} \quad (14c)$$

Thus, we can see that the two SAFT EoS contain the physical, SAFT terms (hard sphere, chain, dispersion, and association for SAFT-VR Mie and hard sphere, chain, dispersion, association, and polar in ePPC-SAFT), the electrostatic term (DH in eSAFT-VR Mie or MSA in ePPC-SAFT), and the Born term. The e-CPA model has the DH equation for ion-ion interactions, the Born term, as well as the SRK and association terms for the remaining contributions. Short-range ionic interactions are approached in different ways in the three EoS. In eSAFT-VR Mie, ions are assumed to interact with dispersion forces (both ion-ion and ion-water), while the association term accounts only for the water-water interaction. In ePPC-SAFT, the dispersion term accounts only for water-water interaction (as the special case of Li^+ is not considered here), while the association term accounts for water-water, water-ion, and cation-anion interactions. For e-CPA, different parameterizations have been employed; in some cases association is considered only for water molecules and in other cases for water-water, ion-water and cation-anion. The different parameterizations are presented later.

In explicit molecular simulations (EMS) [27], as already mentioned, only two contributions are identified, the LJ and Cb. The ideal gas (IG) part is very small both for EoS and MS and it will not be discussed here. In EMS, the RSP of the electrolyte solution is an output of the calculations, making them directly comparable to a non-primitive model, while all the e-EoS in this work are based on the primitive approach (water as dielectric continuum).

Based on the way simulations have been carried out, LJ from MS is equivalent to the “physical forces” from e-EoS models and Cb is equivalent to the combined “ion-ion + Born” terms from e-EoS. This is the case because molecular simulations do include the “Born term” as part of the free energy. To determine the free energy of an ion, an LJ core of the ion is inserted gradually, from zero to full size, while no charges are present. This term is clearly the “LJ” part and is reported as such. The ion is then slowly charged from zero to full value. The free energy calculated from this second stage includes the energy required to charge the ion, which is the origin of Born term, the electrostatic interactions of this ion with other ions, which is the ion-ion term, and the energy due to the rearrangement of solvent molecules around the new charged entity, which does not have a direct equivalent to e-models. The latter is indirectly incorporated into the e-EoS by using a salt-concentration-dependent RSP.

Classification of the association contributions is not as straightforward. As association resembles a chemical bond, which involves the exchange of charge, it can be included in the Cb part of the model. Although we consider this as the most likely scenario, we have also assumed that the association term can be, together with other non-ionic effects, combined with physical forces and compared to the LJ part from the EMS. The difference between these two approaches is small for eSAFT-VR Mie (ions are non-associating species) and for those parameterizations of e-CPA for which no ion-ion association is considered. In these cases, these models only account for water-water association, which is a much smaller contribution compared to all others. The difference is significant for ePPC-SAFT (and for some e-CPA parameterizations), in which the ion-ion and water-ion associations are also accounted for by the association term. Due to the expression of non-bonded fractions, $X^{A_i} = \left(1 + \rho N_{AV} \sum_{B_j} X^{B_j} \Delta^{A_i B_j}\right)^{-1}$, the ion-ion and water-ion associations cannot be separated from the water-water interaction (which more probably does not correspond to the Cb contribution).

5.2. Activity coefficient contributions from eSAFT-VR Mie

In this section, we compare the EMS with the eSAFT-VR Mie calculations. In the EMS, the RSP of the electrolyte solution is an output of the calculations making them directly comparable to a non-primitive model. The eSAFT-VR Mie model, on the other hand, incorporates a primitive model for electrolytes. The model can have three different relations for the RSP, a mild salt concentration dependency, in the form of the mole fraction mixing rule (MFMR) [52], a correlation of RSP experimental data by Zuber et al. [75], and a constant RSP value, equal to that of the solvent (water for aqueous electrolyte solutions). All these approaches are described by Novak et al. [68,72]. All these models have been parameterized using both MIAC and IIAC, and the order of IIAC (whether cations or anions have larger values) agree with the EMS and experimental data by Wilczek-Vera et al. [21]. An interesting addition to previous work is the comparison with the individual contributions to the calculation of IIAC shown here.

Figs. 11 and 12 show the results for NaCl and KCl, while results for other salts (NaF and KF) are shown in the Supplementary Material. The agreement of the EoS and EMS contributions greatly depends on the value of the RSP. When eSAFT-VR Mie is used with the RSP of water (Fig. 11a, d), the agreement between EoS and EMS is quite satisfactory, both qualitatively and quantitatively. Typically, the EMS values are (in absolute values) higher than those from the model (when the RSP of solvent or the MFMR are used).

When the MFMR is used with eSAFT-VR Mie, then the contributions from EoS and EMS do not agree quantitatively, but the qualitative behavior is reproduced. On the other hand, when the experimental RSP is used through the correlation by Zuber et al., then the EoS predicts the exact opposite behavior: the Cb term is in excellent agreement with the SAFT without association, whereas the LJ term is essentially equal to the DH + Born + Association term. Furthermore, in this case, there is a minimum predicted in the DH + Born term that is not present in the EMS. In the case of eSAFT-VR Mie, we have association only between water molecules and the contribution of this term is quite small.

The study of IIAC reveals some interesting observations. The Cb term for IIAC has a minimum for the smaller ion within a salt, usually the cation (Fig. 12). Apart from the minimum, the agreement between EoS and EMS for IIAC, is similar to MIAC; the correct trend is captured in the case of the constant RSP, while the use of the experimental RSP leads to

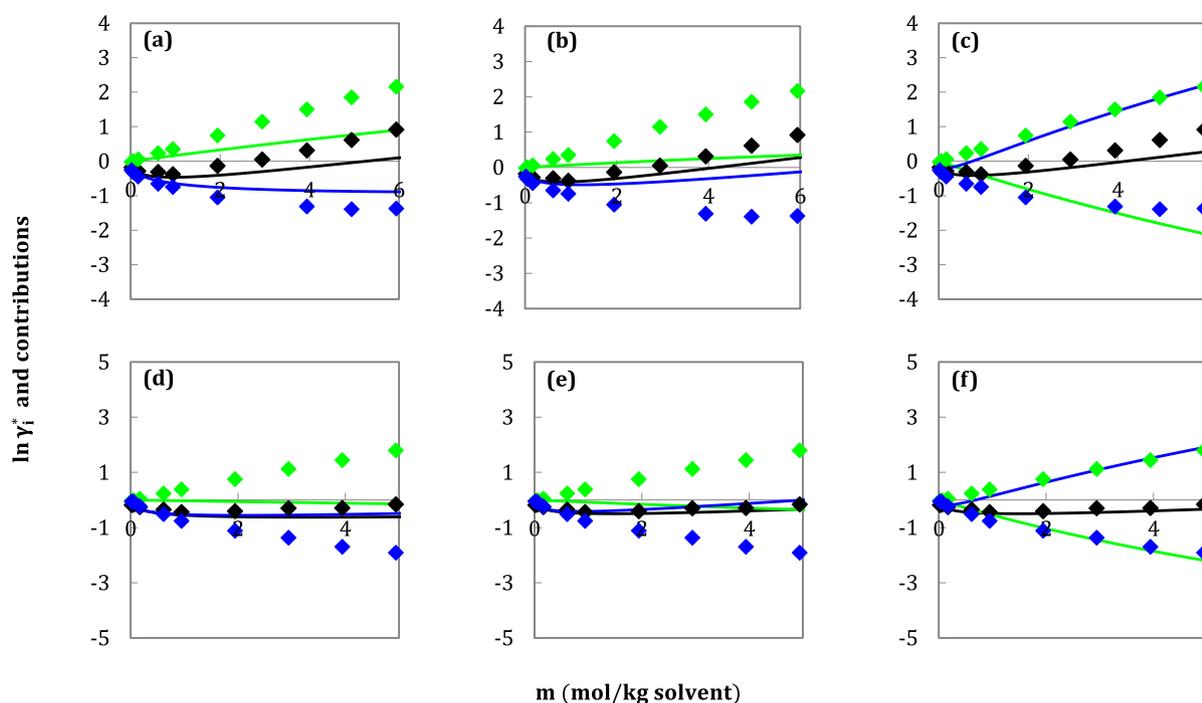


Fig. 11. $\ln \gamma_i^*$ and contribution of the various terms from explicit molecular simulation and eSAFT-VR Mie using (a, d) a constant RSP, (b, e) the MFMR and (c, f) the experimental RSP in the form of Zuber et al. [75] for NaCl (a-c) and KCl (d-f) at 298.15 K. Points are explicit molecular simulations, lines are eSAFT-VR Mie calculations. Green lines correspond to hard sphere + dispersion + chain contribution, blue lines correspond to the DH + Born + Association contribution and black is the total MIAC. Green points correspond to the LJ contribution in EMS, blue points to Cb contribution in EMS, black correspond to the total value of MIAC from EMS.

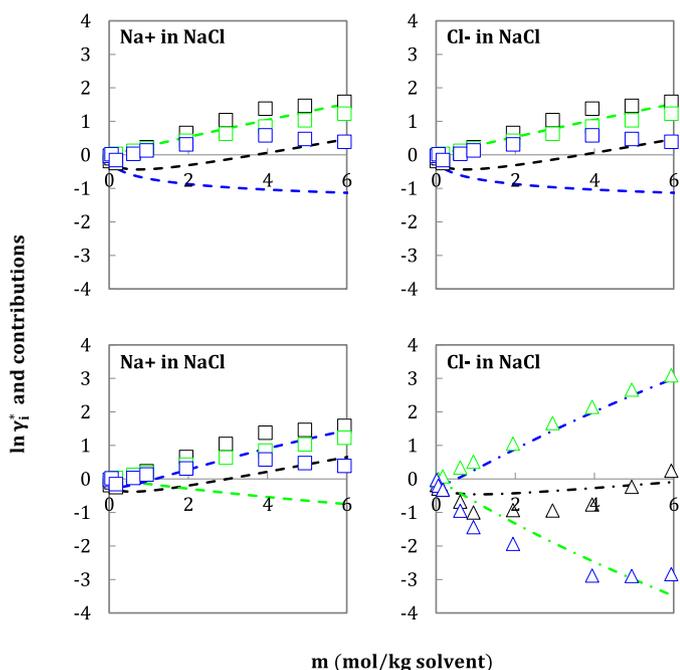


Fig. 12. $\ln \gamma_i^*$ and contribution of the various terms from explicit molecular simulation and eSAFT-VR Mie for individual ions for NaCl at 298.15 K. Top plots correspond to eSAFT-VR Mie (constant) and bottom plots to eSAFT-VR Mie (Zuber et al. [75]). Points are explicit molecular simulations, lines are eSAFT-VR Mie calculations. Green lines correspond to hard sphere + dispersion + chain contribution, blue lines correspond to the DH + Born + Association contribution and black is the total MIAC. Green points correspond to the LJ contribution in EMS, blue points to Cb contribution in EMS, black correspond to the total value of MIAC from EMS. Squares correspond to cation, triangles to anion.

the opposite trend between EoS and EMS. This is probably a side effect of “blindly” fitting parameters to experimental data and reinforces the need for understanding the relative trends between the different terms in e-EoS.

Finally, comparing the results for the four salts, we observe a better agreement between the EMS and the model (in the case of water RSP and MFMR) for the two Na^+ salts (NaCl, NaF) compared to the two K^+ salts (KCl, KF).

5.3. Activity coefficient contributions from ePPC-SAFT

Activity coefficients are calculated with the ePPC-SAFT model [54, 55] using the Schreckenber RSP model [60]. The association, dispersion, and full (association + dispersion) approaches were compared in previous works [54,55] for the short-range ion-ion and ion-solvent interactions. Among these approaches, only the association approach was able to predict the reversed relative magnitudes of the IIAC of cation and anion of the aqueous NaCl and KCl solutions, when the IIAC was not used in the parameterization. Thus, this is the methodology adopted here and association is considered for both ion-ion and ion-water interactions.

Fig. 13–16 show the results for NaCl and KCl, while results for the other salts are presented in the Supplementary Material. Figs. 13 and 14 show the contributions plotted when the (MSA + Born) terms combined correspond to the Cb contribution. Figs. 15 and 16 show the contributions plotted when the (MSA + Born + association) terms combined correspond to the Cb contribution.

In the first combination (where MSA + Born are compared to Cb from the EMS), the LJ and Cb contributions are much larger in magnitude compared to the EoS contributions, although in the end they also cancel each other out. This indicates that the contributions are more non-ideal in the EMS. For IIAC, both the EMS and ePPC-SAFT predict the correct relative magnitudes of the cation and anion IIACs for NaCl and KCl. The EMS results deviate further from the experimental data. However, the

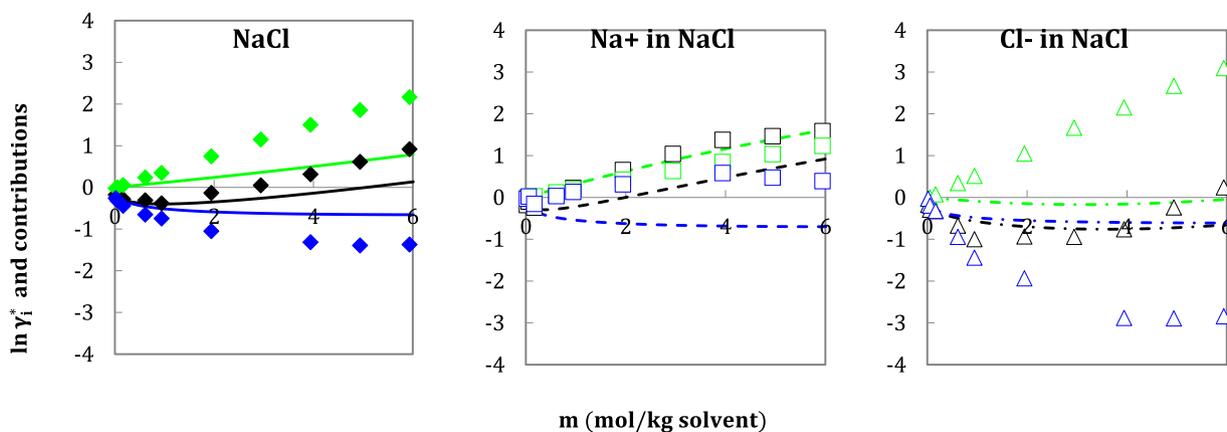


Fig. 13. $\ln \gamma_i^*$ and contributions of the various terms from explicit molecular simulation and ePPC-SAFT for NaCl at 298.15 K. Points are explicit molecular simulations, lines are ePPC-SAFT calculations. Green points are LJ contributions. Blue points are Cb contributions. Squares correspond to cation, triangles to anion and diamonds to the salt. Blue lines are the MSA + Born contributions. Green lines are Hard Chain + Dispersion + Polar + Association. Black points and lines are the total $\ln \gamma_i^*$.

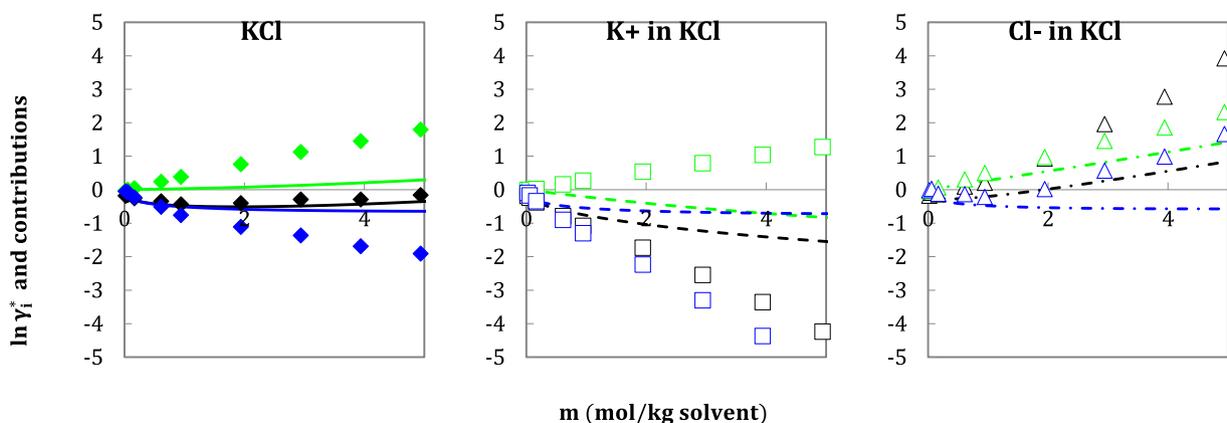


Fig. 14. $\ln \gamma_i^*$ and contributions of the various terms from explicit molecular simulation and ePPC-SAFT for KCl at 298.15 K. Points are explicit molecular simulations. Lines are ePPC-SAFT calculations. Green points are LJ contributions. Blue points are Cb contributions. Squares correspond to cation, triangles to anion and diamonds to the salt. Blue points are Cb contributions. Blue lines are the MSA + Born contributions. Green lines are Hard Chain + Dispersion + Polar + Association. Black points and lines are the total $\ln \gamma_i^*$.

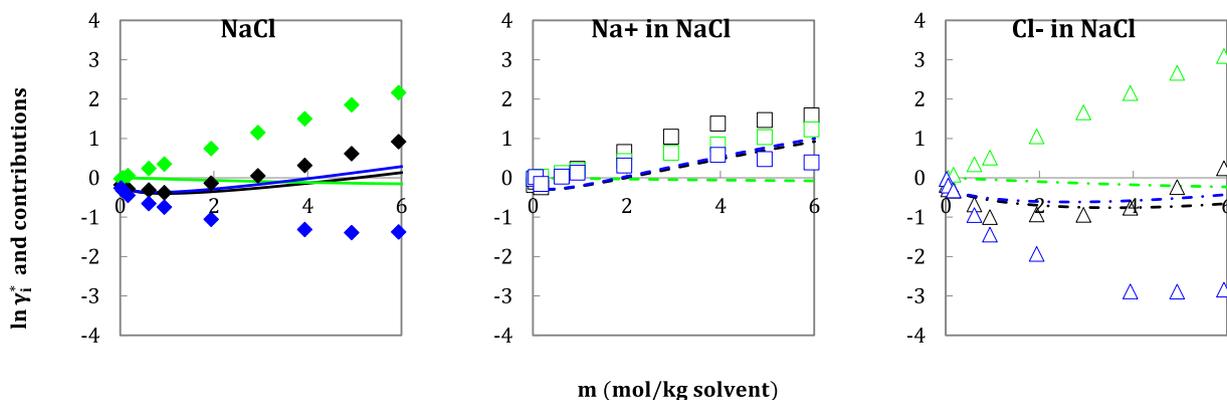


Fig. 15. $\ln \gamma_i^*$ and contributions of the various terms from explicit molecular simulation and ePPC-SAFT for NaCl at 298.15 K. Points are explicit molecular simulations. Lines are ePPC-SAFT calculations. Green points are LJ contributions. Blue points are Cb contributions. Squares correspond to cation, triangles to anion and diamonds to the salt. Blue lines are the MSA + Born + Association contributions. Green lines are Hard Chain + Dispersion + Polar. Black points and lines are the total $\ln \gamma_i^*$.

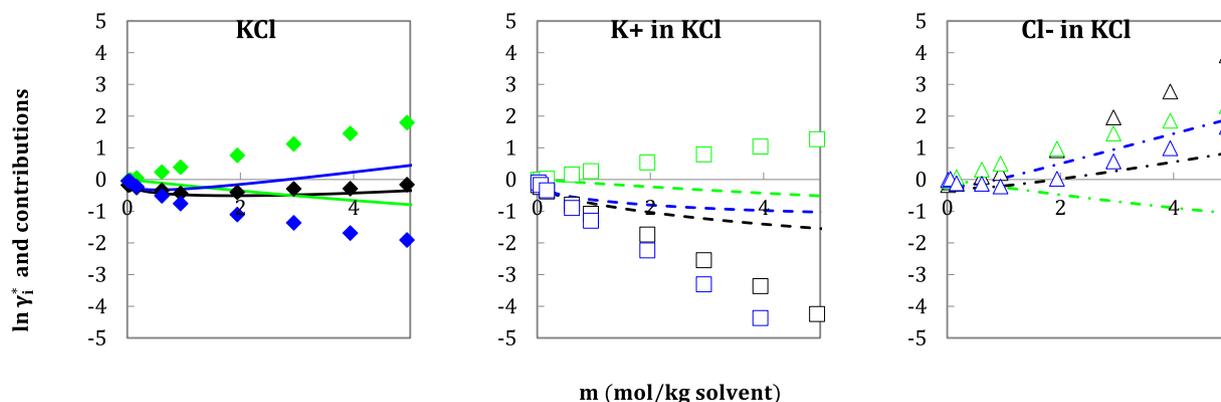


Fig. 16. $\ln \gamma_i^*$ and contributions of the various terms from explicit molecular simulation and ePPC-SAFT for KCl at 298.15 K. Points are explicit molecular simulations. Lines are ePPC-SAFT calculations. Green points are LJ contributions. Blue points are Cb contributions. Squares correspond to cation, triangles to anion and diamonds to the salt. Blue lines are the MSA + Born + Association contributions. Green lines are Hard Chain + Dispersion + Polar. Black points and lines are the total $\ln \gamma_i^*$.

Cb contribution in the EMS and the MSA contribution in the ePPC-SAFT behave quite differently. In the EMS, the Cb contribution presents a minimum, and is positive at larger salt composition for Na^+ in NaCl and Cl^- in KCl, but is negative for Cl^- in NaCl and K^+ in KCl; while the MSA contribution presents curves of similar shapes for MIAC and all IACs.

According to the results for the association and dispersion strategies of the ePPC-SAFT, the association term plays an important role in correctly predicting the relative magnitudes of the IACs of the cation and anion for NaCl and KCl. Though only qualitative, the EMS Cb contribution behavior suggests that the rest of the terms in the EoS needs to account for the ion-ion interaction that is significantly different from how the MSA term typically behaves. In the ePPC-SAFT, the additional ion-ion interaction is accounted for by the Wertheim association.

We should mention that since the Schreckenber RSP model is used and, thus, since the salt-composition dependency is quite small and implicit through the volume dependency, the effect of the Born term is also quite small. Similar results are shown (in supplementary material) for NaF and KF, where we observe that the model's "physical" contribution (with the first combination) is very small, especially for NaF, and as for the other salts, much smaller than the EMS results.

In the second combination (where MSA + Born + association is compared to Cb from EMS), the (MSA + Born + association) IAC curves of Na^+ in NaCl and Cl^- in KCl present trends alike to the Cb contributions for the IACs in the EMS. This is, however, not the case of the other ions and overall, the results for MIAC contributions are less in agreement with EMS compared to first combination (when association is included in the physical term). More specifically, for MIAC the second combination results in smaller, compared to the first combination, absolute values for the negative electrolyte and positive physical terms. These are even smaller than the first contribution compared to the EMS.

In this second combination, and for both NaCl and KCl, the model's physical contribution decreases with increasing salt concentration, which is not in agreement to the EMS results. This is because of the inclusion of the water-water association in the electrolyte contribution. Similar conclusions are seen for KF, while for NaF the agreement between model and EMS is slightly better with the second combination.

Although the water-water association could not be separated from the association term, the contribution is expected to be much smaller than the ion-ion and ion-water association contributions. Therefore, although the water-water association likely caused the negative physical contributions that are very small in magnitude, it does not change that the magnitude of the contribution of the (MSA + Born + association)

Table 2

An overview of the e-CPA parameterizations.

Name	Reference	RSP-dependency ¹	IAC trend ⁴	Comments ⁵
Set 4	Olsen et al., 2021 [69]	Constant	Wrong	Density in objective function SRK vs. DH Born, Association, etc. very small
Case2/ Model 6	Olsen et al., 2023 [73]	Experimental	Correct	Fitted to IAC Ion association Born & SRK vs. DH & Association Born > SRK DH > Association
Scenario 1/ MMB ²	Olsen et al., 2023 [74]	Mild	Wrong	Dispersion parameters SRK vs. DH Born almost zero
Scenario 3/ Simonin	Olsen et al., 2023 [74]	Experimental	Correct	Association parameters Ion association Born vs. DH SRK small, Association negative, important
Scenario 5/ MM ³ solvent	Olsen et al., 2023 [74]	Mild	Wrong	Dispersion + Association parameters SRK vs. DH Born of some importance Association small negative

1: The salt-concentration dependency of the RSP.

2: MMB=Mollerup-Michelsen-Breil expression for the RSP.

3: MM=Maribo-Mogensen expression for the RSP.

4: The IAC trend is in comparison to the experimental data.

5: When we write e.g. "SRK vs. DH", we mean that the largest positive and negative contributions, roughly balancing each other are the SRK and Debye-Hückel terms respectively (similarly in other cases).

combination is smaller than the first combination (MSA + Born), and deviates further to the EMS data. To conclude, when the ion-ion and ion-water associations are included in the EoS, we note that the combined contributions of the association and MSA terms are closer to the Cb contribution in the EMS, compared to that of the MSA term on its own.

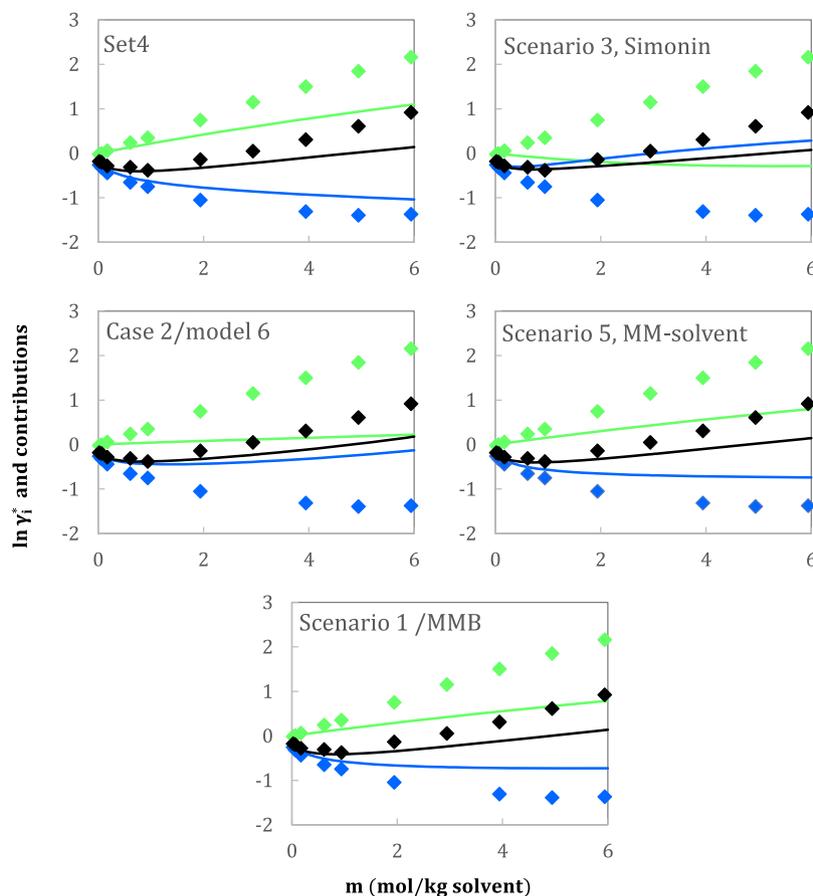


Fig. 17. Trends of the e-CPA contributions (terms) for various e-CPA parameterizations shown in Table 2 against the molecular simulation data from [27] at 298.15 K. Green points are LJ contributions, blue points are Cb contributions, black points are MIAC. Green lines are SRK + Association, blue lines are DH + Born, black lines are total MIAC.

In addition, the behavior of the MIAC contributions is less challenging to reproduce, at least qualitatively, as the Cb contribution presents a curve that resembles the MSA. The drastic increase and decrease of the cation and anion activity coefficient in the EMS, respectively, which is not MSA behavior, cancel each other out. Therefore, when only mean properties are included in the parameterization of EoS, a parameter set that fails in representing the trends of IIAC could have no problem in accurately representing MIAC. Once again, the Born term is quite small for the MIAC.

5.4. Activity coefficient contributions from e-CPA

In this section, we present comparisons of the e-CPA results with the EMS for the activity coefficients of NaCl in water. This is the only system parameterized with e-CPA in recent studies [69,73,74]. We have selected several characteristic sets from these works, as presented and discussed in Table 2. We have kept the original terminology of these sets. The results are shown in Figs. 17, 18 and 19. The parameterizations are chosen so that they cover a wide range of parameter estimation methods. The diversity of the parameter estimation methods and differences in the trends of the main terms can be seen under comments in Table 2.

For each of the parameterizations, the contributions to MIAC are shown. For all parameterizations, MIAC, osmotic coefficients, and density of water-NaCl are satisfactorily represented.

We have chosen two options for the terms corresponding to the Cb forces from molecular simulation, either DH + Born or DH + Born + Association. In both cases, the rest of the terms are compared to the LJ forces from the molecular simulations (EMS).

With respect to the contributions from the EMS, it can be seen from

Figs. 17, 18 and 19 that there are large and opposite trends for LJ and Cb for NaCl. In [71], where IIAC results are shown, we see that for Cl^- , there are large and opposite trends for LJ and Cb (like NaCl) whereas both LJ and Cb are positive contributions outside of the very low concentration range for Na^+ . The Na^+ IIAC trends are not predicted by any of the e-CPA versions. These results are not shown here.

Our observations can be summarized as follows:

1. For the MIAC trends, all e-CPA results are in qualitative agreement with the EMS results; SRK is in agreement with LJ and DH + Born + association with Cb. For the sets where ion-association has been included, by far the best agreement with Cb EMS results is obtained when association is included in DH + Born. This may be expected. For Scenario 3, Simonin, the trend is even wrong at higher salt content when association is considered as an LJ contribution.
2. None of the models presented here predict the large difference between the LJ and Cb contributions as shown by the EMS. The EMS results show contributions which are (much) larger than the e-EoS results, especially for the LJ vs. SRK etc. terms. However, it should be noted that the EMS results are not accurate for either MIAC or IIAC of any of the ions, which means that the magnitudes of the LJ and Cb forces should be considered with care. However, it is still interesting that none of the parameterizations are close to match the magnitudes of the EMS, especially for the LJ contributions.
3. There are rather small differences between the various and quite different e-CPA parameterizations when the Cb forces are DH + Born + Association, as can be seen from Fig. 19 where several sets are compared.

Based on this figure, set 4 is the closest to the EMS results and

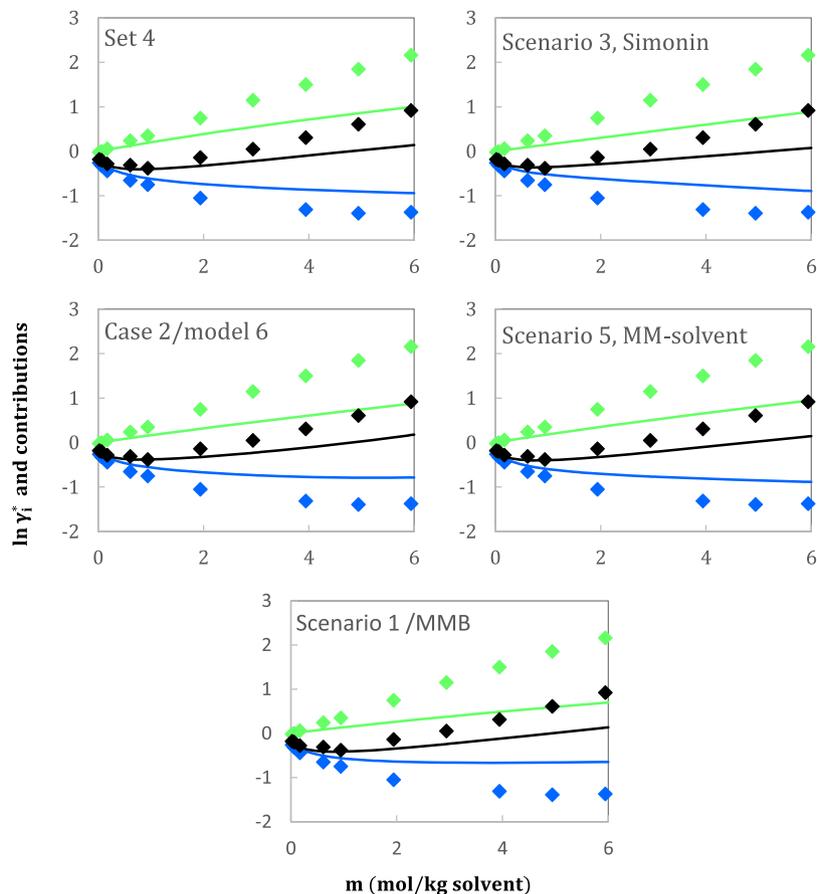


Fig. 18. Trends of the e-CPA contributions (terms) for various e-CPA parameterizations shown in Table 2 against the molecular simulation data from [27] at 298.15 K. Green points are LJ contributions, blue points are Cb contributions, black points are MIAC. Green lines are SRK, blue lines are DH + Born + Association, black lines are total MIAC.

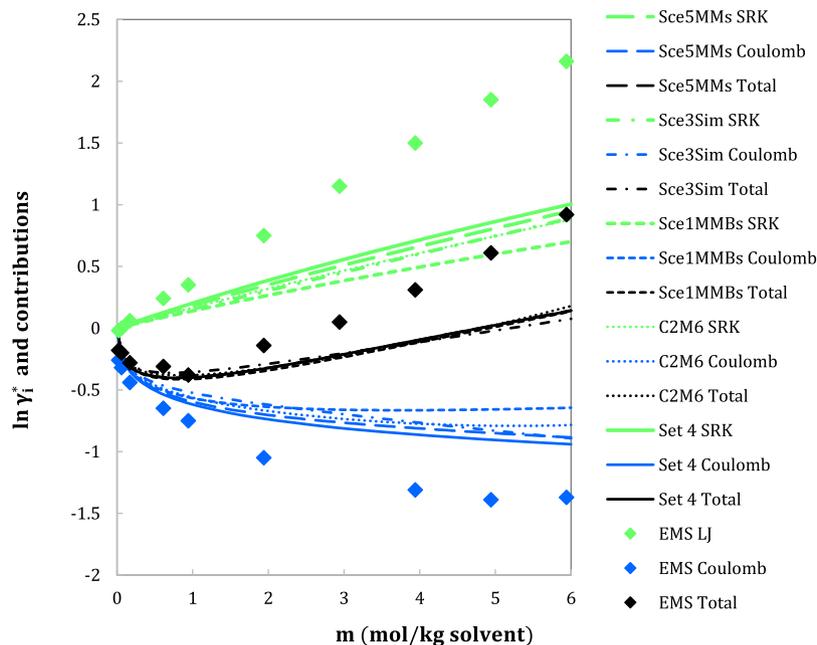


Fig. 19. Comparative representation of the trends of the e-CPA contributions (terms) for various e-CPA parameterizations shown in Table 2 against the molecular simulation data from [27] at 298.15 K. Points are EMS, lines are e-CPA predictions. The Coulomb contributions for e-CPA are in all cases DH + Born + Association.

Scenario 1/MMB is the one that is the furthest away. The second-best set, in terms of agreement between the e-CPA and EMS, is Scenario 5/MMsolvent. For these two sets, the RSP is either that of water or a mild concentration dependency, i.e. the Born term is zero or almost zero. None of the two sets predict the correct IIAC trends. Interestingly enough, the e-CPA sets where ion-association is considered and an experimental RSP dependency is used perform worse with respect to EMS agreement.

However, it should be emphasized, as shown in Fig. 19, that all the parameterization scenarios yield very similar contributions. This similarity is quite interesting considering that in the different scenarios, different RSP models have been used, and completely different parameterization strategies, which result in significantly different balance between the different forces if the terms are examined individually. Set 4 and Scenario 5/MM are both basically just a balance between SRK and DH (fully or partially), while several of the other sets have significant individual contributions from all the terms and yet they are all so similar when the terms are combined as done here. This suggests that it is correct to consider association as a part of the Cb contribution. However, it is possible that it is specific to e-CPA (and ePPC-SAFT).

6. Discussion

We will now try to draw some conclusions from the results and comparisons shown in Section 5. It is not easy, and perhaps not even possible, to generalize our conclusions as we have only studied four 1:1 strong aqueous electrolyte solutions at 25 °C at atmospheric pressure (though only NaCl-water for e-CPA). Our conclusions may differ at higher temperatures and for non-aqueous solvents and other electrolytes. Nevertheless, we anticipate that the underlying physical basis and careful parameterization of these EoS will result in good extrapolations to a broader range of conditions. Additional molecular simulation results at elevated temperature, pressure and alternative solvents would be valuable to confirm the robustness of the EoS beyond the thermodynamic conditions examined in the present study. These observations may differ at higher temperatures and for non-aqueous solvents and other electrolytes. Correspondence between e-EoS and EMS contributions is not entirely clear either as, by ignoring one term in the molecular force field, the system changes and a particular property refers to this different system. Still, MS possibly is the only tool currently available to make some reasoning behind the trends of the various contributions from thermodynamic models for electrolytes. For e-EoS, in addition to the various types of possible interactions that have been incorporated in the models, the parameter estimation procedure can also have an influence on the results. In the case of e-CPA, we have considered several estimation methods, as reported in the literature and reproduced in the previous section.

With the above reservations, we can conclude that the deviations between the three e-EoS and EMS are similar; there are some differences, but they do not appear to be very important. In all cases, the model contributions are much smaller than those of MS; the physical term is small in almost all cases; actually, it seems that the models sometimes have an “acceptable” agreement to EMS for the electrostatic terms, but not for the physical term (compared to the LJ term from the EMS).

The results for eSAFT-VR Mie indicate that good correspondence with the EMS is obtained only with zero Born term, i.e. no RSP concentration dependency at all. Acceptable results are obtained when a weak salt-concentration-dependency of the RSP is used (with the MFMR). Using the Zuber model for RSP, i.e. an expression that represents well the experimental RSP concentration dependency, yields poor results, with essentially “reverse trends” for all contributions. It is clear that having the correct concentration dependency of RSP does not perform well when compared to the EMS results (neither quantitatively nor qualitatively). It is interesting to recall that the Lewis-Randall/McMillan-Mayer framework consistency “demands” that the RSP is salt-concentration independent, as recently shown in [76].

Recent studies with eSAFT-VR Mie [68,72] have shown that these approaches (water’s RSP, MFMR or Zuber et al. expression for the RSP) perform equally well for the MIAC of aqueous salt solutions after the ion-water energy and ion diameter parameters have been fitted to experimental data. On the other hand, for extension to non-aqueous and mixed solvent electrolyte solutions a weak salt-concentration-dependency of the RSP is needed (MFMR), while representing the RSP accurately (Zuber et al. expression) does not yield good MIAC results in non-aqueous solvents [68,72].

In the case of e-CPA, only NaCl-water have been considered but with five parameter estimation procedures (Table 2). As with eSAFT-VR Mie, the model shows lower values for the various contributions compared to the EMS results. There are some similarities and differences compared to eSAFT-VR Mie. For both models, the best agreement with the EMS is obtained using water’s RSP and acceptable one using mild salt-concentration dependency for the RSP. Unlike eSAFT-VR Mie, e-CPA results using experimental RSP dependencies are, while worse compared to using water’s RSP, not catastrophic (as with eSAFT-VR Mie using the Zuber et al. expression). Still, in the case of e-CPA and for the single system considered, the differences between the various parameterizations are much smaller compared to eSAFT-VR Mie.

In the case of ePPC-SAFT, which combines the polar PC-SAFT with MSA, the parameter estimation includes ion-ion association and ion-water association as well. The Born term is small due to the choice of the RSP expression, so the major contributions are MSA, physical terms and the association term (between ions, water and ion-water). We have considered two combinations, first (association together with physical forces) and second (association together with MSA + Born). In both cases, the model activity coefficients are much smaller in magnitude than the EMS, but only in the first we have qualitatively good agreement with the EMS for MIAC contributions. In the second combination, including the ion-ion association in ePPC-SAFT correctly represents the IIAC minimum. However, it makes the MIAC results of the model to be further away from the EMS.

Results with all three models indicate, taking the EMS results at face value, that improvements are needed in all three e-EoS, possibly both in the physical and electrostatic terms. Considering the differences between the models, both in terms of various terms but also on their parameterization strategies, and the results of this work, one might be tempted to state that some of these models are overfitted, as much simpler models result in similar MIAC predictions. However, we consider this view oversimplistic, as there is more to electrolyte thermodynamics than MIAC predictions, studied in this work, and all three models were parameterized also based on various other properties. It is our view that our models capture the essential physics, rather than overfit the experimental data, especially considering that even after all the new developments in electrolyte thermodynamics, we still do not have a clear answer as to the terms/parameters that are actually required for a complete electrolyte model. For example, when solvation energies or extension to non-aqueous solutions are considered, a Born term is required for accurate predictions [59,68,77], while to capture electrical conductivity, an ion-pairing term is required [78]. But there are models that capture MIAC correctly even without a Born term. It all comes down to what terms are needed for specific properties. What we can without a doubt prove with this work is that we need at least two opposing terms (and their corresponding parameters) to describe contributions and MIAC accurately. Molecular simulation shows that these terms are a physical one and an electrolyte one and this approach is adopted by most electrolyte models, both EoS and activity coefficient models.

6.1. Reflections of the comparisons of the three e-EoS with literature models and trends

In this section, we compare the trends of the three e-EoS against MS with the literature models presented in Section 2. First, several activity

coefficient models like those from Validsko-Boda, Shilov-Lyashenko, Hückel and others contain only ion-ion (DH or other methods) and Born terms and several of these models provide good results for MIAC (some qualitatively correct also for IIAC).

It is absolutely essential for such models (with only ion-ion + Born contributions and no other additional terms) to use a salt-concentration-dependent RSP and a Born term to obtain realistic activity coefficients. This conclusion does not necessarily mean that a salt concentration dependent RSP is the correct choice for all models, but if only ion-ion + Born terms constitute the model, such a dependency is absolutely necessary. It also does not confirm the necessity to use the Born term for aqueous electrolyte systems. Indeed, as seen with all three e-EoS (e-CPA, ePPC-SAFT and eSAFT-VR Mie) investigated here, it is entirely possible to obtain excellent results for MIAC of aqueous electrolyte systems (but not for other properties) when the effect of the Born term on MIAC disappears due to a salt-concentration-independent RSP or if its contribution is very small due to a very mild concentration dependency for RSP [39,50,51,53–55,59,60,68,69,72–74]. In this case, the “physical terms” of the models increase with concentration and to some extent counterbalances the ion-ion (DH or MSA) contributions at high concentrations. The same behavior is observed for activity coefficient models that do not include the Born term like the extended UNIQUAC. We can conclude that this result agrees with MS studies which contain both electrostatic (ion-ion and Born) and physical (LJ) terms. Using the RSP of pure water or a mild salt concentration dependency of RSP is the best approach. In some sense, EMS studies confirm what we have observed with all three e-EoS, when their performance for MIAC and densities is considered. It is interesting to note that Walker et al. [67] found that in eSAFT-VR Mie the experimental salt concentration dependency of RSP may be the optimum approach, but their work is entirely predictive without fitting any parameters and properties like densities and MIAC are represented only qualitatively correct with the predictive version of the model. This “importance” of using the experimental RSP dependency seems to be lost when the model parameters are fitted to experimental data (densities and MIAC), possibly because the “physical term” of the model is increased in importance and magnitude.

Moreover, as shown in several studies by Liang, Silva and co-workers [43,44], the way the concentration dependency of RSP is considered in the various e-EoS may not be optimum from a physical point of view. The models have been derived under the assumption that RSP is constant, and then this assumption is relaxed, and a salt concentration dependency is included (in some cases). It would be more correct to include the concentration dependency before the charging process and the derivation of the electrostatic contribution to the Helmholtz energy, as shown by Shilov-Lyashenko and Silva et al. [28,29,43,44]. In the latter case, it appears that for ion-ion + Born models alone, the performance is better.

7. Conclusions

In this work, three equations of state (EoS) suitable for electrolytes (eSAFT-VR Mie, ePPC-SAFT and e-CPA) have been compared with explicit molecular simulations (EMS) for the contributions of the various terms to MIAC and IIAC of some aqueous electrolyte solutions. Four 1:1 electrolytes are considered at 25 °C and 1 bar, for which MS data are available. We expect the conclusions of this study to be valid for similar systems and conditions, but may differ at higher temperatures and for non-aqueous solvents and other electrolytes. For this reason, additional molecular simulation results at elevated temperature, pressure and alternative solvents and salts would be a valuable addition to the literature.

First, we have shown how MS contributions (Cb and LJ) are generated from MS data. We have investigated the correspondence of the EoS terms to the LJ and Cb contributions produced by EMS studies. Considering how the MS are performed, we suggest that the most probable analogy between the EoS and EMS terms is (i) DH/MSA + Born

corresponding to the Coulombic term (Cb) from the EMS, and (ii) the rest of the EoS terms (SAFT/CPA) corresponding to the Lennard-Jones term (LJ). Some e-EoS parameterizations consider ion-ion association and this results in a significant association term. This can be considered either as “electrostatic” or “physical” and thus is compared accordingly with the corresponding MS-generated data.

The main conclusion is that, in qualitative terms and when considering all results, the performance of all three e-EoS is overall similar when compared to the EMS. All models predict significantly lower values for MIAC/IIAC compared to simulations, but they are in qualitative agreement with the simulation data. This agreement is more evident, in most cases, for the electrostatic term rather than the physical contributions. It is interesting to note the similarities in the performance of all three models considering they are based on different physical terms, different ion-ion theories, and different parameterizations.

Despite the small differences between the models, overall eSAFT-VR Mie is closer to the EMS compared to the other two e-EoS considered for MIAC. For IIAC, however, the DH and MSA contributions do not capture the minimum shown in explicit MS, and the EoS contributions continue to decrease with increasing molality. In ePPC-SAFT, assuming that the association (ion-ion, ion-water, and water-water), MSA and Born terms combined correspond to the Cb contribution, the minimum in the IIAC is reproduced qualitatively.

Different expressions for the RSP are considered and these affect the contribution of the Born term. When only the water’s RSP is used, the Born term does not contribute to the values of the activity coefficients. For eSAFT-VR Mie and ePPC-SAFT, using no or very mild concentration dependencies of RSP (thus no or very small Born contribution) results in the best performance against EMS – and the same was concluded in previous studies when the models were compared against experimental activity coefficient data. For e-CPA, water’s RSP performs also very well, but the effect of RSP is smaller compared to the other two e-EoS for the only system considered with this model (NaCl). In two of the models (e-CPA and ePPC-SAFT), ion-ion association is explicitly considered, although the improvement in terms of models’ agreement against the EMS is not significant for the MIAC, there is improvement for the IIAC for ePPC-SAFT.

All thermodynamic models considered here were parameterized against experimental MIAC data and the EMS were not used in parameter estimation. Previous studies demonstrated with various models that composition dependent RSP and the Born term may be of significance for electrolyte EoS and for certain activity coefficient models for electrolytes, especially those containing mostly/only ion-ion and Born terms. This study, only focusing on aqueous solutions at room temperature, demonstrated - also when compared to simulations - that the Born/RSP effects may be small at least for e-EoS that contain a variety of terms (physical, association, ion-ion, Born). The parameter estimation procedures may somewhat account for Born/RSP effects, as other terms e.g. physical or association counterbalance the significant ion-ion contributions at higher concentrations. It remains to be seen whether such conclusions will change for other conditions (higher temperatures and non-aqueous solvents).

CRedit authorship contribution statement

Nefeli Novak: Writing – review & editing, Writing – original draft, Investigation, Formal analysis. **Fufang Yang:** Writing – review & editing, Writing – original draft, Investigation, Formal analysis. **Martin Due Olsen:** Investigation, Formal analysis. **Xiaodong Liang:** Writing – review & editing, Supervision. **Nicolas von Solms:** Writing – review & editing, Supervision. **Ioannis G. Economou:** Writing – review & editing, Supervision. **Marcelo Castier:** Writing – original draft, Supervision. **Jean-Charles de Hemptinne:** Writing – original draft, Supervision, Investigation. **Athanassios Z. Panagiotopoulos:** Writing – review & editing, Supervision. **Georgios M. Kontogeorgis:** Writing – review & editing, Writing – original draft, Supervision, Funding acquisition,

Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Comparison between Explicit Molecular Simulations and eSAFT-VR Mie and ePPC-SAFT for fluoride salts.

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.fluid.2025.114339](https://doi.org/10.1016/j.fluid.2025.114339).

Data availability

Data will be made available on request.

References

- G.M. Kontogeorgis, R. Privat, J.N. Jaubert, Taking another look at the van der Waals equation of state-almost 150 years later, *J. Chem. Eng. Data* 64 (2019) 4619–4637, <https://doi.org/10.1021/acs.jced.9b00264>.
- G.M. Kontogeorgis, G.K. Folas, Thermodynamic Models for Industrial Applications: From Classical and Advanced Mixing Rules to Association Theories, John Wiley & Sons, 2009, <https://doi.org/10.1002/9780470747537>.
- G.M. Kontogeorgis, P. Coutsikos, Thirty years with EoS/G E models-what have we learned? *Ind. Eng. Chem. Res.* 51 (2012) 4119–4142, <https://doi.org/10.1021/ie2015119>.
- G.M. Kontogeorgis, I.G. Economou, Equations of state: from the ideas of van der Waals to association theories, *J. Supercrit. Fluids* 55 (2010) 421–437, <https://doi.org/10.1016/j.supflu.2010.10.023>.
- G.M. Kontogeorgis, P. Coutsikos, V.I. Harismiadis, A. Fredenslund, D.P. Tassios, A novel method for investigating the repulsive and attractive parts of cubic equations of state and the combining rules used with the vdW-1f theory, *Chem. Eng. Sci.* 53 (1998) 541–552, [https://doi.org/10.1016/S0009-2509\(97\)00274-1](https://doi.org/10.1016/S0009-2509(97)00274-1).
- R. Privat, J.-N. Jaubert, G.M. Kontogeorgis, The secret of the Wilson equation, *Fluid. Phase Equilib.* 114018 (2023), <https://doi.org/10.1016/j.fluid.2023.114018>.
- J.M. Prausnitz, R.N. Lichtenthaler, E.G. De Azevedo, *Molecular Thermodynamics of Fluid-Phase Equilibria*, Pearson Education, 1998, [https://doi.org/10.1016/0378-3812\(87\)80022-5](https://doi.org/10.1016/0378-3812(87)80022-5).
- G.M. Kontogeorgis, P.M. Vlamos, An interpretation of the behavior of EoS/GE models for asymmetric systems, *Chem. Eng. Sci.* 55 (2000) 2351–2358, [https://doi.org/10.1016/S0009-2509\(99\)00472-8](https://doi.org/10.1016/S0009-2509(99)00472-8).
- P.A. Sacomani, E.A. Brignole, Predictions of activity coefficients of nearly Athermal binary mixtures using cubic equations of State, *Ind. Eng. Chem. Res.* 42 (2003) 4143–4145, <https://doi.org/10.1021/ie030028u>.
- M.-J. Huron, J. Vidal, New mixing rules in simple equations of state for representing vapour-liquid equilibria of strongly non-ideal mixtures 3 (1979) 255–271.
- D.S.H. Wong, S.I. Sandler, A theoretically correct mixing rule for cubic equations of state, *AIChE Journal* 38 (1992) 671–680, <https://doi.org/10.1002/aic.690380505>.
- G.M. Kontogeorgis, P.M. Vlamos, An interpretation of the behavior of EoS/GE models for asymmetric systems, *Chem. Eng. Sci.* 55 (2000) 2351–2358, [https://doi.org/10.1016/S0009-2509\(99\)00472-8](https://doi.org/10.1016/S0009-2509(99)00472-8).
- J. Ahlers, J. Gmehling, Development of a universal group contribution equation of state. 2. Prediction of vapor-liquid equilibria for asymmetric systems, *Ind. Eng. Chem. Res.* 41 (2002) 3489–3498, <https://doi.org/10.1021/ie020047o>.
- W.G. Chapman, K.E. Gubbins, G. Jackson, M. Radosz, New reference equation of state for associating liquids, *Ind. Eng. Chem. Res.* 29 (1990) 1709–1721.
- K. Thomsen, Modeling electrolyte solutions with the extended universal quasichemical (UNIQUAC) model, *Pure Appl. Chem.* (2005) 531–542, <https://doi.org/10.1351/pac200577030531>.
- J.-L. Cruz, H. Renon, A new thermodynamic representation of binary electrolyte solutions nonideality in the whole range of concentrations, *AIChE J.* 24 (1978) 817–830, <https://doi.org/10.1002/aic.690240508>.
- L. Blum, Mean spherical model for asymmetric electrolytes I. Method of solution, *Mol. Phys.* 30 (1975) 1529–1535, <https://doi.org/10.1080/00268977500103051>.
- P. Debye, E. Hückel, The theory of electrolytes: I. lowering of freezing point and related phenomena, *Phys. Z* 24 (1923) 185–206.
- M. Born, Volumen und Hydratationswärme der Ionen, *Zeitschrift Für Physik* 1 (1920) 45–48, <https://doi.org/10.1007/BF01881023>.
- N. Bjerrum, Investigations on association of ions. I. The influence of association of ions on the activity of the ions at intermediate degrees of association, *Kgl. Danske Videnskab. Selskab.* 7 (1926) 1–48.
- G. Wilczek-Vera, E. Rodil, J.H. Vera, On the activity of ions and the junction potential: revised values for all data, *AIChE Journal* 50 (2004) 445–462, <https://doi.org/10.1002/aic.10039>.
- G. Wilczek-Vera, J.H. Vera, On the measurement of individual ion activities, *Fluid. Phase Equilib.* 236 (2005) 96–110.
- J. Vera, G. Wilczek-Vera, *Classical Thermodynamics of Fluid Systems: principles and Applications*, 2016. <https://books.google.com/books?hl=en&lr=&id=dw4NDgAAQBAJ&oi=fnd&pg=PP1&dq=Classical+Thermodynamics+of+Fluid+Systems+Principles+and+Applications&ots=1mU2o33H5C&sig=dTuIL20VWDsDtNv-EAine0Yxdmk> (accessed December 12, 2022).
- F. Malatesta, On the experimental determinations of ionic activity coefficients, *Fluid. Phase Equilib.* 239 (2006) 120–124, <https://doi.org/10.1016/j.fluid.2005.11.009>.
- F. Malatesta, The impossibility of measuring individual ion activity coefficients using ion selective electrodes, *J. Solution. Chem.* 29 (2000) 771–779, <https://doi.org/10.1023/A:1005137929282>.
- F. Malatesta, On a recent purported determination of individual ion activity coefficients, *AIChE J.* 52 (2006) 785–791, <https://doi.org/10.1002/aic.10651>.
- S.H. Saravi, A.Z. Panagiotopoulos, Individual ion activity coefficients in aqueous electrolytes from explicit-water molecular dynamics simulations, *J. Phys. Chem. B* 125 (2021) 8511–8521, <https://doi.org/10.1021/acs.jpcc.1c04019>.
- I.Yu. Shilov, A.K. Lyashchenko, The role of concentration dependent static permittivity of electrolyte solutions in the Debye-Hückel theory, *J. Phys. Chem. B* 119 (2015) 10087–10095, <https://doi.org/10.1021/acs.jpcc.5b04555>.
- I.Yu. Shilov, A.K. Lyashchenko, Modeling activity coefficients in alkali iodide aqueous solutions using the extended Debye-Hückel theory, *J. Mol. Liq.* 240 (2017) 172–178, <https://doi.org/10.1016/j.molliq.2017.05.010>.
- M. Valiskó, D. Boda, Unraveling the behavior of the individual ionic activity coefficients on the basis of the balance of ion-ion and ion-water interactions, *J. Phys. Chem. B* 119 (2015) 1546–1557, <https://doi.org/10.1021/jp509445k>.
- J. Vincze, M. Valiskó, D. Boda, The nonmonotonic concentration dependence of the mean activity coefficient of electrolytes is a result of a balance between solvation and ion-ion correlations, *J. Chem. Phys.* 133 (2010) 154507, <https://doi.org/10.1063/1.3489418>.
- N. Khomutov, Activity coefficients of ions and their solvation, *Russian J. Phys. Chem.* 41 (1967) 1216.
- E. Hückel, Zur theorie konzentrierter wässriger lösungen starkerelektrolyte, *Physikalische Zeitschrift* 26 (1925) 93–147.
- L.A. Bromley, Thermodynamic properties of strong electrolytes in aqueous solutions, *AIChE Journal* 19 (1973) 313–320, <https://doi.org/10.1002/aic.690190216>.
- G.M. Silva, X. Liang, G.M. Kontogeorgis, The true Hückel equation for electrolyte solutions and its relation with the Born term, *J. Mol. Liq.* 368 (2022), <https://doi.org/10.1016/j.molliq.2022.120554>.
- H.C. Helgeson, D.H. Kirkham, G.C. Flowers, Theoretical prediction of the thermodynamic behavior of aqueous electrolytes by high pressures and temperatures; IV, Calculation of activity coefficients, osmotic coefficients, and apparent molal and standard and relative partial molal properties to 600 °C and 5kb, *Am. J. Sci.* 281 (1981) 1249–1516.
- L. Sun, X. Liang, N. von Solms, G.M. Kontogeorgis, Analysis of some electrolyte models including their ability to predict the activity coefficients of individual ions, *Ind. Eng. Chem. Res.* 59 (2020) 11790–11809, <https://doi.org/10.1021/acs.iecr.0c00980>.
- L. Sun, Q. Lei, B. Peng, G.M. Kontogeorgis, X. Liang, An analysis of the parameters in the Debye-Hückel theory, *Fluid. Phase Equilib.* 556 (2022) 113398, <https://doi.org/10.1016/j.fluid.2022.113398>.
- Q. Lei, B. Peng, L. Sun, J. Luo, Y. Chen, G.M. Kontogeorgis, X. Liang, Predicting activity coefficients with the Debye-Hückel theory using concentration dependent static permittivity, *AIChE Journal* 66 (2020) e16651, <https://doi.org/10.1002/aic.16651>.
- E.A. Guggenheim, L. The specific thermodynamic properties of aqueous solutions of strong electrolytes, *London, Edinburgh, and Dublin Philosoph. Magazine J. Sci.* 19 (1935) 588–643, <https://doi.org/10.1080/14786443508561403>.
- A.C. Tikanen, W.R. Fawcett, The role of solvent permittivity in estimation of electrolyte activity coefficients for systems with ion pairing on the basis of the

- mean spherical approximation, *Berichte Der Bunsengesellschaft Für Physikalische Chemie* 100 (1996) 634–640, <https://doi.org/10.1002/bbpc.19961000515>.
- [42] W.R. Fawcett, A.C. Tikanen, Role of solvent permittivity in estimation of electrolyte activity coefficients on the basis of the mean spherical approximation, *J. Phys. Chem.* 100 (1996) 4251–4255, <https://doi.org/10.1021/jp952379v>.
- [43] G.M. Silva, X. Liang, G.M. Kontogeorgis, How to account for the concentration dependency of relative permittivity in the Debye-Hückel and Born equations, *Fluid. Phase Equilib.* (2022) 113671, <https://doi.org/10.1016/j.fluid.2022.113671>.
- [44] G.M. Silva, X. Liang, G.M. Kontogeorgis, The connection between the Debye and Güntelberg charging processes and the importance of relative permittivity: the ionic cloud charging process, *J. Chem. Eng. Data* (2023), <https://doi.org/10.1021/acs.jced.3c00168>.
- [45] H.-G. Simon, H. Kistenmacher, J.M. Prausnitz, D. Vortmeyer, An equation of state for systems containing electrolytes and nonelectrolytes, *Chem. Eng. Process. Process Intensif.* 29 (1991) 139–146.
- [46] R. Inchekele, J.C. de Hemptinne, W. Fürst, The simultaneous representation of dielectric constant, volume and activity coefficients using an electrolyte equation of state, *Fluid. Phase Equilib.* 271 (2008) 19–27, <https://doi.org/10.1016/j.fluid.2008.06.013>.
- [47] W. Fürst, H. Renon, Representation of excess properties of electrolyte solutions using a new equation of state, *AIChE J.* 39 (1993) 335–343, <https://doi.org/10.1002/aic.690390213>.
- [48] B. Maribo-Mogensen, G.M. Kontogeorgis, K. Thomsen, Modeling of dielectric properties of complex fluids with an equation of state, *J. Phys. Chem. B* 117 (2013) 3389–3397, <https://doi.org/10.1021/jp310572q>.
- [49] B. Maribo-Mogensen, G.M. Kontogeorgis, K. Thomsen, Comparison of the Debye-Hückel and the mean spherical approximation theories for electrolyte solutions, *Ind. Eng. Chem. Res.* 51 (2012) 5353–5363, <https://doi.org/10.1021/ie2029943>.
- [50] B. Maribo-Mogensen, G.M. Kontogeorgis, K. Thomsen, Modeling of dielectric properties of aqueous salt solutions with an equation of state, *J. Phys. Chem. B* 117 (2013) 10523–10533, <https://doi.org/10.1021/jp403375t>.
- [51] S. Ahmed, N. Ferrando, J.C. de Hemptinne, J.P. Simonin, O. Bernard, O. Baudouin, Modeling of mixed-solvent electrolyte systems, *Fluid. Phase Equilib.* 459 (2018) 138–157, <https://doi.org/10.1016/j.fluid.2017.12.002>.
- [52] M. Bülow, M. Ascani, C. Held, ePC-SAFT advanced - Part I: physical meaning of including a concentration-dependent dielectric constant in the born term and in the Debye-Hückel theory, *Fluid. Phase Equilib.* 535 (2021) 112967, <https://doi.org/10.1016/j.fluid.2021.112967>.
- [53] J. Rozmus, J.C. De Hemptinne, A. Galindo, S. Dufal, P. Mougin, Modeling of strong electrolytes with ePPC-SAFT up to high temperatures, *Ind. Eng. Chem. Res.* 52 (2013) 9979–9994, <https://doi.org/10.1021/ie303527j>.
- [54] F. Yang, T.D. Ngo, J.S. Roa Pinto, G.M. Kontogeorgis, J.-C. de Hemptinne, Systematic evaluation of parameterization approaches for the ePPC-SAFT model for aqueous alkali halide solutions, *Fluid. Phase Equilib.* 570 (2023) 113778, <https://doi.org/10.1016/j.fluid.2023.113778>.
- [55] F. Yang, G.M. Kontogeorgis, J.-C. de Hemptinne, Systematic evaluation of parameterization approaches for the ePPC-SAFT model for aqueous alkali halide solutions. II. Alkali bromides, iodides, fluorides, and lithium halides, *Fluid. Phase Equilib.* 573 (2023) 113853, <https://doi.org/10.1016/j.fluid.2023.113853>.
- [56] F. Yang, G.M. Kontogeorgis, J.-C. de Hemptinne, Composition-dependence of relative static permittivity in ePPC-SAFT for mixed-solvent alkali halides, *Fluid. Phase Equilib.* 583 (2024) 114103, <https://doi.org/10.1016/j.fluid.2024.114103>.
- [57] F. Yang, A. Raespour Shirazi, J.S. Roa Pinto, G.M. Kontogeorgis, N. Ferrando, A. Galindo, J.-C. de Hemptinne, Ion Pairing in ePPC-SAFT for Aqueous and Mixed-Solvent Alkali Halide Solutions, *Ind. Eng. Chem. Res.* 63 (2024) 12999–13015, <https://doi.org/10.1021/acs.iecr.4c01579>.
- [58] A.R. Shirazi, F. Yang, T.D. Ngo, N. Ferrando, O. Bernard, J.P. Simonin, J.C. de Hemptinne, Thermodynamic modeling of aqueous and mixed-solvent alkali chloride solutions using an ion-pairing equation of state, *Fluid. Phase Equilib.* 588 (2025), <https://doi.org/10.1016/j.fluid.2024.114231>.
- [59] J.S. Roa Pinto, N. Ferrando, J.-C. de Hemptinne, A. Galindo, Temperature dependence and short-range electrolytic interactions within the e-PPC-SAFT framework, *Fluid. Phase Equilib.* 560 (2022) 113486, <https://doi.org/10.1016/j.fluid.2022.113486>.
- [60] J.M.A. Schreckenber, S. Dufal, A.J. Haslam, C.S. Adjiman, G. Jackson, A. Galindo, Modelling of the thermodynamic and solvation properties of electrolyte solutions with the statistical associating fluid theory for potentials of variable range, *Mol. Phys.* 112 (2014) 2339–2364, <https://doi.org/10.1080/00268976.2014.910316>.
- [61] J.P. Simonin, O. Bernard, L. Blum, Real ionic solutions in the mean spherical approximation. 3. Osmotic and activity coefficients for associating electrolytes in the primitive model, *J. Phys. Chem. B* 102 (1998) 4411–4417, <https://doi.org/10.1021/jp9732423>.
- [62] K. Giese, U. Kaatz, R. Pottel, Permittivity and dielectric and proton magnetic relaxation of aqueous solutions of the alkali halides, *J. Phys. Chem.* 74 (1970) 3718–3725, <https://doi.org/10.1021/j100715a005>.
- [63] F. Yang, J. Qu, G.M. Kontogeorgis, J.-C. de Hemptinne, Reference density database for 20 aqueous alkali halide solutions, *J. Phys. Chem. Ref. Data* 51 (2022) 043104, <https://doi.org/10.1063/5.0124173>.
- [64] F. Yang, T.D. Ngo, G.M. Kontogeorgis, J. De Hemptinne, A Benchmark Database for Mixed-Solvent Electrolyte Solutions : consistency Analysis Using E NRTL, *Ind. Eng. Chem. Res.* 61 (2022) 15576–15593, <https://doi.org/10.1021/acs.iecr.2c00059>.
- [65] N. Novak, G.M. Kontogeorgis, M. Castier, I.G. Economou, Modeling of gas solubility in aqueous electrolyte solutions with the eSAFT-VR Mie Equation of State, *Ind. Eng. Chem. Res.* 60 (2021) 15327–15342, <https://doi.org/10.1021/acs.iecr.1c02923>.
- [66] M.A. Selam, I.G. Economou, M. Castier, A thermodynamic model for strong aqueous electrolytes based on the eSAFT-VR Mie equation of state, *Fluid. Phase Equilib.* 464 (2018) 47–63, <https://doi.org/10.1016/j.fluid.2018.02.018>.
- [67] P.J. Walker, X. Liang, G.M. Kontogeorgis, Importance of the relative static permittivity in electrolyte SAFT-VR Mie equations of state, *Fluid. Phase Equilib.* 551 (2022) 113256, <https://doi.org/10.1016/j.fluid.2021.113256>.
- [68] N. Novak, G.M. Kontogeorgis, M. Castier, I.G. Economou, Extension of the eSAFT-VR Mie equation of state from aqueous to non-aqueous electrolyte solutions, *Fluid. Phase Equilib.* 565 (2023) 113618, <https://doi.org/10.1016/j.fluid.2022.113618>.
- [69] M.D. Olsen, G.M. Kontogeorgis, X. Liang, N. Von Solms, Investigation of the performance of e-CPA for a wide range of properties for aqueous NaCl solutions, *Fluid. Phase Equilib.* (2021) 113167, <https://doi.org/10.1016/j.fluid.2021.113167>.
- [70] N. Novak, G.M. Kontogeorgis, M. Castier, I.G. Economou, Mixed Solvent Electrolyte Solutions: a Review and Calculations with the eSAFT-VR Mie Equation of State, *Ind. Eng. Chem. Res.* 62 (2023) 13646–13665, <https://doi.org/10.1021/acs.iecr.3c00717>.
- [71] S.H. Saravi, A.Z. Panagiotopoulos, Activity coefficients of aqueous electrolytes from implicit-water molecular dynamics simulations, *Journal of Chemical Physics* 155 (2021), <https://doi.org/10.1063/5.0064963>.
- [72] N. Novak, G.M. Kontogeorgis, M. Castier, I.G. Economou, Mixed solvent electrolyte solutions: a review and calculations with eSAFT-VR Mie EoS, (2023).
- [73] M.D. Olsen, G.M. Kontogeorgis, X. Liang, N. von Solms, Comparison of models for the relative static permittivity with the e-CPA equation of state, *Fluid. Phase Equilib.* 565 (2023) 113632, <https://doi.org/10.1016/j.fluid.2022.113632>.
- [74] M.D. Olsen, G.M. Kontogeorgis, J.C. de Hemptinne, X. Liang, N. von Solms, Comparisons of equation of state models for electrolytes: e-CPA and e-PPC-SAFT, *Fluid. Phase Equilib.* 571 (2023), <https://doi.org/10.1016/j.fluid.2023.113804>.
- [75] A. Zuber, L. Cardozo-Filho, V.F. Cabral, R.F. Checoni, M. Castier, An empirical equation for the dielectric constant in aqueous and nonaqueous electrolyte mixtures, *Fluid. Phase Equilib.* 376 (2014) 116–123, <https://doi.org/10.1016/j.fluid.2014.05.037>.
- [76] N. Novak, G.M. Kontogeorgis, M. Castier, I.G. Economou, Theoretical considerations on single and mixed solvent electrolyte solutions, *Fluid. Phase Equilib.* 576 (2024) 113924, <https://doi.org/10.1016/j.fluid.2023.113924>.
- [77] M. Ascani, C. Held, Prediction of salting-out in liquid-liquid two-phase systems with ePC-SAFT: effect of the Born term and of a concentration-dependent dielectric constant, *Z. Anorg. Allg. Chem.* 647 (2021) 1305–1314, <https://doi.org/10.1002/zaac.202100032>.
- [78] S.Naseri Boroujeni, B. Maribo-Mogensen, X. Liang, G.M. Kontogeorgis, Theoretical and practical investigation of ion-ion association in electrolyte solutions, *J. Chem. Phys.* 160 (2024), <https://doi.org/10.1063/5.0198308>.