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Comparison of models for the relative static permittivity with the e-CPA equation of state

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This study compares five different models of the relative static permittivity when they are used in the electrolyte Cubic Plus Association (e-CPA) equation of state. To get the best possible performance of the models, the parameters of e-CPA are readjusted for every model. Two different combinations of adjustable parameters are tested. The static permittivity models that are compared include both simple correlations and theoretically derived expressions. A new theoretically based model, that has not been applied to e-CPA before, is also investigated. The novel model describes the impact ions have on the relative static permittivity based on water–ion association. The model is parameterized in two ways: firstly, so that the model describes the reported experimental relative static permittivity data, and secondly to describe the permittivity when kinetic depolarization is not included. All the models are tested for their quantitative agreement with mean ionic activity coefficients (MIAC), osmotic coefficients and density. The model that describes the experimental data the best is the one based on ion association, when it is parameterized to describe the experimental relative static permittivity data. The prediction of the individual ion activity coefficients (IIAC) is also investigated. The only model that is capable of describing the qualitative trend of the IIAC data is the ion association model, but the quantitative agreement with the IIAC data is quite poor. Because of this, an additional parameterization of the ion association model is performed based on an altered parameter optimization strategy. It is shown that with the new parameterization it is possible to describe the IIAC data well, without significant loss of performance for any of the other properties.

1. Introduction

Electrolytes are present in many applications of great interest to different industries [1]. This is highlighted in a review of the industrial needs from thermodynamics and transport properties from 2010 by Hendriks et al. [2]. In this review many companies from a variety of different sectors comment on the issues they have regarding electrolytes and they state that improved models, that can describe properties in a wider range of conditions, are needed. A need for further parameterization of the current models is also mentioned so more systems can be modelled. Alternatively a clear description of the parameterization approach would let the companies parameterize the models themselves so new compounds can be included. This is mentioned because it was viewed as unclear what should be done when parameters of important compounds of a system are missing. In a follow-up review from 2020 by Kontogeorgis et al. [3], the same needs for improvements of electrolyte models are still present, and might even be more important due to new applications being in focus at the companies, including increasing relevance of electrolytes to biotechnology.

There is therefore a great need to improve the thermodynamic models for electrolytes to be able to properly predict the behaviour of processes where ions are present. This is especially important because the impact of the ions can be significant even at low concentrations. This is both due to the long range nature of ion–ion interactions and ions ability to disrupt the structure of the solvent. Even though the electrolyte systems are important, the thermodynamic modelling is still not at a point, where it can be reliably used for a wide range of systems, without special care [2,3].

A difficulty when modelling electrolyte is that the fundamentals of electrolyte thermodynamics are not fully understood and agreed upon by the scientific community, so it is necessary to attempt to provide answers to some fundamental questions on electrolytes. Some of these fundamental questions have been brought up in a earlier review by Kontogeorgis et al. [4], and while these were attempted to be answered based on the current literature, it was not possible to obtain concrete answers to all the questions.

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The lack of answers to fundamental questions regarding electrolytes coupled with a need for better models from industry, made it clear that more research into the fundamentals of electrolytes were needed. Our previous work [5] was also contributing to this. In the paper [5] several previously published [6–8] parameterizations of the equation of state (EoS) electrolyte Cubic Plus Association (e-CPA) model were evaluated for their ability to describe many different properties of the aqueous sodium chloride system in a wide range of conditions. This was done to test the limitations and capabilities for a state of the art model.

With the previously published parameter sets [6–8] the density was found to be described fairly inaccurately. While the density description was improved with the addition of a constant (temperature-, pressure- and concentration independent) Peneloux volume translation parameter [9], the temperature dependence was still unsatisfying. An objective of the previous work [5] was to be able to describe the density at the same time as the other properties without the use of a volume translation parameter. This was accomplished by adding the density to the objective function. The new parameter set was successful as it was shown that many properties were described equally well or better than the previously published parameter sets. In [10] it was also shown that the parameter set was capable of predicting the density at high pressures (up to 2000 bar), even though such data had not been included in the parameter optimization.

Another aspect of the previous work [5] was that the ability of e-CPA to predict individual ion activity coefficients (IIAC) was investigated. It was found that all the previously published parameter sets and the new parameter set that could predict the density correctly would all describe IIAC qualitatively incorrect. With qualitatively it is meant which ion is higher (and lower) than the mean ionic activity coefficients (MIAC). For NaCl e-CPA would predict the opposite trend compared to the experimental data.

The reason for the wrongly predicted trend of IIAC with e-CPA was found to be related to the parameterization strategy of the model. The way the model was parameterized the only type of parameter that had a real influence on the IIAC was the ion size. In our previous work [5] it was shown that it is possible to describe the IIAC correctly with e-CPA without much loss of precision for the other properties. However, to get this result the relative size of the ions had to be opposite of what it is supposed to be, so Na+, would need to be larger than Cl-, which is not the actual case. It was therefore clear that either more physics or a different parameterization strategy was needed to distinguish between the two ions, if the IIAC data are to be described correctly without using unphysical values of the ion size. Because of this IIAC is also investigated in this work.

Another feature of our previous work was that the model for the relative static permittivity from [11], made it impossible to describe the density together with the relative static permittivity. This was because the model is dependent on the volume and with correct density the model (unfortunately) predicts the relative static permittivity of pure water. In this study the role of the relative static permittivity will be investigated, by comparing several different models of the relative static permittivity when the parameters of e-CPA are re-fitted to ensure the best possible performance of each of the models.

This is an important aspect of electrolyte thermodynamics as one of the unanswered fundamental questions [4] is how the relative static permittivity should be considered in a primitive model, where the relative static permittivity is required as an input from either a model or experimental data. The key fundamental question regarding the modelling of the relative static permittivity is related to which variables it should be considered dependent on. It is especially not clear if the relative static permittivity should be dependent on the salt concentration, even though experimentally a trend of decreasing relative static permittivity with increasing concentration of salt is clear.

The literature regarding the dependencies of the relative static permittivity for e-EoS’s or electrolyte activity coefficient models is divided, as models have been presented that include a salt concentration dependency [12–15] and others do not include such a dependency [16–19]. With both methods the models are capable of describing some properties well under some conditions. The role of the relative static permittivity cannot be determined from these studies because the models vary in numerous other ways than just the used relative static permittivity models. The various models also differ in what properties they investigate and what conditions the models are tested against. Furthermore, it is tough to make a fair comparison when the number and type of adjustable parameters are not the same among the investigated methods. This highlights that there is a need for systematic comparisons of different relative static permittivity models on a “fair” basis, where it is the impact of the relative static permittivity models that is compared.

The only study to our knowledge that attempts to make a fair comparison of several relative static permittivity models is a recent study by Walker et al. [20]. In that work SAFT-VR-Mie is the non-electrolyte EoS and the ionic interactions are described by either DH or MSA terms combined with a Born term. The relative static permittivity models are compared without readjusting parameters of the EoS. A lot can be learned from this study especially in terms of what properties are heavily influenced by the choice of the relative static permittivity model, but also, which properties are not significantly influenced by this choice.

The study of Walker et al. [20] can sadly not be used to conclude on which model for the relative static permittivity that should be used in connection with an EoS. This is due to the lack of parameterization of the EoS, which would always be a part of a model that is used in applications. A models parameterization could easily change the outcome of which model performs the best. This is why the comparison of the relative static permittivity models in this work, will include a systematic parameter fitting of the full e-CPA model with each of the models for the relative static permittivity.

The aim of this work is therefore to provide a fair comparison for several different models of the relative static permittivity, when they are implemented within the same EoS (e-CPA) with the same adjustable parameters optimized to the same objective function using the same set of experimental data. Two combinations of adjustable parameters are tested. The models for the relative static permittivity will therefore be consistently tested in a way that allows for a true comparison of the impact of the relative static permittivity models. The investigated models of the relative static permittivity are developed on different theoretical backgrounds and importantly different amount of fitting parameters. This will have an impact on the accuracy of the models. The fitting parameters of the relative static permittivity models are generally available for the water–NaCl system and are not refitted in this work, when they are already available.

A new theoretically-based model for the relative static permittivity that relies on water–ion association to describe the impact of ions will also be investigated. A comparable model has been used with ePC-SAFT [21], but it has not been applied to e-CPA. Because it is a new model, it is necessary to fit parameters of the model in this work. The association parameters of the ions, which are mainly impacting the predicted relative static permittivity of the model, will be separately optimized to an objective function that only includes relative static permittivity data. This is done to make sure the model is comparable to the other relative static permittivity models investigated in this work as they are also parameterized (by others) to capture the experimental permittivity data.

The manuscript is organized as follows: Section 2 contains a description of the methodology of this work, which includes a short description of the e-CPA model, descriptions of all the used relative static permittivity models and the methods of parameterizing e-CPA. Section 3 is a combined results and discussion section, which first describes the quantitative performance of all the relative static permittivity models with two different parameterizations. The models are analysed by comparing balance of contribution plots for MIAC. The performance of all the models are also evaluated for IIAC, and afterwards the balance
of contributions for IIAC are discussed for some of the models. Section 4
describes a different way to parameterize the new ion association model
to obtain better results for IIAC, without significant loss of the other
properties.

2. Methods and theory

2.1. The e-CPA model

The e-CPA model that is used in this work contains four terms
describing different forces as can be seen in Eq. (1).

\[ A^{\text{eCPA}} = A^{\text{SRK}} + A^{\text{Assoc}} + A^{\text{DH}} + A^{\text{Born}} \]  

where SRK is the cubic EoS by Soave–Redlich–Kwong [22], which is
considered the physical term that describes the short range interactions
of the molecules, Assoc is short for association, which describes the
hydrogen bonding and is calculated from Wertheim's theory [23],
DH is the full Debye–Hückel equation [24], which describes ion–ion
interactions and Born is a term that describes the solvation of ions. The
equations of the model have been described in a previous work [5] and
the model is the same except for the used relative static permittivity
model. All the investigated relative static permittivity models will be
described in the next sections.

2.2. Permittivity models

In this work several models for the relative static permittivity are
investigated. An overview of the models considered in this work are
shown in Table 1 and the details of each model are given in the
following sections. Several of the models only describe the impact of
ions and they therefore require an input of the pure solvent value. The
same model for the relative static permittivity of pure water is used
in all cases and it is described in Section 2.2.1. One of the models
is an extension of an approach that can describe the relative static
permittivity of liquids to also include the impact of ions. This model
will therefore reduce to the solvent model, if no ions are present. The
two solvent models will be compared in order to investigate if this
case gives rise to significant differences. The models for the impact
of the ions vary in terms of required input variables and both a model
without any additional parameters and models with adjustable paramet-
ers are considered. When possible previously published parameters for
the water–NaCl system are used.

2.2.1. Pure water model

Some of the models for the relative static permittivity that will
be investigated in this work require an input of the value for pure
water. These models require an equation that can describe the relative
static permittivity of pure water accurately. In this work the model
for the relative static permittivity of pure water is from the book of
Michelsen and Mollerup [25]. It is derived based on theory, but it
also includes an adjustable parameter, which improves the accuracy.
The model includes both a temperature and volume dependency. It is
chosen because it has been shown to correlate experimental data for
the relative static permittivity of water in a wide temperature range.
The relative static permittivity of pure water is given by:

\[ \varepsilon_{r,0}(T, V) = \varepsilon_{r,0}^0(T_0) + \frac{1}{2} \left( \frac{\mu_{\text{mot}},0}{k_B T_0} \right) \]  

where \( T_0 \) is the reference temperature (273.15 K), \( \varepsilon_{r,0}^0(T_0) \) (87.82) is
the static permittivity of water at the reference temperature, \( \mu_{\text{mot}},0 \) (2.5
D -value from Chen et al. [26]) is the dipole moment of liquid water, \( \beta_1 \)
(3.1306) is a fitting constant, \( \rho_w \) is the molar density of water and \( \rho_{\text{mot}} \)
is the molar density of water at \( T_0 \). The volume dependency is found in
the molar density of water (\( \rho_w = n_w/V \)) where the volume is calculated
from e-CPA. All the investigated models that rely on this model for the
relative static permittivity of water will therefore have a temperature-
and volume dependency.

2.2.2. Mollerup–Michelsen–Breil model

In this section the model for the static permittivity based on the
approach by Mollerup, Michelsen and Breil [25] is described. The
model only describes the impact of the ions, and it is dependent on
volume and ion concentration. The pure water model is temperature
dependent. It therefore provides a realistic static permittivity in e-CPA
at various temperatures, volumes and salt concentrations. It also relies
on several fitting parameters, which ensure good agreement with the
experimental data. The model is given by:

\[ \varepsilon_i = \varepsilon_{r,0} \cdot \left( 1 + \sum_{j=1}^{i} \beta_j c_j - \frac{\alpha_j c_j}{1 + \beta_j c_j} \right) \]  

where \( \beta_j = 0.160 \text{ L/mol} \) and \( \beta_j = 0.010 \text{ L/mol} \) are fitting parameters
for the solvent and \( \alpha_j \) is an ion-specific parameter with the values: \( \alpha_{\text{Na}^+} = 0.1062 \text{ L/mol} \) and \( \alpha_{\text{Cl}^-} = 0.0172 \text{ L/mol} \). The volume and concentration
dependencies are expressed as \( c_j \) which is the concentration of the ion
\( i \) given by \( c_j = n_j/V \).
2.2.3. Pottel model
The model by Pottel [27] is a predictive model that is based on the size of the ions, without any additional adjustable parameters. The model has previously been applied in e-EoS like e-CPA [12] and ePPC-SAFT [28]. The expression for the relative static permittivity by Pottel is given by:

\[ \epsilon_r - 1 = (\epsilon_{r,w} - 1) \frac{1 - \epsilon''_\infty}{1 + \frac{4\pi}{3} r_i^3/2} \]

where \( \epsilon''_\infty \) is the volume of low permittivity, that the ions occupy in the solution. By assuming that the ions are spherical, which is a good assumption for Na+ and Cl−, \( \epsilon''_\infty \) can be approximated by:

\[ \epsilon''_\infty = \frac{\pi N A}{6} \sum_{i} n_i d_i^3 \]

\( d_i \) refers to the diameter of the ion. There are several parameters in e-CPA that in some way describe the size of the ions so there is a choice involved in the selection of the value for this diameter. In the current parameterization of e-CPA either \( \sigma \) or \( 2R_{\text{Icen}} \) effectively describe a diameter of an ion. If the co-volumes of the ions were independently estimated, it would be possible to calculate a diameter from it, that could be used as well. None of these parameters would actually describe the diameter in Eq. (5). The latter is the diameter of the spherical space that is experiencing a low permittivity due to the ions, and that diameter (expected to be used in Eq. (5)) is likely larger than the diameters already used in the model.

In this work it is chosen to use \( \sigma \) (distance of closest approach in Debye–Hückel) to describe the diameter in Eq. (5). This should be the smallest possible diameter of the ions. This will also lead to an effectively predictive model for the relative static permittivity, which would be good in the comparisons of this work. Since the diameter is smaller, it will lead to the reduction of the relative static permittivity to be smaller than the experimental data. However, fitting the diameter to the data is also undesirable, because the model only accounts for one of the effects of the reduction of the permittivity due to the ions, namely the dilution of the permittivity. The effect that the ions influence the solvent structure is neglected so from a theoretical standpoint the model is not supposed to match the data, so the fitted diameter would also be arbitrary. For sodium chloride a significant reason for the reduction of the relative static permittivity should be from destabilizing the solvent structure, because of the high charge density of the ions especially for sodium.

2.2.4. Simonin model
The model by Simonin [29] is a simple model that can accurately describe the decrease of the relative static permittivity with increasing salt concentration, by the use of a single ion-/salt-specific parameter. It is designed to correlate the data, and does not have any theoretical derivations. The model is only dependent on the composition of the mixture. The expression for Simonins model for the relative static permittivity is:

\[ \epsilon_r = \frac{\epsilon_{r,w}}{1 + \sum_{i} n_i x_i} \]

where \( x_i \) is a ion/salt specific adjustable parameter which for NaCl previously has been estimated to be 5.08 [12] and it is not re-estimated as a part of this work. The relative static permittivity of pure water (\( \epsilon_{r,w} \)) is calculated from Eq. (2). The model has previously been successfully applied in e-CPA [12,13], but the parameterizations of e-CPA in these works are different compared to the current study.

2.2.5. Maribo-Mogensen solvent model
The solvent model by Maribo-Mogensen et al. [11] is a theoretical model that describes the relative static permittivity based on the sum of the dipole moment of all molecules in the mixture and the association of the molecules in the solution. In the original work of Maribo-Mogensen et al. [11] the model is shown to describe the relative static permittivity of several pure solvents in a wide temperature range. The model also readily extends to mixtures, where the relative static permittivity is predicted with good accuracy. The relative static permittivity is calculated from:

\[ \frac{(2\epsilon_r + \epsilon_{\infty}(\epsilon_r - \epsilon_{\infty}))}{\epsilon_r} = \left( \frac{\epsilon_{\infty} + 2}{3} \right)^2 \frac{N A}{\epsilon_r \theta_i k_B T} \sum_{i} x_i \theta_i \mu_i^2 \]

where \( \theta_i \) is the dipole moment of component \( i \). The infinite frequency permittivity, \( \epsilon_{\infty} \), is calculated from the Clausius–Mossotti [30] equation:

\[ \epsilon_{\infty} - 1 = \frac{1}{3} \frac{N A}{\epsilon_r \theta_i k_B T} \sum_{i} x_i \theta_i \mu_i^2 \]

The model presented above was used in a previous work [5], where it was shown that e-CPA performed well for many properties in a wide range of conditions, when this model was used to calculate the relative static permittivity. A consequence of the model is that when it is applied to an electrolyte mixture, it will calculate the relative static permittivity of the salt free solution, when the volume is accurately described. This is because the ions are not taken into account, because they do not have a dipole moment. A parameter set (called set 4 in [5]), is considered as a comparison to the estimated parameter sets of this work. For this parameter set the relative static permittivity is effectively independent of the salt concentration and it therefore serves as a comparison to a model that considers the relative static permittivity as independent of salt concentration. This parameter set from literature [5] is called “model 0” in the results and discussion section.

2.2.6. Maribo-Mogensen modified electrolyte model
This relative static permittivity model is a modification of the theoretical model developed by Maribo-Mogensen et al. [31]. The model is a direct extension of the solvent model described in the previous section by accounting for the effect that ions have on a polar solvent within the framework of the solvent model. The equation for calculating the relative static permittivity is given by:

\[ \frac{(2\epsilon_r + \epsilon_{\infty}(\epsilon_r - \epsilon_{\infty}))}{\epsilon_r} = \left( \frac{\epsilon_{\infty} + 2}{3} \right)^2 \frac{N A}{\epsilon_r \theta_i k_B T} \sum_{i} x_i \theta_i \mu_i^2 \]

(10)

Eq. (10) is similar to the solvent model (Eq. (7)) with the difference being the addition of \( \theta_i \), which is the fraction of component \( i \) that is not bound to an ion. Therefore, if there is no water–ion association the model is the same as the solvent model. The key assumption to arrive at the expression given in Eq. (10) is that any solvent molecule that is associating to an ion will have its dipole moment cancelled and that solvent molecule will therefore not contribute to an increase of the permittivity of the solution. The expression for \( \theta_i \) is:

\[ \theta_i = 1 - \sum_{j} P_{ij} \]

(11)

where \( P_{ij} \) is the probability that two sites are hydrogen bonded. It is calculated by:

\[ P_{ij} = \rho X_i A_{i,j} \]

(12)

where \( X \) is the site fraction and the subscripts refer to different sites. The site fraction is calculated in the same way as in the association term where it is determined by:

\[ \frac{1}{X_i} = 1 + \sum_{j} \rho_j \sum_{i<j} X_j A_{i,j} \]

(13)
\( \Delta_{A,B} \) is the association strength between two sites. In the paper of Maribo-Mogensen et al. [31] the water–ion association strength is calculated based on the ion–water coordination number and the equation is:

\[
\Delta_{A,B} = \frac{1}{\rho_i} \left( \frac{N_{ij}}{N_i - N_{ij}} \right)
\]

where \( N_j \) is the number of sites on ion \( j \) and \( N_{ij} \) is the apparent coordination number of molecule \( i \) around ion \( j \), \( \rho_i \) is the pure component molar density of component \( i \). This expression is derived assuming infinite dilution of the ions, where all associations sites on the ions will be bound to a water molecule, which is a valid assumption at infinite dilution. A consequence of this is that the association constant will be independent of salt concentration.

In this work the association strength is calculated from the Wertheim formalism instead of Eq. (14). This is also how association is generally treated in (e-)CPA [32,33]. This means that all types of associations (water–water, water–ion and ion–ion) are treated in the same way mathematically, which keeps the model self-consistent. This method also includes a realistic concentration dependency in the association strength, which is missing in the original method of Maribo-Mogensen et al. [31] (Eq. (14)). The association strength in the Wertheim formalism is given as:

\[
\Delta_{A,B} = g(\rho) \left[ \exp \left( \frac{\varepsilon_{A,B}}{RT} \right) - 1 \right] b_{ij} \beta_{A,B}
\]

From this expression two additional parameters need to be determined for each type of cross association: the cross association volume \( (\beta_{A,B}) \) and the cross association energy \( (\varepsilon_{A,B}) \). If each of the cross association parameters were independently estimated, 8 additional association parameters would need to be optimized for the water–NaCl system. This is because 3 association pairs are considered for the ions (water–cation, water–anion and cation–anion), which require two parameters each.

To reduce the number of adjustable parameters the association parameters are estimated by assigning a number of sites, association energy and association volume to the ions. The cross association parameters are calculated from the combining rule given in Eq. (16). The ions will not associate with themselves (as in cation–cation or anion–anion) because ions only have either negative or positive sites. This method will therefore only include water–ion and cation–anion association. The combining rule used for these association types is the so-called CR1 [34] which is given by:

\[
\varepsilon_{A,B} = \frac{\varepsilon_{A,R} + \varepsilon_{A,B}}{2} \quad \text{and} \quad \beta_{A,B} = \sqrt{\beta_{A,R} \beta_{B,B}}
\]

This reduces the number of new adjustable parameters to 4 (2 per ion), and to further reduce the number of adjustable parameters, it is chosen that the association volume of the ions is set equal to the self-association volume of water. It is common in SAFT type e-EoS to set the association volume of the ions to a constant value either close to or equal to the association volume of water [21,28,35]. This is done to reduce the number of adjustable parameter, and we expect it could also be a valid approach for e-CPA. Furthermore, the association energy of both cation and anion is set to the same value. This is done because only NaCl-systems are considered and we cannot tell the difference between the ions. The resulting value can be considered an average value of the two ions. With these choices in the parameterization only a single new parameter needs to be adjusted for the water–NaCl system, which is the association energy of the ions. This makes the model comparable to the other models of the relative static permittivity described in the previous sections.

2.2.7. Performance of pure water permittivity models

The relative static permittivity models of Mollerup–Michelsen–Breil, Pottel and Simonin require an input of the pure solvent relative static permittivity at a given temperature and pressure, so it is important that the model used to calculate this value is accurate. The ion association model described in Section 2.2.6 is a direct extension of the solvent model by Maribo-Mogensen et al. [11] to include electrolytes, so it cannot be decoupled from the non-electrolyte version. It is important for the performance of the electrolyte version that the non-electrolyte version performs well.

In Fig. 1 the two models for the relative static permittivity of pure water are compared to experimental data in a wide temperature and pressure range. It can be seen that both models perform well in the investigated range. It is also important for a proper comparison, that the performance is similar between the models for pure water, so this is not the reason for any discrepancies for the electrolyte systems. The temperature dependency is especially important in this work, as the relative static permittivity vary a lot in the investigated temperature range, and this variation will affect the calculation of other properties. The pressure dependency on the relative static permittivity of water is less impactful compared to the temperature dependency.

2.3. Thermodynamic part of the permittivity

When salts are added to a liquid solution the relative static permittivity will usually decrease. The reduction of the relative static permittivity due to the addition of ions can be described by two effects that ions have on a solution. The first effect is that the space that the ions takes up do not contribute to the static permittivity with a significant value, so the addition of ions will dilute the average permittivity of the solution. The other impact is that the ions will usually disrupt the hydrogen-bonding network which will reduce the relative static permittivity because the water molecules surrounding the ions will contribute less to the permittivity of the solution.

In several papers [37–41] it has been discussed that when measuring the relative static permittivity of an electrolyte solution, the measured reduction of the relative static permittivity, that is observed when the concentration of ions is increased, is due to both a equilibrium/thermodynamic part and a kinetic part.

The thermodynamic part is due to the two effects, dilution of the permittivity and disruption of the hydrogen-bonding network, that have already been described. The kinetic part is due to kinetic depolarization which arises from the method of measuring the relative static permittivity. When measuring the relative static permittivity a current is applied to the solution. This current will make the ions in the solution move towards the opposite charge. The movement, that is induced by the current, will destabilize the hydrogen-bond network more than if the current was not applied. This means that, while the relative static permittivity should be lower when ions are added to the solution, the measured relative static permittivity is lowered additionally due to the measurement itself because of kinetic depolarization and the additional decrease is considered to be the kinetic part.

Based on a review of previous works [37–40] it is estimated by Maribo-Mogensen et al. [31] that the kinetic part accounts for 25%–75% of the measured reduction of the relative static permittivity for electrolyte solutions. The kinetic part is therefore a significant contribution to the experimental relative static permittivity value for electrolyte solutions and cannot be neglected. The reason for the large deviation in the estimate is because it is currently not possible to split the thermodynamic and kinetic part experimentally, so the contribution from the kinetic part is estimated based on theoretical modelling, where assumptions made when developing the model play a significant role.

In this work, it is of interest to consider a model where the modelled relative static permittivity only contains the thermodynamic part. It is assumed that the thermodynamic part of the reduction is around 50% of the experimental reduction. This has been chosen because 50%
is in the middle of the aforementioned estimated range. Because the range of the reduction of the experimental relative static permittivity due to kinetic depolarization is rather broad, it is difficult to fully investigate the case where only the thermodynamic part is considered. However, it is an important aspect to investigate, considering that, from a theoretical standpoint, the kinetic part of the reduction of the relative static permittivity is due to kinetic effects induced by the measurement itself. The kinetic part is therefore only present when the permittivity is measured. It is therefore important to attempt an investigation of how the model behaves for other properties when the relative static permittivity only contains the thermodynamic part.

2.3.1. Estimation of kinetic depolarization

In this section a method for estimating the size of the kinetic depolarization will be described. The values that are calculated with this method will be compared to a model that will be parameterized to only describe the thermodynamic part of the relative static permittivity. When calculating a theoretical value of the kinetic depolarization of an electrolyte solution, several additional properties have to be measured at the same time as the relative static permittivity is measured. There are very few salts/conditions where these additional properties have been reported, so the conditions, where the kinetic depolarization is calculable, are limited. However, in the work of Buchner et al. [41], all the necessary properties are reported for the water–NaCl system, so the size of the kinetic depolarization can be estimated. The thermodynamic part of the relative static permittivity can therefore also be calculated. It is assumed that the kinetic (kd) and thermodynamic (eq) contributions are additive as follows:

$$\Delta \varepsilon(c) = \Delta_{eq}\varepsilon(c) + \Delta_{kd}\varepsilon(c)$$  \hspace{1cm} (17)

where $\Delta \varepsilon(c)$ is the change of the static permittivity at salt concentration, $c$, compared to the salt free static permittivity. The subscripts eq and kd stands for equilibrium (the thermodynamic part) and kinetic depolarization (the kinetic part) respectively. According to Buchner et al. [41] the kinetic depolarization can be calculated by:

$$\Delta_{kd}\varepsilon_{ir} = \kappa(c) \cdot \frac{\varepsilon_i(0) - \varepsilon_{in}(c)}{\varepsilon_i(0)}$$  \hspace{1cm} (18)

where $\kappa(c)$ is the conductivity of the electrolyte solution at the salt concentration $c$, $\varepsilon_i(0)$ is the relative static permittivity of the salt free solution, $\varepsilon_{in}(c)$ is the infinite frequency of the electrolyte solution and $\varepsilon_i(0)$ is the relaxation time of the salt free solution. The hydrodynamic boundary condition of ionic motion is accounted for with the factor $p$, which is either considered to be stick ($p = 1$) or slip ($p = 2/3$). The two conditions describe the limits of the kinetic depolarization, and it is expected that the real value of the kinetic depolarization is somewhere in between. Based on an analysis of estimated solvation numbers of NaCl by Buchner et al. [41], the kinetic depolarization should be closer to the value calculated with the slip-condition, because the stick-condition yields effective solvation numbers that are negative.

2.4. Investigated cases

Two cases, which consist of different combinations of adjustable parameters, are tested. The first case includes the same adjustable parameters as in our previous work [5], which are a scaling factor for the ion diameters, $\sigma$, and the parameters of a temperature dependent interaction parameter in the Huron–Vidal infinite pressure mixing rule, $U_{ref}$, $T_0$, and $\alpha$. This allows for a fair comparison with the solvent relative static permittivity model parameterized in our previous work [5]. The ion diameters are adjusted by scaling the ion diameter values of Marcus [42] (2.36 Å and 3.19 Å for Na$^+$ and Cl$^-$ respectively) with the same scaling factor for both ions. This is an artificial way to make sure the ions have a reasonable size relative to each other. This is necessary because the water–NaCl system is the only considered system and none of the properties distinguish between the ions.

The second case includes the same four adjustable parameters as the first case, with the addition of the Born radius as an adjustable parameter, which for simplicity will be set to the same value for both ions. This is done because none of the data in the objective function can distinguish between the cation and anion so the only way to get a difference between the Born radii would be to arbitrarily introduce it. As mentioned, this was done for $\sigma$, but because the Born radius only affect the Born term in a additive fashion, this was deemed less important. As described in our previous work [5], $\sigma$ affects the DH-term and the co-volume ($b = 1/6 \pi \sigma^3$) used in the SRK-term, and $\sigma$ therefore affects more of the model.

The reason for choosing to adjust the Born radius as an additional parameter, is because with a concentration dependent relative static permittivity there will be a large contribution to the activity coefficients from the Born term. This contribution will be heavily influenced by the size of the Born radii, so the adjustment of the Born radii should have a significant impact on the results. The solvent model will not have adjusted Born radii as the parameter does not have any significant impact on any of the properties in the used objective function, when the relative static permittivity is independent of the salt concentration.

The models of the relative static permittivity are named in Table 1, and the models will be parameterized according to both cases 1 and 2. This will provide a good overview of the impact that the relative static permittivity has on a model like e-CPA. Inclusion of several models that describe the relative static permittivity similarly important because the derivatives (first and second order) of the models will be different, and the derivatives of the permittivity will

![Fig. 1. Performance of water models for their temperature (T) and pressure (P) dependencies for the relative static permittivity. Maribo-Mogensen is from [11] (see Section 2.2.5) and MMB is short for Mollerup–Michelsen–Breil [25] (see Section 2.2.1). For the T-dependency (left) the pressure is atmospheric below 373 K and the saturation pressure above 373 K. For the P-dependency (right) the temperature is 293.15 K. All the experimental data are from [36].](image)
influence other properties. Testing several models that describe the relative static permittivity similarly will reveal the possible effects of the concentration derivatives.

2.5. Parameter estimation

The c-CPA parameters of cases 1 and 2 are found by minimizing the following objective function (OF):

\[
OF = \frac{1}{N} \sum_i \left( \frac{\gamma_i^{exp} - \gamma_i^{calc}}{\gamma_i^{exp}} \right)^2 + \frac{1}{N} \sum_i \left( \frac{\Phi_i^{exp} - \Phi_i^{calc}}{\Phi_i^{exp}} \right)^2
\]

\[
+ \frac{1}{N} \sum_i \left( \frac{\rho_i^{exp} - \rho_i^{calc}}{\rho_i^{exp}} \right)^2 \frac{m_i}{m_{max}}
\]

(19)

where \( N \) is the number of experimental points of the property, \( \gamma_i \) is the mean ionic activity coefficients (MIAC), \( \Phi \) is the osmotic coefficient and \( \rho \) is the density. The superscripts \( exp \) and \( calc \) refer to experimental and calculated values respectively. \( m_i \) and \( m_{max} \) are the molality of experimental point \( i \) and the largest molality value at the temperature respectively. The reason that the term \( m_i/m_{max} \) is included for the density data is because the density is mainly determined by the description of water, but the water parameters are not altered. This means that at lower molality the impact of the adjustable parameters is lower and the impact of the salt parameters will likewise be larger at higher molality. This phenomenon is taken into account by the term \( m_i/m_{max} \).

2.5.1. Estimating ion association parameters

The estimation of the association parameters for models 4 and 5 have to be treated separately, as the parameters need to be estimated from the relative static permittivity data and not the properties in the objective function (Eq. (19)). This is important to ensure that the results of the ion association model are comparable to the other models, as the objective function (Eq. (19)) is still minimized. The "experimental data" used are shown in Fig. 3, compared to the recalculated experimental values used to optimize the parameter. It can be seen that the agreement is good at both temperatures.

In Fig. 4 the results are compared to the thermodynamic part of the relative static permittivity where the contribution from kinetic depolarization is removed. It can be seen that the resulting model is quite close to the results with the slip condition of the hydrodynamic boundary condition. This is good since as shown by Buchner et al. [41], the stick condition yields unreasonable (negative) coordination numbers of the ions. The estimated association energy parameter is therefore considered to describe the thermodynamic part of the relative static permittivity well. It can also be seen that there is a difference between the experimentally measured values of the relative static permittivity from the two data sources (Shcherbakov et al. [43] and Buchner...
from Shcherbakov et al. [43] to correspond to a 50% reduction of the relative static permittivity. The circles are the reported experimental data from Shcherbakov et al. [43].

Fig. 3. The concentration dependency of the relative static permittivity for the water–NaCl system at two temperatures with the ion association model (see Section 2.2.6) with the ion parameters of $\varepsilon_A/i / R = 349.2$ K (optimized value) and $\beta_{i,R} = 69.2 \cdot 10^{-3}$ (water value) and experimental values for the volume. The crosses are adjusted experimental data from Shcherbakov et al. [43] to correspond to a 50% reduction of the relative static permittivity. The circles are the reported experimental data from Shcherbakov et al. [43].

Fig. 4. The concentration dependency of the relative static permittivity for the water–NaCl system at 298.15 K showing both experimental values and the experimental values when only the thermodynamic part (called Thermo) is considered. The model is the ion association model (See Section 2.2.6, $\varepsilon_A/i / R = 349.2$ K) with experimental volumes. Thermo (stick) and (slip) refers to the boundary conditions in the calculation of the kinetic depolarization (Eq. (18)) and they are calculated from data of Buchner et al. [41]. The experimental data are from Shcherbakov et al. [43] and Buchner et al. [41].

et al. [41]). The reason for the discrepancy of the data is that the relative static permittivity measurement involves various frequencies and the reported values are the extrapolated ones to zero/low frequency. In the data sources we observe different methods for measuring in terms of available frequencies and the extrapolation of the data. It has not been possible to determine which source is the most credible, but possible reasons for the difference of such measurements are discussed in [43].

3. Results and discussion

The parameters found with the parameterizations described in Section 2.5 are shown in Tables 2 and 3 for cases 1 and 2 respectively. Case 1 has the same adjustable parameters as in the previous work [5] (the ion diameter and 3 parameters for the temperature dependent salt-water interaction parameter) whereas case 2 has the same 4 parameters as case 1 and additionally the Born radius i.e. in total 5 adjustable parameters. For case 1 (Table 2) it can be seen that the optimized parameters are varying a lot for the various relative static permittivity models. This variation makes it difficult to make comparisons between the models in terms of the impact that they have on the optimized parameters. The actual performance of the models with the optimized parameters can still be compared. Especially, Model 5, which is the ion association model that describes the experimental relative static permittivity, has very large values of the $U_{rel}$ which is the value at 298.15 K, while it also has very small values for the ion size.

Looking at Table 3, the parameters are a lot more similar between the different relative static permittivity models for case 2. First of all, the interaction parameter is negative for all models and the ion sizes are relatively similar and relatively close to Marcus values [42]. Regarding the Born radius it is clear that when it is considered an adjustable parameter with a concentration dependent relative static permittivity, a much larger value is obtained compared to usual literature values, which often are estimated from thermal infinite dilution properties. The values for the Born radii in case 1 are from [6] and they are estimated from enthalpy of hydration at infinite dilution. Generally, the values of case 2 seem to be around 3 Å, which is much larger than the average value used in case 1 (around 1.7 Å). Valisko and Boda [45] estimated the Born radius from Gibbs energy of hydration at infinite dilution. In that case the average value is around 1.9 Å (for Na+ it is 1.62 Å and for Cl- it is 2.26 Å). This means that the case 2 Born radii are increased by over 50%, which is significant. The much larger Born radii will lead to a reduced impact of the Born term for MIAC and osmotic coefficients, because the Helmholtz energy from the Born term is inversely proportional to the Born radii.

In Fig. 5 the results for the concentration dependency of the relative static permittivity are shown for all the models with parameters from case 2. The results of case 1 are quite similar as any differences arise from small deviations in the density/volume that is predicted with the model. It can be seen that the models (2 (Simonin), 3 (Mollerup–Michelsen–Breil) and 5 (ion association model parameterized to experimental relative static permittivity data)) that were expected to describe the experimental data well are fairly close to the experimental data. Model 1 (Pottel) yields larger values of the relative static permittivity than model 4, which was parameterized to only consider the thermodynamic part of the permittivity, by omitting the contribution from kinetic depolarization. It makes sense that the model of Pottel, would not describe the full decrease of the experimental relative static permittivity data or even just the thermodynamic part, given that the model was developed by only considering the dilution of the permittivity field, which is only a part of the effect of the experimental decrease.

In Table 4 the deviations are given for the properties in the objective function. The deviations are calculated as relative average deviations (RAD) by:

$$RAD = \frac{1}{N} \sum \frac{|X^{exp} - X^{calc}|}{X^{exp}} \cdot 100\% \quad (21)$$
Table 2
The optimized parameters for e-CPA with the different relative static permittivity models (Described in Table 1) with the adjusted parameters of case 1 (defined in Section 2.4). The a’s are scaled from Marcus values [42] (2.36 Å and 3.19 Å for Na+ and Cl− respectively) with the same factor for both ions. The number of association sites for the ions are 8 positive sites for sodium and 7 negative sites for chloride when association parameters are given. Model 0 parameters are from a previous work [5].

| Name | ϵ, model | Interaction parameters | Ion diameter, σ | Born radius, \( R_{\text{ion}} \) | Association parameters* |
|------|----------|------------------------|----------------|-------------------------------|------------------------|
|      |          | \( \frac{U_{\text{eff}}}{R} \) | \( T_a \) | Na+ | Cl− | Na+ | Cl− | \( \beta \) | \( r_{\text{e,a}}/R \) |
| Model 0 | Solvent | −947.9 | 408.2 | 5503 | 2.58 | 3.49 | 1.67 | 1.83 |
| Model 1 | Pottel | −643.6 | 355.3 | 5183 | 2.33 | 3.16 | 1.67 | 1.83 |
| Model 2 | Simonin | 1258.6 | 349.9 | 4771 | 1.71 | 2.31 | 1.67 | 1.83 |
| Model 3 | MMB\(^b\) | 1417.7 | 452.4 | 4571 | 1.50 | 2.03 | 1.67 | 1.83 |
| Model 4 | IA\(^a\) | 125.2 | 366.5 | 4102 | 2.39 | 3.23 | 1.67 | 1.83 |
| Model 5 | IA\(^a\) | 4677.9 | 489.4 | 8242 | 1.15 | 1.56 | 1.67 | 1.83 |

*The association parameters are the same values for both ions. Cross-association is calculated from Eq. (16).

\(^b\)MMB is short for Mollerup–Michelsen–Breil. See Eq. (3).

\(^a\)IA is short for ion association and is the model described in Section 2.2.6.

Table 3
The optimized parameters for e-CPA with the different relative static permittivity models (Described in Table 1) with the adjusted parameters of case 2 (defined in Section 2.4). The a’s are scaled from Marcus values [42] (2.36 Å and 3.19 Å for Na+ and Cl− respectively) with the same factor for both ions. The number of association sites for the ions are 8 positive sites for sodium and 7 negative sites for chloride when association parameters are given. Model 0 parameters are from a previous work [5]. The last set (model 6) is described in Section 4.

| Name | ϵ, model | Interaction parameters | Ion diameter, σ | Born radius, \( R_{\text{ion}} \) | Association parameters* |
|------|----------|------------------------|----------------|-------------------------------|------------------------|
|      |          | \( \frac{U_{\text{eff}}}{R} \) | \( T_a \) | Na+ | Cl− | Na+ | Cl− | \( \beta \) | \( r_{\text{e,a}}/R \) |
| Model 0 | Solvent | −947.9 | 408.2 | 5503 | 2.58 | 3.49 | 1.67 | 1.83 |
| Model 1 | Pottel | −1218.2 | 487.3 | 4951 | 2.38 | 3.22 | 3.37 | 3.37 |
| Model 2 | Simonin | −971.9 | 456.7 | 4514 | 2.32 | 3.13 | 3.08 | 3.08 |
| Model 3 | MMB\(^b\) | −797.3 | 466.5 | 4003 | 2.25 | 3.04 | 2.90 | 2.90 |
| Model 4 | IA\(^a\) | −590.5 | 426.6 | 4289 | 2.45 | 3.31 | 2.87 | 2.87 |
| Model 5 | IA\(^a\) | −197.3 | 407.4 | 4746 | 2.70 | 3.65 | 3.17 | 3.17 |
| Model 6 | IA\(^a\) | −239.6 | 391.6 | 4929 | 2.63 | 3.55 | 3.05 | 3.05 |

*The association parameters are the same values for both ions. Cross-association is calculated from Eq. (16).

\(^b\)MMB is short for Mollerup–Michelsen–Breil. See Eq. (3).

\(^a\)IA is short for ion association and is the model described in Section 2.2.6.

Fig. 5. The results of the concentration dependency of the relative static permittivity with e-CPA for the water–NaCl system at 298.15 K, of case 2 (defined in Section 2.4) for all the models (defined in Table 1). The experimental data are from Shcherbakov et al. [43] and Buchner et al. [41]. Model 6 is presented in Section 4.

From Table 4 it can be seen that for case 1, the best performing model is the solvent model that effectively does not have a salt concentration dependency of the relative static permittivity. The second best performing model is model 1 (Pottel) and the third best is model 4, which is the ion association model that is parameterized to describe the thermodynamic part of the relative static permittivity. The worst performing models are models 2, 3 and 5, which all describe the experimental relative static permittivity data well. This means that with the adjustable parameters used in case 1, the results of the three properties, mean ionic activity coefficients, osmotic coefficients and density get worse with improved representation of the relative static permittivity.

When looking at the deviations of case 2 (model 6 is discussed separately in Section 4), it can be seen that the trend of the general performance found for case 1, is not seen in case 2, where the Born radii are optimized together with the other parameters. It can be seen that the best performing model for case 2 is model 5, which describes the relative static permittivity data well with the ion association model. This is quite an interesting observation given that the other models that describe the relative static permittivity data well (models 2 and 3) are significantly worse than model 0. The models that only describe part of the decrease of the relative static permittivity (models 1 and 4) are also not improved enough to perform better than the solvent model (model 0). The possible reasons that model 5 is the best performing parameter set will be explored in the later sections.

Based on the deviations of the models shown in Table 4 it is possible to discuss the difference of the two models that both more or less corresponds to the thermodynamic part of the relative static permittivity (models 1 and 4) within the previously discussed large uncertainty [31]. As discussed in Section 2.5.2 model 4 corresponds to a 50% split between the kinetic and thermodynamic parts (Fig. 5) and model 1, that predicts a slightly larger permittivity (Fig. 5), which corresponds to a model that effectively assumes that the contribution from thermodynamic part is around 10% smaller. It can be seen that with case 1 parameters there is a significant difference between the models in favour of model 1 (Pottel) that has the smaller decrease of the permittivity, which means that the parameterization of case 1 is not able to absorb a 10% change of the relative static permittivity. However, for case 2 it can be seen that results are very similar and are only slightly better for model 4, which means that the parameterization of
Table 4
The deviation in percent (Eq. (21)) for the water–NaCl system with e-CPA with different relative static permittivity models (see Table 1 for definitions) for cases 1 and 2 (Section 2.4 for description). Model 0 results are from a previous work [5]. Model 6 is described in Section 4.

| Name       | 𝜀-𝑟-model | Case 1 | Case 2 |
|------------|------------|--------|--------|
|            | MIAC       | Osmotic coef. | Density | MIAC       | Osmotic coef. | Density |
| Model 0    | Solvent    | 1.95   | 1.62   | 0.58 | 1.95   | 1.62   | 0.58 |
| Model 1    | Pottel     | 2.56   | 1.50   | 0.92 | 2.22  | 1.51   | 0.79 |
| Model 2    | Simonin    | 7.96   | 6.43   | 1.18 | 5.15  | 3.81   | 0.89 |
| Model 3    | MMB       | 7.97   | 6.92   | 0.91 | 6.13  | 4.53   | 0.99 |
| Model 4    | IA         | 3.48   | 2.04   | 0.87 | 2.14  | 1.31   | 0.81 |
| Model 5    | IA         | 7.16   | 3.21   | 0.73 | 1.19  | 0.79   | 0.34 |
| Model 6    | IA         | 1.21   | 0.78   | 0.59 |       |        |      |

aMIAC is short for mean ionic activity coefficients.
bMMB is short for Mollerup–Michelsen–Breil. See Eq. (3).
cIA is short for ion association and is the model described in Section 2.2.6.

case 2 is able to capture this difference in the relative static permittivity of the two models.

In Table 4 it can be seen that the different approaches both in terms of relative static permittivity models and adjustable parameters, mostly affect the mean ionic activity coefficients and osmotic coefficients, whereas the density is affected to a much smaller degree. This shows that the density is not affected much by the choice of model used for the relative static permittivity. This was also observed in the work of Walker et al. [20], where many models of the relative static permittivity were compared without refitting of the parameters, and deviations of the density data were much smaller compared to other properties like mean ionic activity coefficients and osmotic coefficients.

The deviations of the mean ionic activity coefficients and osmotic coefficients are similar as these properties are linked by the Gibbs–Duhem equation [46]:

\[
\ln \gamma_m^\pm = \phi - 1 + \int_0^{m_r} \frac{\phi - 1}{m} \, dm \tag{22}
\]

where \( \gamma_m^\pm \) refers to the mean ionic activity coefficient in the molality based state, \( \phi \) is the osmotic coefficient, and \( m \) is the molality. The reason to include both properties is that there are different data available and the qualitative agreement should be better, because the model is required to match the shape of both properties, as for example the minimum is found at a different molality. The reason that some models show quite a large difference in the deviations between the activity and osmotic coefficients is because of differences in the available data. The data set for the osmotic coefficients includes a lot more data points at 298.15 K compared to activity coefficients, so if this temperature is described well the overall deviation of the osmotic coefficients will be reduced.

The results of case 2/model 5 in a wide temperature range are shown in Figs. 6–8 for the density, MIAC and osmotic coefficients respectively. The good quantitative agreement of the model shown in terms of deviation in Table 4 is also apparent in the figures. What the figures show is that the deviations appear to be spread across the temperature range for both density and MIAC (Figs. 6 and 7).

For the osmotic coefficients (Fig. 8) it can be seen that especially the agreement at 298.15 K is good, and it is a bit worse at higher temperatures. While it is a bit difficult to tell the difference between 298.15 K and 373.15 K, because the data are close, it can be seen that at both temperatures the minimum of the osmotic coefficients is found at approximately the correct molality. The data also indicate that there should be two intersections for the two temperatures (298.15 K and 373.15 K), and the model is also able to (barely) capture this trend. The molality of these intersections are impossible to find accurately due to scattering in the data. The model is therefore able to capture some fine qualitative details of a quite sensitive property (osmotic coefficients).

It has been highlighted by others [47] that the MIAC data for NaCl show a maximum at a temperature of around 323.15 K. This maximum

![Fig. 6. The results for the density for the water–NaCl system at different temperatures with e-CPA with parameters of case 2/model 5 (see Table 3). The points are from a correlation of experimental data by Al-Ghafri et al. [44].](image)

![Fig. 7. The results for the mean ionic activity coefficients for the water–NaCl system at different temperatures with e-CPA with parameters of case 2/model 5 (see Table 3). The points are experimental data.](image)

![Fig. 8. The results for the osmotic coefficients for the water–NaCl system at different temperatures with e-CPA with parameters of case 2/model 5 (see Table 3). The points are experimental data.](image)
also results to the fact that the MIAC data at 273 K and 373 K are very similar. In Fig. 9 the results for case 2/model 5 are shown, in the relevant temperature range of 273.15–373.15 K. It can be seen that the model is able to capture the behaviour around the maximum very well, as the data at both 313.15 K and 333.15 K are captured very well. The figure also shows that the model behaves less satisfactorily at the lowest included temperature of 273.15 K.

### 3.1. Balance of contributions to the activity coefficients

The mean ionic activity coefficients can be split into the contributions of the various terms in the model. This analysis has been done before in several works by various groups [12,28,48,49], also including our previous work [5]. The full details of how the contributions are derived are given in our previous work [5]. The short description is that the model is split into 5 terms: the 4 terms shown in Eq. (1) (SRK, Association, DH and Born) plus an additional term called permittivity (Perm in the figures). The permittivity term describes the impact of the derivatives of the static permittivity, and the plotted values are the sum of the impacts from both the DH and Born terms. These derivatives are not included in the DH and Born contributions.

In general a “correct” balance of contributions is not known (and this will be the case for many years to come). Regardless of this, it is still a highly valuable tool to understand how various models/parameterizations work, as it provides information on what terms of the model are actually important.

In Fig. 10 the contributions to MIAC of some of the cases/models are shown and in the supplementary material results for all of the models of cases 1 and 2 can be found. For all cases/models the DH term is the most negative contribution to MIAC and this is usually what is observed for electrolyte models [5,12,28,48,49]. What is generally seen when looking at the contributions to the activity coefficients, is that if the static permittivity is concentration dependent, the Born term will be a positive contribution and counterbalance the electrostatic term (here: DH). When the static permittivity is concentration independent, the Born term will be zero, and usually the physical term (here: SRK) will counterbalance the electrostatic term, which is also seen for model 0 [5]. For model 1 (and 4) where the permittivity is between the solvent value and the experimental value both the Born and SRK term have a contribution from the permittivity term will generally be positive. For the solvent model, the addition of ions in the system will decrease the mole fraction of water and that leads to a negative contribution due to the structure of the model.

Comparing results from cases 1 and 2 (Fig. 10 (c)–(d) or (e)–(f)) it can be seen that the general impact of adjusting the Born radius of the ions leads to smaller contributions from the Born term. This has already been discussed as being because the Born radii have much larger values. For model 1 (and 4) which has a decrease of the permittivity that is between the solvent value and the experimental relative static permittivity data, the SRK term becomes larger than the Born term, but the contribution from the Born term is not negligible. For models where the relative static permittivity is describing the experimental values it is typically seen that the DH term is significantly reduced in magnitude as exemplified in Fig. 10 (c)–(f) for model 5. The trend is the same for models 2 and 3 as can be seen in the supplementary material.

What can be observed for the permittivity term when comparing between cases 1 and 2 is that the direction is the same but the magnitude has decreased due to the smaller magnitudes of the DH and Born terms. Regarding the association term it is mostly relevant for model 5. However, the association term changes significantly from case 1 to 2 for model 5. In case 1 the association term is a large positive contribution, but for case 2 it is a significant negative contribution. The reason for this large difference between cases 1 and 2, where the same association parameters are used, can be found in Eq. (15), which describes the association strength of the model. The association strength in the Wertheim based methodology is not just dependent on the association parameters, but also on the co-volumes of the associating molecules. Since the co-volume of the ions are calculated from the ion diameter (σ), the large difference of the ion size between cases 1 and 2, will also lead to large differences in the co-volumes, which will also affect the association strength and therefore the association term.

When comparing cases 1 and 2 for model 5 it can also be seen that the SRK term switches sign, where it is a negative contribution for case 1 and a positive contribution for case 2. It is generally seen that the SRK term becomes more positive from case 1 to case 2, and this must be a side effect of adjusting the Born radius. This is because it is found that the adjustment of the Born radii leads to much larger values for the Born radii, which means that the impact of the Born term is reduced. A more positive SRK term is therefore likely necessary to compensate for some of the reduced size of the Born term. This is especially the case for the models that describe the experimental relative static permittivity (models 2, 3 and 5), as these models have the largest decrease of the permittivity.

The large impact of the association term for model 5 for both cases, is also something that sets it apart from the other models as they do
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Fig. 10. The 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 permittivity models (defined in Table 1) of cases 1 and 2 (defined in Section 2.4). Model 0 results are also shown in a previous work [5].

not have this significant contribution from the association term. This might be part of the reason why model 5 performs significantly better than the other models with adjustable parameters according to case 2 (see Table 4).

3.2. Individual ion activity coefficients

Reported measurements of individual ion activity coefficients (IIAC) have been considered controversial for a long time, because critics believe that such measurements are impossible. The disagreement has been especially clear in the discussions of Vera/Wilczek-Vera [50,54, 55] versus Malatesta [56] and Zarubin [57–59]. It should be stressed that the controversies are only regarding the legitimacy of the measurements, given that when the mean ionic activity coefficients are calculated with an EoS, they will usually be calculated from the IIAC, because the ions usually are defined as two separate ions in an e-EoS. IIAC is a well defined thermodynamic quantity in the framework of a thermodynamic model, but the issue is that it is unclear if the measured data actually reflect the same quantity. In this work, the experimental data are assumed valid, but the focus is mostly on qualitative agreement, because the reported IIAC data from different groups vary significantly.

Despite the mentioned controversies, papers that investigated the modelling of IIAC have been published. Valisko and Boda [45] did a review of the literature in 2014 and cited around 20 papers modelling this property. Most of these were molecular dynamics simulations studies, which are not considered particularly controversial. Only 4 of the studies actually compare their results to the measured values of IIAC, which is probably because of the discussed controversies. In later years a new study has been conducted by Sun et al. [49], and a new
molecular dynamics simulations study has been published by Saravi and Panagiotopoulos [60], which is able to confirm the qualitative trends of the published IIAC data for many salts.

In our previous work [5], a comparison with the IIAC data was also done with various parameter sets of e-CPA including model 0 of this work. It was found that all the investigated parameterizations of e-CPA were predicting the opposite qualitative trend of the IIAC compared to the experimental data. What is meant by qualitative trend is in regards to which ion has higher (and lower) IIAC compared to MIAC. It was found that the only parameter that had a significant impact on the qualitative trend of IIAC was the relative difference of the ion size, $\sigma$, between the two ions. The relative difference of the co-volumes would also impact the IIAC, but because the co-volume is calculated from $\sigma$ in all the parameterizations, the relative difference of the co-volume had a comparable trend to the value of $\sigma$.

This lead to the result that the larger ion would always be predicted to have a larger IIAC than the smaller ion. For NaCl this means that Na$^+$ will be predicted lower and Cl$^-$ will be predicted higher because of their relative sizes, however experimentally the trend is opposite. It was shown in our previous work that the IIAC can be correlated with e-CPA, with a similar parameterization procedure, but it was required that the size of the ions was flipped so Na$^+$ was considered larger than Cl$^-$.

This was an undesirable approach as it is well-known that Na$^+$ should be the smaller ion, so the model was clearly missing some physics in order to correctly describe the IIAC.
3.2.1. Results for individual ion activity coefficients

The results with models 3 and 5 for both cases are shown in Fig. 11 and results of all of the models are shown in the supplementary material. It can be seen that case 1/model 3 (Fig. 11 (a)) have IIAC values that are fairly close to the average (MIAC) values, but still with the opposite trend. This is seen for many of the case 1 results (shown in supplementary material) aside from with model 5. The reasons for this will be discussed in Section 3.3, where the contribution of the terms to IIAC are shown. In Fig. 11 (b) the results with case 2/model 3 is shown and compared to case 1 (Fig. 11 (a)) it can be seen that the difference between the MIAC and IIAC is larger. The relative difference between MIAC and IIAC that is exemplified in Fig. 11 (b) is similar for models 0–4 as can be seen in the supplementary material and it is likely related to the Born radii being the same for both ions.

Finally, the results of model 5, which is the ion association model describing the experimental relative static permittivity data needs to be thoroughly discussed (Fig. 11 (c) and (d)). This is the only model that is able to correctly capture the qualitative trend of the IIAC data. The quantitative agreement is clearly poor for both cases and the absolute difference 

$$|\ln \gamma_{\text{calc}} - \ln \gamma_{\text{exp}}|$$

between the model and experimental data.
does not seem to be much better for model 5 compared to the other models. The correct qualitative agreement is still very interesting as it deviates significantly from the results of all the other models. The reason for this will be explored further in a later section by investigating the contributions to IIAC. While case 2/model 5 significantly improves the description of the MIAC data compared to case 1 together with slightly better quantitative agreement for IIAC, it is still far from accurately describing the experimental IIAC data.

3.3. Contributions to individual ion activity coefficients

In a similar fashion to MIAC, it is possible to split IIAC into the contributions from the different terms of the model. This will help in understanding why the IIAC of the different models behave as they do. This was also done in our previous work [5], and what was generally seen was that the behaviour of the IIAC was generally similar to what was observed for MIAC, with some general differences in the size of the different terms based on the relative size of the ions. Larger ions would have a more positive contribution from the SRK term and a less negative contribution from the DH term. These consequences of the ion size are the two main factors that caused the trend that larger ions have higher IIAC, which is the reason for the wrong qualitative trend for NaCl.

In Fig. 12 the results for the contributions to IIAC for model 1 (Pottel) with case 1 parameters are shown. These results show the same general trends that were mentioned above: the IIAC contributions are quite similar to the MIAC contributions (Fig. 10 (c)), with the main differences being slight changes in the magnitude of the SRK and DH term, which leads to the wrong qualitative trend of the IIAC. The permittivity term is slightly different for the two ions, because the Pottel model depends on the ion diameter, \( \sigma \), which is different between the ions. However, the contribution from the permittivity term also pushes in the direction of larger ions resulting in higher IIAC.

In Fig. 13 the results of model 3 with case 1 parameters are shown. The IIAC were shown to be fairly close to the MIAC for both ions (Fig. 11 (a)). The difference in the contributions of the two ions is quite small, but in this case they are not all in the same direction. The difference in the DH term is as usual, with the smaller ion having a more negative contribution. However, the SRK term is now more negative for the larger ion, whereas for model 1 (Fig. 12) the larger ion would be more positive. This is an effect that will make the IIAC of the two ions closer to each other compared to what is seen for the solvent model. The difference in the Born contribution also plays a role, as the larger ion is less positive. The difference between the ions for the Born term is less significant than the DH difference, but a bit more than the SRK difference.

The SRK term being a negative contribution is related to the very small values of the ion diameter, \( \sigma \), because the co-volume is calculated from the ion diameter by assuming that the ions are perfectly spherical, and that the co-volume corresponds to the volume of the sphere. The interaction parameter will also affect the SRK term, but when \( \sigma \) is changed by some factor, the co-volume will be affected by the same factor to the third power, due to the conversion between diameter and volume. The large differences of the \( \sigma \)-values seen for some of the models of case 1 (Table 2), will have a very large impact on the co-volume.

To sum up the discussion of Fig. 13, while the different Born radii of the ions do have an impact, the very small \( \sigma \)-values of the ions are also a significant reason for the different behaviour of the IIAC, compared to the other models. It is therefore a mix of “strange” parameters of model 3 case 1 (very small \( \sigma \)-values) and the different Born radii of the two ions. One of these two effects are alone not enough to make the IIAC almost equal to the MIAC.

Another very interesting result of the analysis of the IIAC of the different models was that, model 5 for both cases 1 and 2 was able to get the qualitative correct trend of the IIAC, even through the quantitative agreement with the data was unsatisfactory (Fig. 11 (c) and (d)). In Figs. 14 and 15 the results of the contribution of the different terms to the IIAC of the ions are shown for model 5 with parameters from cases 1 and 2 respectively. These figures can explain why the model is able to describe the IIAC qualitatively correct, while still maintaining a correct relative size difference, where chloride is larger than the sodium-ion.

Looking at Fig. 14 (case 1/model 5) it can be seen that for most of the terms, the difference between the ions is quite small for the same terms and follow the same trends compared to ion size as already discussed. However, this is not the case for the association term, which shows a very significant difference of over 2 for \( \ln \gamma \) at 6 mol/kg. The large difference of the association term between the ions is what makes the IIAC qualitatively correct, because the value is larger for sodium than for chloride. The fact that the association term for chloride is close to 0 is likely just a result of some opposite acting forces cancelling out and not an indication that chloride is not associating. It should be mentioned that the association term is due to the ions being considered associating species and is a combination of water–ion association and ion–ion association.

In Fig. 15 the results of the contribution from the various terms are shown for model 5 case 2. The analysis is similar to the case 1 results above; terms other than the association term are generally similar in size between ions, with the SRK and DH terms being affected by the different ion diameter of the two ions. The association term is again significantly different between the two ions, with it being slightly positive for sodium and very negative (comparable size to the DH term) for chloride. This also confirms that the association being close to zero for chloride in case 1 (Fig. 14), was just a coincidence.

It should be discussed why the association term varies so much between the ions and cases 1 and 2 despite the association parameters of both the ions being the same. It has already been discussed why the association term of the MIAC contributions, was so different from cases 1 and 2. The reasoning for the IIAC is the same. It is because the association strength is also calculated from the co-volume, which is calculated from the \( \sigma \)-values. Since the \( \sigma \)-values are different for the two ions, this is reflected in the size of the association contribution.

4. Re-parameterizing the ion association model

From the results shown and discussed in the previous sections a lot has been learned about the impact of different concentration dependent relative static permittivity models. It was clear that the best performing
method for e-CPA is when the ion association model is used to calculate the relative static permittivity and the adjustable parameters are the same as case 2 (σ, U_{eoff}, \gamma_{\text{ref}}, a \text{ and } R_{\text{water}}). This method provides the best quantitative agreement (lowest deviations with experimental data) for the properties mean ionic activity coefficients, osmotic coefficients and density, while being able to describe the experimental relative static permittivity. It was also the only method that was able to describe the qualitative trend of the individual ion activity coefficients, although the quantitative agreement was poor.

The goal of this section is to describe a method for improving the quantitative description of the IIAC data, without significant loss of predictability for any of the other properties with the ion association model for calculating the relative static permittivity. The method for obtaining better quantitative agreement for IIAC is through an alternative way of parameterizing the ion association model within e-CPA, which is as follows: The optimized parameters are like case 2, with the addition of the association energy of the ions as an additional adjustable parameter. The association volume of the ions is still considered to have the same value as the association volume of water to reduce the complexity of the parameter optimization. The IIAC data are also added to the objective function, which therefore is:

\[
OF = \frac{1}{N_{\text{II}}} \sum_{i} \left( \frac{\gamma_{\text{exp}} - \gamma_{\text{calc}}}{\gamma_{\text{II},i}} \right)^2 + \frac{1}{N_{\Phi}} \sum_{i} \left( \frac{\Phi_{\text{exp}} - \Phi_{\text{calc}}}{\Phi_{\text{I},i}} \right)^2 + \frac{1}{N_{\rho}} \sum_{i} \left( \frac{\rho_{\text{exp}} - \rho_{\text{calc}}}{\rho_{\text{I},i}} \right)^2 + \frac{0.1}{N_{\gamma}} \sum_{i} \left( \frac{\gamma_{\text{II},i} - \gamma_{\text{calc}}}{\gamma_{\text{II},i}} \right)^2 \]

(23)

The subscript II refers to individual ions and refers to data for both sodium and chloride. The IIAC data have been given a smaller weight than the other properties for two reasons: The data used include a lot of scattering, which decreases the trust in the individual data points. The second reason for reducing the weight is because IIAC only makes sense as a quantitative property when the mean ionic activity coefficients, osmotic coefficients and density, while being able to describe the experimental relative static permittivity. It was also the only method that was able to describe the qualitative trend of the individual ion activity coefficients, although the quantitative agreement was poor.

The optimized parameters are shown in Table 3 with the name “model 6” and it can be seen that most of the parameters are quite comparable to the model 5 parameters, except for the association energy, which is smaller. The calculated deviations are shown in Table 4 again with the name “model 6” and it is clear that the performance of the new parameterization compares well to the model 5 results. The biggest difference between models 5 and 6 is observed for the density, which shows a slightly worse quantitative agreement. Overall, the agreement with experimental data is considered to be satisfactory.

In Fig. 16 the results for the IIAC are shown. The model results agree well with the experimental data, when considering the large amount of scattering of the data. This means that one of the objectives of this parameterization is obtained, because good agreement with the IIAC data was the reason that the IIAC data were added to the objective function in the first place.

Another aspect of this method is that there is no direct knowledge of the relative static permittivity data in the parameter optimization, so it is important to check that this property is predicted correctly. In Fig. 5, it can be seen that the agreement with the experimental data is good. It is therefore shown that with the ion association model it is possible to describe the relative static permittivity data without including it in the parameter estimation, because the association energy that is required to describe the IIAC is also sufficient to describe the experimental relative static permittivity.

Similarly to the other models/cases, the balance of contributions from e-CPA to both MIAC and IIAC will be analysed for the new parameterization, which is presented in this section. The results are primarily compared to the results of case 2/model 5, because the basis of both parameterizations are similar as the same model is used for the relative static permittivity, and the same adjustable parameters are optimized. The only difference is regarding how the association energy of the ions is obtained. In Fig. 17 the contributions to MIAC are shown. Compared to case 2/model 5 (Fig. 10 (f)) it can be seen that the contributions of this parameterization is very similar. Only small changes are observed, as the general direction (e.g. positive or negative contributions) is the same. The main difference is that the contributions of the new parameterization are of slightly smaller magnitudes for all terms.

In Fig. 18 the contributions to the IIAC of both ions are shown for the new parameterization. Compared to the results of case 2/model 5 (Fig. 15), most of the apparent trends from the contributions to MIAC are also observed for the contributions to IIAC. For the SRK, DH, Born and permittivity terms the differences between the two parameterizations are small, with a general trend of the new parameterization showing slightly smaller magnitudes for these contributions. The only term that shows a significant change between the two parameterizations is the association term. For Na+ with case 2/model 5 parameters, the association term was a contribution that was comparable to the SRK term while it for the new parameterization is close to zero. For Cl−, the association term is no longer the most negative contribution at higher molalities as it was for case 2/model 5 parameters and it is instead “just” a large negative contribution. The fact that it is the association term that has changed the most from case 2/model 5 to the new parameterization is also reflected in the parameters (see Table 3), where it can be seen that the biggest difference of the parameters of models 5 and 6 is the association energy of the ions.
5. Conclusion

In this work the performance of several models of the relative static permittivity was compared when the models were used as input to the e-CPA equation of state for the water–NaCl system. The parameters of e-CPA were refitted for each of the models. Two combinations of adjustable parameters were investigated, which were called case 1 and 2. Case 1 included the ion diameter and a temperature dependent interaction parameter. Case 2 included the same parameters with the addition of the Born radius, which was assumed to be the same value for both ions. A comparison to a model from a previous work that did not include the salt concentration dependency of the relative static permittivity was also made.

When case 1 parameters were optimized, it was found that the best results were obtained when the relative static permittivity was independent of the salt concentration. The results of case 1 even suggested that there is a trend that the prediction of other properties would get worse as the relative static permittivity was described better.

The best performing model was found when case 2 adjustable parameters were optimized for the various models. It was the model that was based on water–ion association and describes the relative static permittivity data correctly, that was found to perform the best. Based on an analysis of the balance of contributions to the mean ionic activity coefficients, it was found that the association term and the derivatives of the permittivity model played significant roles in why this model performed the best. The trend where better description of the relative static permittivity would lead to worse description of the other properties, that was found for case 1 was therefore not observed with a different combination of adjustable parameters.

Individual ion activity coefficients (IIAC) were also investigated as a part of this study, and it was found that the only static permittivity model that was capable of describing the correct qualitative trend of the IIAC, was the ion association model. Even with the correct qualitative trend, the quantitative agreement with experimental data was still poor. From balance of contribution plots for IIAC it was found that the reason for the correct qualitative trend was that the contribution from the association term was very different between the two ions.

Finally, it was shown that the ion association model could be parameterized to also get reasonable quantitative agreement with the experimental IIAC data without significantly impacting any of the other investigated properties. This was accomplished by including the IIAC data in the objective function and adding the association parameter as an adjustable parameter. This meant that data of the relative static permittivity were not considered in the parameter optimization. It was found that with this method the relative static permittivity would still be reasonably described.
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List of Greek symbols

\( T \) \hspace{1cm} \text{Temperature}
\( T_a \) \hspace{1cm} \text{Parameter for temperature dependency of interaction energy in Huron–Vidal mixing rule}
\( U_{ref} \) \hspace{1cm} \text{Interaction energy at reference temperature in Huron–Vidal mixing rule}
\( V \) \hspace{1cm} \text{Volume}
\( x \) \hspace{1cm} \text{Mole fraction}
\( X \) \hspace{1cm} \text{Any property}
\( \lambda_{i} \) \hspace{1cm} \text{Site fraction}
\( z_{ij} \) \hspace{1cm} \text{Coordination number of molecule } j \text{ around central molecule } i

List of subscripts

\( \alpha \) \hspace{1cm} \text{Fraction of component } i \text{ that is not associated to ions}
\( \beta_{i,j} \) \hspace{1cm} \text{Association volume}
\( \cos \gamma_{ij} \) \hspace{1cm} \text{Angle between dipole moments of molecules } i \text{ and } j
\( \cos \theta_{ij} \) \hspace{1cm} \text{Rotation angle between shells in the hydrogen bond network}
\( \Delta_{i,j} \) \hspace{1cm} \text{Association strength}
\( \epsilon_{0} \) \hspace{1cm} \text{Vacuum permittivity}
\( \epsilon_{A,B} \) \hspace{1cm} \text{Association energy}
\( \epsilon_{\infty} \) \hspace{1cm} \text{Infinite static permittivity of solvent (water)}
\( \gamma \) \hspace{1cm} \text{Individual ionic activity coefficient}
\( \gamma_{\pm} \) \hspace{1cm} \text{Mean ionic activity coefficient in molality scale}
\( \gamma_{\infty} \) \hspace{1cm} \text{Mean ionic activity coefficient in molality scale}
\( \kappa \) \hspace{1cm} \text{Conductivity}
\( \mu_{0} \) \hspace{1cm} \text{Dipole moment}
\( \mu_{w,0} \) \hspace{1cm} \text{Dipole moment of solvent}
\( \nu \) \hspace{1cm} \text{Molar volume}
\( \Phi \) \hspace{1cm} \text{Osmotic coefficient}
\( \rho \) \hspace{1cm} \text{Mass density}
\( \rho_{w} \) \hspace{1cm} \text{Molar density of solvent}
\( \sigma \) \hspace{1cm} \text{Ion diameter}
\( \tau \) \hspace{1cm} \text{Relaxation time}
\( \Theta_{i} \) \hspace{1cm} \text{Fraction of component } i \text{ that is not associated to ions}
\( \varphi_{i,j}^{\infty} \) \hspace{1cm} \text{Ionic compacity}

List of superscripts

\( max \) \hspace{1cm} \text{Largest value}
\( \Phi \) \hspace{1cm} \text{Osmotic coefficient}
\( \rho \) \hspace{1cm} \text{Mass density}

CRediT authorship contribution statement

Martin Due Olsen: Methodology, Software, Formal analysis, Writing – original draft, Visualization.
Georgios M. Kontogeorgis: Conceptualization, Writing – review & editing, Funding acquisition.
Xiaodong Liang: Software, Writing – review & editing.
Nicolas von Solms: Project administration, Supervision.

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.

Data availability

All data used in this work is available in the literature.

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Appendix A. Supplementary material

Supplementary material related to this article can be found online at https://doi.org/10.1016/j.fluid.2022.113632.

The supplementary material contains figures showing the plots for the contributions of terms and for the individual ion activity coefficients for all of the models of this work.

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