

# Predicting the thermodynamic properties of experimental mixed-solvent electrolyte systems using the SAFT-VR+DE equation of state

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## ABSTRACT

We apply the SAFT-VR+DE equation of state to the study of experimental mixed-solvent electrolyte solutions. In the non-primitive model based SAFT-VR+DE approach (Zhao et al., JCP 2007, 126, 244503) the ions are considered fully dissociated within the solvent that is explicitly treated within the model and the theoretical framework. Typically in the study of electrolyte systems the simpler primitive model is used, which requires knowledge of the experimental dielectric constant. With the non-primitive model the dielectric constant is calculated as part of the theory, which is a particularly attractive feature in the study of mixed-solvent electrolyte systems as data for the experimental dielectric constant of such systems is more scarce. Here for the first time as far as the authors are aware, a non-primitive based equation of state has been used for the study of mixed-solvent electrolytes. The solvents considered (water, methanol and ethanol) are modeled using the SAFT-VR+D approach (Zhao et al., JCP 2007, 127, 084514; Zhao et al., JCP 2006, 125, 104504) in which the contribution of the dipole to the thermodynamics and structure of the fluid are explicitly accounted for. The theory is found to accurately predict the vapor-liquid equilibrium, as well as dielectric properties of the salt free alcohol-water mixtures both at room and elevated temperatures. Ternary mixtures of salt/water/alcohol are then studied using the SAFT-VR+DE parameters for the salts determined in earlier work (Das et al., AIChE Journal 2015, 61, 3053–3072) and a cation-alcohol unlike dispersive energy parameter obtained by fitting to mean ionic activity coefficient data at room temperature and pressure. Thus, with only one adjustable parameter, a predictive SAFT-VR+DE equation to study mixed-solvent electrolyte systems is developed. The SAFT-VR+DE predictions are found to be in good quantitative agreement with mean ionic activity coefficient data for several mixed-solvent electrolyte systems over a wide range of molalities and different solvent ratios. The model is parameterized to allow the molecular level interactions between different cations and the surrounding solvent molecules to be explored.

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## 1. Introduction

Advances in equations of state and activity coefficient models enable a quantitative representation of the thermophysical properties and phase behavior of mixtures, which serve as a foundation for process modeling and process and product design tools [1]. For example, the Peng-Robinson and Soave-Redlich-Kwong equations are widely used as the equation of state of choice for many thermodynamic property and phase behavior calculations (e.g. vapor

liquid equilibrium (VLE)) in the petrochemical industry. However, molecular-based equations of state, such as versions of the statistical associating fluid theory [2–4], are now available in process simulators, allowing these advanced tools to find more mainstream use. As a molecular-based equation, SAFT accounts for the structural and physical anisotropies that exist in complex chemical systems and in return results in a more predictive approach as compared to classical cubic equations of state. Thus far, SAFT has been applied to a wide range of important systems, as mentioned in several review articles [5–7].

While the success of SAFT as a predictive tool has led to the study of increasingly complex systems, one area in which a predictive theoretical tool still lacks is electrolytes, and in particular mixed-solvent systems. Mixed-solvent electrolyte solutions find

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applications in several industrial and natural biological processes. Examples include extractive distillation with salt, solution crystallization, waste and drinking-water purification, and fertilizer synthesis among many others [8–12]. Often these processes involve salt solutions over wide ranges of composition (e.g., aqueous, organic or mixed-solvent, dilute or concentrated solutions) and state conditions (e.g., from ambient temperatures to supercritical conditions). Thus the design of such processes requires a precise quantitative description of relevant thermodynamic properties such as salt solubility and mean ionic activity coefficient. There are two means of addressing this need; one is by performing experimental measurements and the other through theoretical predictions. As experimental studies on the thermodynamic properties of mixed-solvent electrolyte systems are limited [13], theoretical approaches provide an alternate means to study such systems and generate “pseudo” experimental data.

The desire to develop a theoretical framework for the calculation of the thermodynamic properties and phase behavior of mixed-solvent electrolyte systems dates back to the 1960's. In the first such study, Johnson and Furter [14] proposed a quantitative correlative equation, based on the relation between the relative volatility of solvents and salt concentration, to calculate the vapor-liquid equilibrium (VLE) of eighteen different alcohol (methanol/ethanol/1-propanol)/water + salt mixed-solvent electrolyte systems. However, the model parameters were dependent upon the salt and solvent compositions, and the approach limited to cases where the solubility of salt was low and caused an insignificant increase in the boiling point of the solvent. Ohe [15] later proposed an empirical model for water-alcohol- $\text{CaCl}_2$  vapor-liquid equilibrium calculations. The approach, based upon solvation number (i.e., ratio of the number of solvent molecules to salt molecules in the preferential solvate) assumed that no solvated salt molecules take part in vaporization. Rousseau et al. [16,17] were the first to apply activity coefficient models (i.e., van Laar, Wilson, and UNIQUAC) to mixed-solvent electrolyte systems and studied ternary mixtures of salt + two solvents as a binary mixture of two pseudo components; one salted-out component (non-preferential solvent component) and one salted-in component (preferential solvent component + salt). The approach was found to accurately correlate (~2% deviations in mole fractions) the vapor phase mole fraction data for methanol/ethanol/1-propanol + water + NaBr/KCl/NaF/LiCl/HgCl<sub>2</sub> systems. Subsequently, others used activity coefficient models to describe the salt as a fully associated third component. For example, Mock et al. [18] and Kolker et al. [19,20] with NRTL and Dahl and Macedo [21] with UNIFAC studied mixed-solvent electrolyte systems; however, only the short-ranged dispersive effects of the electrolytes were captured through these models.

While the methods discussed above can correlate the thermodynamics of electrolytes, they completely ignore any long-range electrostatic interactions, which play a central role in determining the properties of electrolyte solutions [22–24]. Thus, in later studies, a number of models, were proposed that combined the Gibbs free energy due to long-range electrostatic interactions with activity coefficient models [12,89,90]. The Debye–Hückel (DH) theory proved to be the most influential and forms the basis of several equations for mixed-solvent electrolytes [24–32]. In the DH approach, ions are considered to be point charges in a dielectric continuum, thus the solvent is considered implicitly. The approach of treating solvent molecules implicitly using a representative dielectric constant in an electrolyte solution is in the McMillan-Mayer (MM) framework [33], also known as a primitive model (PM) of electrolyte solutions.

In an effort to improve the predictive ability of equations of state for the study of mixed-solvent electrolyte systems, SAFT based equations have been applied to their study. In perhaps the first such

study, the SAFT-VRE [34] equation developed by combining SAFT-VR with an electrostatic interaction contribution to the free energy obtained by using mean spherical approximation (MSA) at the level of the restrictive primitive model (i.e., an equimolar mixture of equal-diameter hard spheres are assumed in a dielectric continuum), was applied to the study of water + alkane + salt systems [35]. The water and electrolyte model parameters were used in a transferable manner from a previous SAFT-VRE study of aqueous electrolyte systems [34] and the alkane parameters taken from the work of McCabe et al. [36]. The approach was able to provide a qualitative representation of the experimental phase behavior data (coexisting compositions of the water-rich and n-alkane-rich liquid phases, salting out, and solution densities of the water rich phase) for water + n-alkane + salt systems (MX, M = Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, and X = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>) rather than a quantitative one. Unlike cross interaction energy range and depth parameters between the water and alkane molecules, obtained by fitting to ternary phase behavior data, were then used to improve the agreement between the theory and experimental results. In more recent developments, other SAFT based equations of state have also been applied to the study of mixed-solvent electrolyte solutions. For example, Held et al. [13] applied the previously developed primitive model based ePC-SAFT [37] equation of state to study mixed-solvent electrolyte systems. The ePC-SAFT equation of state is an extension of the PC-SAFT [2] equation with an electrostatic contribution to the free energy that is represented by a simple DH term. Two alcohol based (i.e., salt-independent, but solvent-dependent) ion parameters, the solvated ionic diameter and dispersion energy parameter, were determined by simultaneously fitting to experimental solution densities and osmotic coefficients for various electrolyte solutions composed of Na<sup>+</sup>, Li<sup>+</sup>, K<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup> ions in ethanol or methanol. The water based ion parameters were taken from a previous study [91]. For the ternary salt + water + alcohol systems, no ion-ion dispersion interactions were considered; only ion-solvent dispersion interactions were included and obtained from Lorenz-Berthelot combining rules. The ionic radii were obtained from an averaging scheme based upon salt free solvent compositions in solution. The relative permittivity (expressed as a ratio to the permittivity of free space) of salt free solvent mixtures was modeled by an empirical formula obtained from fitting to experimental dielectric constant values. Using these parameters, solution densities and mean ionic activities of KCl, NaBr, NaCl, NaI, LiCl in ethanol + water, methanol + water, and methanol + ethanol + water mixed solvents were predicted across different weight fractions of solvent with considerable accuracy (~1% for solution densities and <5% in most cases for mean ionic activity coefficient); however, one should note that for most systems, solution densities were limited to only the very dilute limit (<1 m). In more recent work, Schreckenberget al. [38] proposed an improved formulation of the SAFT-VRE equation [34] that incorporates a Born contribution in order to better capture solvation effects. Additionally, the implicit solvent within the PM framework of SAFT-VRE [34] was represented through an empirical solution dielectric constant model, following the work of Uematsu and Franck [39], which takes into account the temperature, density and composition of the solvent, and in turn makes the dielectric constant a differentiable variable. The study examined VLE and LLE of mixed-solvent electrolyte systems (methanol/n-butanol and water + salt systems) along with single and multi-salt aqueous electrolytes. The electrolytes were described using a fully dissociated model with ion-specific interaction parameters, with the effective ionic diameter, ion-water and ion-ion dispersive energy parameters obtained by fitting to vapor pressure, solution density, and mean ionic activity coefficient data for fifteen different aqueous alkali halide salts at temperatures below 523 K (critical region). The cross ion-ion dispersive interaction energy was estimated using a

procedure proposed by Hudson and McCoubrey [40]. For mixed-solvent systems, the alcohol-ion unlike dispersion energy was obtained by fitting to experimental water + alcohol + salt VLE/LLE data and was able to provide a good representation of the experimental results, although the effect of the salt on the solvent dielectric is not captured in this approach.

In this work, the non-primitive model based SAFT-VR+DE equation of state [41], has been applied to study the thermodynamic properties of real mixed-solvent electrolyte systems. The non-primitive model of electrolyte solutions explicitly considers the solvent species, as opposed to the primitive model in which the solvent-ion and solvent-solvent dipolar interactions are implicit; it is thus a Born-Oppenheimer (BO) [33] approach. For the simplest of cases the BO model is conceptualized as a mixture of charged hard spheres in a solvent of hard spherical molecules with a point dipole embedded in the center. In previous work, the thermodynamic properties, such as osmotic coefficient, water activity, Gibbs free energy of hydration, dielectric decrement, solution densities, of nineteen different aqueous electrolytes were predicted with considerable accuracy using a single salt-dependent parameter obtained by fitting to experimental mean ionic activity coefficient data [42]. Subsequently, an extended version of the SAFT-VR+DE equation of state was proposed for mixed-solvent electrolyte systems [43], with the incorporation of a one-fluid-like approximation into the theoretical formulation of the ion-dipole and dipole-dipole interactions through an effective solvent diameter and dipole moment. The approximation was extensively tested against PVT data obtained from Monte Carlo (MC) simulations of model mixed-solvent electrolyte systems with different solvent polarities, and ionic and solvent compositions. Excellent agreement between the simulation results and theoretical predictions was obtained and thus the applicability of the one-fluid approach in capturing ion-dipolar interactions validated.

Due to the explicit consideration of the solvent species within the SAFT-VR+DE approach, the dielectric constant is not required as an input and is instead calculated within the theory from the dipole moment of the solvent and is a function of ionic concentration and solvent composition. Explicit treatment of solvent species is certainly advantageous compared to the primitive model based implicit treatment, as it eliminates any dependence on experimental data or empirical correlative equations for the determination of the dielectric constant. In previous work [43], it was observed while comparing against the primitive model that an ion concentration and solvent composition dependent dielectric constant is essential to obtain accurate predictions of PVT data. Additionally, a non-primitive based model provides a contribution to the chemical potential and pressure from ion-dipole and dipole-dipole interactions, which is not possible when using the primitive model. We note that in the modified SAFT-VRE equation [38] the effect of long-range electrostatic and dipolar interactions (ion-dipole, dipole-dipole) on pressure and chemical potential was taken into account in an implicit manner through the use of an empirical composition and density dependent dielectric constant in the Born term.

The focus of this study is the theoretical representation of the mean ionic activities of mixed-solvent electrolyte systems, including the mean ionic activity coefficient, using a minimum number of fitted parameters (i.e., rather than ensuring quantitative accuracy for all systems studied by using and fitting all possible model parameters). Mean ionic activity coefficients have a pronounced effect in many applications. For example, mixed-solvent electrolytes are used in extractive distillation processes in which the salt enables the separation of two miscible compounds that form an azeotropic mixture. In liquid-liquid equilibrium the mean ionic activity coefficient plays a dominating role to produce salting in/salting out behavior [29,44]. It is therefore essential to capture

the mean ionic activity coefficients accurately and in this regard, the SAFT-VR+DE equation has been used in a predictive manner to study the mean ionic activity coefficients of several mixed-solvent electrolyte systems over a range of salt and solvent compositions. The remainder of the paper is organized as follows: in section 2 the molecular model and theory are discussed, in section 3 we report the parameters used for the alcohols, water and electrolytes studied and discuss the results and conclusions from this work in section 4.

## 2. Molecular model and theory

In the SAFT-VR+DE [41] approach mixed-solvent electrolyte systems are described as a mixture of positively and negatively charged ions of arbitrary size in a dipolar solvent of associative chain molecules. Fig. 1, provides a schematic representation of the model system. The ions are represented by hard spheres, half with charge  $+q$  and diameter  $\sigma^+$  and half with charge  $-q$  and diameter  $\sigma^-$ . Two kinds of solvent molecules of arbitrary sizes and polarity are portrayed in Fig. 1: monomeric dipolar molecules with four association sites to represent water and dipolar dimers with two association sites mimicking an alcohol.

Key forces of interaction within mixed-solvent electrolyte systems are: coulombic charged interactions, dipolar-charge and dispersive interactions between ionic and dipolar solvent species, and dipolar, associative and dispersive interactions between solvent species. The potential model for the interactions between species in solution is therefore given by,

$$u(r) = u^{SW}(r) + u^{CC}(r) + u^{CD}(r) + u^{DD}(r) \quad (1)$$

where,  $u^{SW}(r)$ ,  $u^{CC}(r)$ ,  $u^{CD}(r)$  and  $u^{DD}(r)$  represents the dispersive interactions as described by a square-well interaction, the coulombic charge-charge interaction, the charge-dipole interaction, and the dipole-dipole interaction potentials, respectively. The square-well interaction potential is given by,

$$u_{ij}^{SW}(r) = \begin{cases} +\infty & r < \sigma_{ij} \\ -\varepsilon_{ij} & \sigma_{ij} \leq r < \lambda_{ij}\sigma_{ij} \\ 0 & r \geq \lambda_{ij}\sigma_{ij} \end{cases} \quad (2)$$

where,  $\varepsilon_{ij}$  and  $\lambda_{ij}$  are the depth and width of the square-well dispersive pair potential between molecules  $i$  and  $j$  and  $\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2$  with  $\sigma_{ii}$  and  $\sigma_{jj}$  being the hard core diameter of molecules  $i$  and  $j$ . The cross-interaction energy depth and width are computed using the Lorentz-Berthelot combining rule given by,

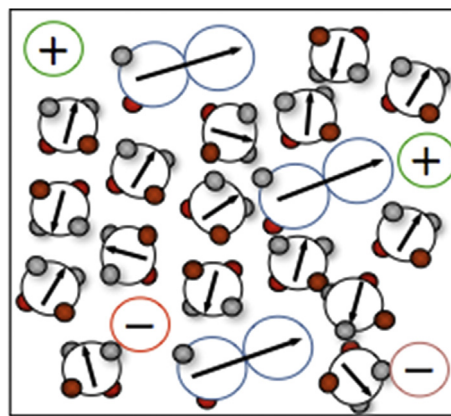


Fig. 1. Schematic representation of molecular model used for mixed-solvent electrolyte solutions containing ions and associating dipolar solvent molecules. Here the ionic species are completely dissociated.

$$\varepsilon_{ij} = \xi \sqrt{\varepsilon_{ii}\varepsilon_{jj}} \quad (3)$$

$$\lambda_{ij} = \gamma \frac{\lambda_{ii}\sigma_{ii} + \lambda_{jj}\sigma_{jj}}{\sigma_{ii} + \sigma_{jj}} \quad (4)$$

where  $\xi$  and  $\gamma$  can be used to modify the cross interaction when deviations from the Lorentz-Berthelot behavior is observed.

The coulombic charge-charge potential between ions is represented by,

$$u_{ij}^{CC}(r) = \begin{cases} +\infty & \text{if } r \leq \sigma_{ij} \\ \frac{z_i z_j e^2}{4\pi\epsilon r} & \text{if } r > \sigma_{ij} \end{cases} \quad (5)$$

where  $r$  is the center-to-center distance,  $z_i$  represents unit charge of the ion  $i$ ,  $e = 1.602 \times 10^{-19}\text{C}$  is the elementary charge of an electron, and  $\epsilon$  the permittivity of the continuous dielectric medium.

The charge-dipole potential between ions and solvent molecules is defined by,

$$u_{ij}^{CD}(r) = \begin{cases} +\infty & \text{if } r \leq \sigma_{ij} \\ \frac{z_i e \mu_i}{4\pi\epsilon r^2} (\hat{r} \cdot \hat{n}) & \text{if } r > \sigma_{ij} \end{cases} \quad (6)$$

where  $\mu_i$  is the dipole moment of the  $i$ -th solvent component and  $\hat{r}$  is the unit vector in the direction of  $r$  joining the center of the segments and  $\hat{n}_i$  is a unit vector parallel to the dipole moment of segment  $i$ .

The dipole-dipole potential between solvent molecules is defined by,

$$u_{ij}^{DD}(r) = \begin{cases} +\infty & \text{if } r \leq \sigma_{ij} \\ -\frac{\mu^2}{4\pi\epsilon r^3} D(n_1 n_2 \hat{r}) & \text{if } r > \sigma_{ij} \end{cases} \quad (7)$$

where,

$$D(n_1 n_2 \hat{r}) = 3(n_1 \cdot \hat{r})(n_2 \cdot \hat{r}) - n_1 \cdot n_2 \quad (8)$$

In the modified SAFT-VR+DE theoretical framework the Helmholtz free energy per molecule in a mixed-solvent electrolyte solution is given by,

$$\frac{A}{Nk_b T} = \frac{A^{ideal}}{Nk_b T} + \frac{A^{mono}}{Nk_b T} + \frac{A^{chain}}{Nk_b T} + \frac{A^{assoc}}{Nk_b T} \quad (9)$$

where  $N$  is a total number of molecules,  $k_b$  is the Boltzmann constant,  $T$  is temperature, and  $A^{ideal}$ ,  $A^{mono}$ ,  $A^{chain}$ , and  $A^{assoc}$  are the Helmholtz free energy contributions due to the ideal, monomer, chain, and association interactions, respectively. Since the general development of the theory and mathematical expressions are elaborately described in previous work, here we focus on the expressions key to the study of mixed-solvent electrolyte systems and for which one the solvents is a chain fluid. For more details the reader is directed to the original papers [42,43,45].

The contribution to the Helmholtz free energy due to the interactions between monomer segments is given as,

$$\frac{A^{mono}}{Nk_b T} = \frac{A^{SW}}{Nk_b T} + \frac{A^{el}}{Nk_b T} \quad (10)$$

where,  $A^{SW}$  and  $A^{el}$  are the free energy contributions due to isotropic square-well dispersion interaction and anisotropic

electrostatic interactions, which contains ion-ion, ion-dipole and dipole-dipole interactions respectively. The attractive square-well dispersive interactions between monomer segments,  $A^{SW}$ , is obtained as in the original SAFT-VR approach from a second order high temperature perturbation expansion [45]. The contribution to the Helmholtz free energy from the electrostatic interactions,  $A^{el}$ , is obtained from Blum and Wei's [46,47] solution to the Ornstein-Zernike equation using integral equation theory within the non-primitive mean spherical approximation (NPMSA) closure for a mixture of ions and dipole of arbitrary size, and is given by,

$$\frac{A^{el}}{Vk_b T} = \frac{E^{el}}{Vk_b T} - J - J' \quad (11)$$

Here,  $V$  is the total volume of the solution, and  $E^{el}/Vk_b T$  is the internal energy per unit volume expressed as,

$$\frac{E^{el}}{Vk_b T} = \frac{1}{4\pi} \left\{ \alpha_0^2 \sum_{k=1}^2 \rho_k z_k N_k - 2\alpha_2 \alpha_0 \rho_n B^{10} - \frac{2\alpha_2^2 \rho_n b_2}{\sigma_n^3} \right\} \quad (12)$$

$N_k$  is a scaling parameter and the virial integral terms  $J$  and  $J'$  are defined as [48],

$$J = \frac{1}{12\pi} \left\{ \alpha_0^2 \sum_{k=1}^2 \rho_k z_k N_k - 4\alpha_0 \alpha_2 \rho_n B^{10} - \frac{6\alpha_2^2 \rho_n b_2}{\sigma_n^3} \right\} \quad (13)$$

$$J' = \frac{\pi}{3} \sum_i \sum_j \rho_i \rho_j \sigma_{ij} \left\{ \sum_{mnl} \frac{(-1)^l}{2l+1} [g_{ij}^{mnl}(\sigma_{ij})]^2 - [g_{ij}^{hs}(\sigma_{ij})]^2 \right\} \quad (14)$$

where  $\alpha_0$  and  $\alpha_2$  are the ion-ion coupling and dipole-dipole strength parameters. The parameters  $B^{10}$  and  $b_2$  corresponds to the ion-dipole and dipole-dipole interactions respectively, and are obtained from the solution of the Ornstein-Zernike equation given by Wei and Blum [47].  $\rho_n$  and  $\sigma_n$  are the density and segment diameter of the dipolar solvent species present in the solution.  $g_{ij}^{mnl}(\sigma_{ij})$  are the contact values of the radial distribution function (RDF) invariant expansion coefficients and  $g_{ij}^{hs}(\sigma_{ij})$  is the hard-sphere contact value. As in earlier work, the dielectric constant of the solution is obtained as

$$\epsilon_A = 1 + \frac{\rho_n \alpha_2^2 \beta_6^2 (1 + \lambda)^4}{16} \quad (15)$$

from the work of Wei et al. [46], where  $\alpha_2^2 = 4\pi\beta\mu^2/3$ ,  $\lambda = \beta_3/\beta_6$ ,  $\beta_3 = 1 + b_2/3$  and  $\beta_6 = 1 - b_2/3$ . We note that the solution of the Ornstein-Zernike equation with the NPMSA closure proposed by Blum et al. [47] is only applicable to ions of arbitrary sizes in a pure dipolar solvent i.e., it does not account for ions of arbitrary size in a solvent composed of more than one type of dipolar species. This limitation to the application of the NPMSA to the study of mixed dipolar solvent electrolytes was overcome in our previous work [43] through the consideration of a one-fluid-like approximation in the theoretical formulation of the ion-dipole and dipole-dipole terms for which an effective segment diameter ( $\sigma_{eff}$ ) and dipole moment ( $\mu_{eff}$ ) was defined. The same approach has been used in this work.

Finally, the Helmholtz free energy contribution due to the formation of a chain containing homogeneous monomeric segments is given by,



**Table 1**

SAFT-VR+D parameters for water, alcohols and the percentage average absolute deviation in vapor pressure (%AAD  $p$ ) and saturated liquid densities (%AAD  $\rho_{liq}$ ) as compared to experimental data.

	$\mu$ (D)	$\sigma$ (Å)	$\epsilon/k_b$ (K)	$\lambda$	$m$	$\epsilon^{HB}/k_b$ (K)	$K^{HB}$ (Å <sup>3</sup> )	%AAD $p$	%AAD $\rho_{liq}$
H <sub>2</sub> O	2.179	3.003	312.36	1.52956	1	758.5521	1.5	1.49	2.43
CH <sub>3</sub> OH	2.730	3.5396	162.17	1.72229	1.2	1800.945	0.81	1.305	0.082
C <sub>2</sub> H <sub>5</sub> OH	3.370	3.728	252.71	1.445	1.5333	2030.0	2.0561	0.474	0.298

$$\frac{A_{chain}}{Nk_bT} = \sum_{i=1}^{n_{solvent}} x_i(1 - m_i) \ln y_{ii}^M(\sigma_{ii}) \quad (16)$$

where, the sum is over all solvent species in the mixture and  $y^M$  is the monomer background correlation function given by,  $y_{ii}^M = \exp(-u_{ij}/k_bT)g_{ii}^M(\sigma_{ii})$ .  $g^M$  represents the contact value of the radial distribution function (RDF) of the dipolar square-well (DSW) monomer segments. Since the Boltzmann factor ( $\exp(-u_{ij}/k_bT)$ ) is independent of density it will not affect the determination of phase equilibria and hence can be ignored without loss of generality [49]. The RDF at contact thus becomes [43,50],

$$g^{DSW}(r\omega_1\omega_1; \rho, T) = g^{SW}(r; \rho, T) \left(1 + g^D(\omega_1\omega_1; \rho, T)\right) \quad (17)$$

where,  $\omega_i$  represents vector angles defining the orientation of the dipole moment in a monomer  $i$ .

### 3. Results & discussion

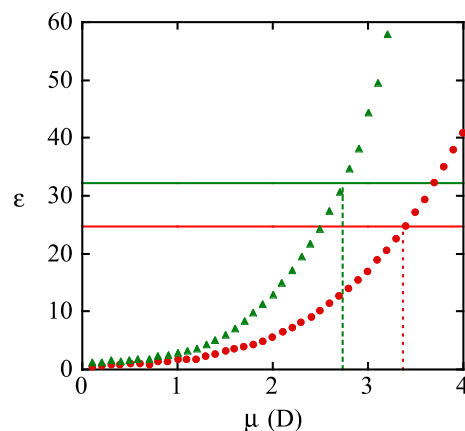
#### 3.1. Pure fluids

Water molecules are modeled as dipolar square-well dispersive hard spheres with four short-range attractive square-well sites describing the association interactions, which mimic hydrogen bonding. The four association sites are of two distinctly different types, with two representing hydrogen atoms and two representing the lone pairs of electrons on the oxygen atom. The SAFT-VR+D [51] parameters for water used here were developed in previous work [42]. Briefly, the hard-core diameter ( $\sigma$ ), square-well potential depth ( $\epsilon$ ), range ( $\lambda$ ), association energy ( $\epsilon^{HB}$ ), and bonding volume ( $\kappa^{HB}$ ) of water were obtained by fitting to experimental vapor pressure and saturated liquid densities using an effective dipole moment of 2.18 D. As discussed in our previous work [42], the effective dipole moment captures the effect of the dipole moment and the polarizability induced by neighboring water molecules. The value used is therefore lower than the typically reported values, since the dispersion energy parameter also partially take into account induced polarizability effects. The SAFT-VR+D approach was found to provide an excellent correlation of the pure water vapor pressure and saturated liquid densities. The SAFT-VR+D parameters used along with the percentage (%) average absolute deviations (AAD) in vapor pressure and saturated liquid densities of water are reported for completeness in Table 1.

The alcohol molecules are described as dipolar square-well chain fluids, again with association sites to capture hydrogen bonding. The association sites of primary alcohols can be described with both 2-site and 3-site association schemes. Gross and Sadowski [52] described primary alcohols with a 2-site association scheme and commented that use of either the 2 or 3-site model provides similar results for phase behavior of pure fluids. Karakatsani and Economou [53] treated primary alcohols with a 2-site scheme and noted that the association scheme effectively captures the experimentally observed linear oligomer formation of heavier alcohols. Kontogeorgis et al. [54] compared three equation of states: cubic-plus-

association (CPA) [55], simplified-PC-SAFT (sPC-SAFT) [56] and non-random hydrogen bonding (NRHB) [57] in a study of the association behavior of alcohols and concluded that methanol is best represented by a 3 site association scheme; however, for ethanol and heavier alcohols the 2 site model provided slightly better results. Hence, a 3-site associating model for methanol and 2-site associating model for ethanol have been employed in this work.

Similar to the treatment of water in previous work [42], a condensed phase effective dipole moment for methanol and ethanol has been used, rather than the gas phase dipole moment (~1.7 D). In the condensed phase, the dipole moment for polar fluids is in general higher than the gas phase isolated molecule dipole moment [58]. The effective dipole moment for methanol and ethanol were obtained by varying the dipole moment as a model parameter and examining the effect on the calculated dielectric constant at room temperature and pressure. As can be seen from Fig. 2, a dipole moment for methanol and ethanol corresponding to 2.73 D and 3.35D respectively, provide a good representation of the liquid phase dielectric constant at room temperature and pressure and so were used in this work. In the SAFT-VR+D framework, associating dipolar chain molecules like alcohols are characterized by a hard-core diameter ( $\sigma$ ), a square-well potential depth ( $\epsilon$ ) and range ( $\lambda$ ), a number of segments per chain ( $m$ ), and the association energy ( $\epsilon_{HB}$ ) and bonding volume ( $\kappa_{HB}$ ). The number of segments per chain ( $m$ ) for each alcohol, has been calculated using the previously developed empirical relationship proposed by Garcia-Lisbona et al. [59] for which  $m = 0.33(C - 1) + 1.2$ . The rest of the SAFT-VR+D parameters were obtained by fitting to experimental vapor pressure and saturated liquid density data between 220 and 475 K for methanol and 215–465 K for ethanol [60]. Experimental data close to the critical region (around 10%) were excluded from the fitting procedure, as SAFT-VR+D like other analytical equation of state



**Fig. 2.** Change in the dielectric constant  $\epsilon$  as a function of dipole moment  $\mu$  for alcohols as predicted by the SAFT-VR+D equation of state at room temperature (298.15 K) and pressure (0.101325 MPa). Solid line represents the experimental dielectric constant for methanol (green) and ethanol (red) at 298.15 K and 0.101325 MPa [65,66], while the dotted lines represent the dipole moments that correspond to the experimental dielectric constant at room temperature. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

exhibits classical critical behavior in the critical region and so over predicts the critical point [61]. Additionally data points near the triple point were also excluded since it has been shown that inclusion of such data can distort the results [62]. Simulated annealing [63,64] was used to fit the model parameters with an objective function defined as a function of vapor pressure and saturated liquid density as given in appendix. The resulting parameters along with the %AAD in pressure and saturated liquid densities are reported in Table 1, and as can be seen from Fig. 3, the theory provides a good representation of the experimental phase data for pure methanol and ethanol.

### 3.2. Water-alcohols mixture phase behavior

We first consider the phase behavior of the binary methanol + water and ethanol + water mixtures to examine the prediction of the binary mixtures before studying salt containing ternary systems. Fig. 4 presents the SAFT-VR+D predictions for the  $P$ - $x$  projection of the  $PTx$  surface for the alcohol-water mixtures over a range of different temperatures. As can be seen from Fig. 4a, the predictions using Lorentz-Berthelot combining rules for methanol-water system are in excellent agreement with the experimental phase behavior data [67] at room temperature (298.15 K) as well as at elevated temperatures of 313.15, 323.15 and 333.15 K. However, in the ethanol-water system, with the Lorentz-Berthelot combining rules the theory fails to predict the constant temperature  $P$ - $x$  phase envelope, suggesting the inclusion of association and dipole interactions alone is not sufficient to capture the molecular interactions, and polarizability effects may be important. An unlike cross-dispersion energy parameter ( $\xi=1.2$ ) obtained by fitting to experimental binary phase equilibrium  $P$ - $x$  data [68] at 298.15 K is found to correct this behavior and is transferrable to the higher temperatures studied. In Fig. 4b,  $P$ - $x$  phase diagrams of water-ethanol mixture correlated at 298.15 K and predicted at higher temperatures using the SAFT-VR+D equation is presented and compared to the experimental data.

In previous work [42], it was discussed how important it is to capture the dielectric behavior of a solution in order to obtain an accurate estimation of the thermodynamic properties of electrolytes. As can be seen in Fig. 5, using condensed phase dipole moments, the theory accurately predicts the dielectric behavior of the water/alcohol mixtures over the entire range of mixture composition. As temperature increases we note that the theory

tends to under predict the solution dielectric constant, especially near the pure water limit as observed in previous work [42].

### 3.3. Mixed-solvent electrolytes

In previous work, two sets of ion parameters, salt independent ionic radii and salt dependent cation-water dispersion interaction energy parameters, were developed in the study of aqueous alkali halide salt solutions [42]. The cation-solvent (water) binary dispersion interaction energy ( $\epsilon_{\text{cation-H}_2\text{O}}$ ) parameter was obtained by fitting to experimental mean ionic activity coefficient data for nineteen different alkali-halide aqueous solution at 298.15 K and 1.01325 bar. The dispersive square-well interaction range ( $\lambda$ ) for the cations was fixed at 1.2 and the Lorentz-Berthelot combining rule was used to determine the cross-interaction range parameters between the cations and solvent water molecules. The ionic radii for the cations  $\text{K}^+$ ,  $\text{Cs}^+$ ,  $\text{Rb}^+$  were taken from the work of Mähler et al. [69], corresponding to the appropriate coordination number, and for the anions ( $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ) from the work of Shannon [70,71]. Ions with smaller radii and higher charge densities, such as  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{F}^-$ , are often referred to as net structure makers, as these ions distort the water structure beyond the first water shell [72,73]. The greater solvation influence of these ions on the surrounding water molecules resulted in the need to determine salt independent ionic radii by fitting to the mean ionic activity coefficient data at 298.15 K and 1.01325 bar. The same set of ionic radii for both cations and anions reported in previous work [42] has been used here to describe the water and ion interactions.

In a mixed-solvent electrolyte solution, the dispersive interaction acts between three kinds of compounds: water, alcohol and salt. Among these the salt (cation)-water and water-alcohol cross-dispersive interaction energy parameters are taken from the binary data of aqueous electrolytes and water-alcohol mixtures, respectively [42]. However, a new salt (cation/anion)-alcohol cross energy parameter is needed to capture the nature of the remaining dispersive interactions. This unlike-cross-interaction energy parameter can be obtained in two ways: by fitting to alcohol-salt binary mean ionic activity coefficient data or by fitting to ternary salt/water/alcohol mean ionic activity coefficient data. Unfortunately, mean ionic activity coefficient data for binary mixtures of alcohol-salt are available for only a few systems, while experimental studies for a number of ternary systems have been reported, and thus ternary data were used. To decide upon which set of data

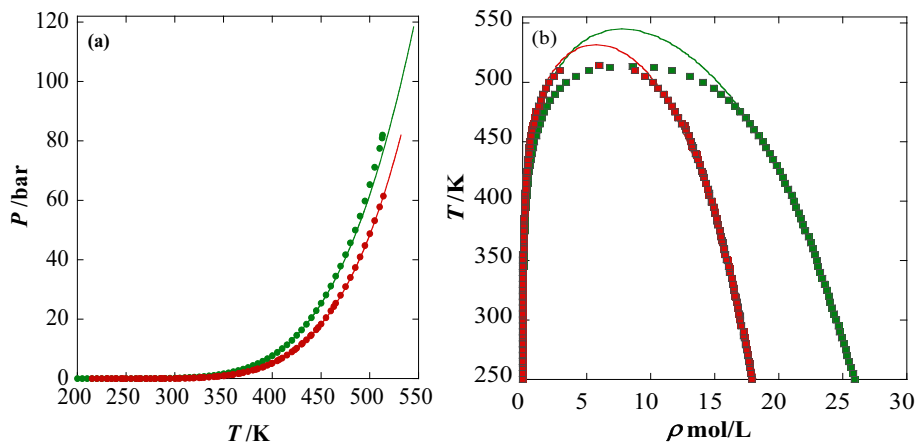
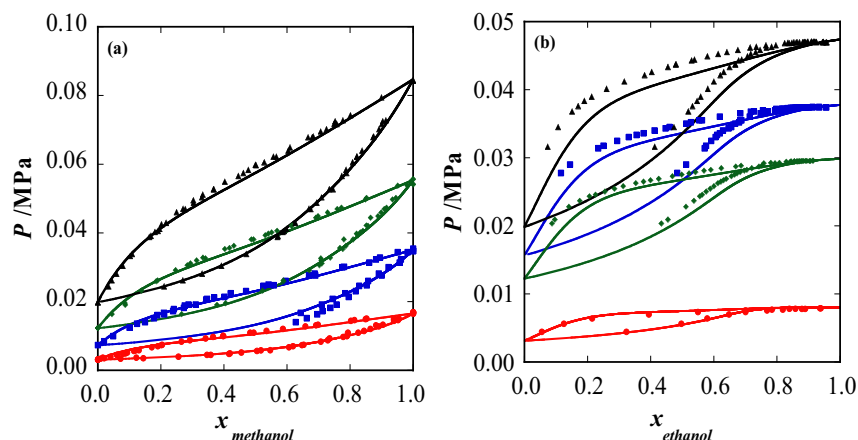


Fig. 3. Comparison of (a) vapor pressure and (b) vapor-liquid coexisting densities for methanol (green) and ethanol (red) from the SAFT-VR+D equation of state and experiment. Symbols represent the experimental data [60] and the theory is represented by the solid lines. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)



**Fig. 4.** Vapor–liquid equilibria for binary mixtures of alcohol + water. (a) methanol + water binary mixture at 298.15 K (red), 313.15 K (blue), 323.15 K (green), 333.15 K (black). (b) ethanol + water at 298.15 K (red), 323.15 K (blue), 328.15 K (green), 333.15 K (black). The solid lines correspond to the theoretical predictions from the SAFT-VR+D approach and the symbols to the experimental data [67,68]. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

to use for parameter optimization (i.e., water-rich or alcohol-rich) and which dispersion energy parameters to fit (i.e., cation-alcohol and/or anion-alcohol) understanding the relative interactions of electrolytes with solvents is necessary. Experimental NMR studies [74] and molecular dynamics (MD) computer simulations [75] of alkali halide + methanol + water systems have indicated preferential solvation of ions within the mixed solvent. Preferential solvation is defined in terms of the local composition of solvent species around the solute electrolytes. These studies concluded that cations of alkali halide salts show preferential hydration even in water-lean (alcohol-rich) solution if a sufficient number of water molecules are present, whereas anions are selectively solvated by alcohol molecules. Based upon this observation, the cation-alcohol dispersive interaction will be screened by water molecules, present in the hydration shell of the cation even in water-lean solutions. Since the one-fluid approximation is used within the proposed theoretical approach, the screened interaction between the cations and alcohol molecules cannot be appropriately captured by the ion-dipole electrostatic interaction term. Therefore a cation-alcohol cross dispersive energy parameter ( $\epsilon_{\text{cation-alcohol}}$ ) has been used

and obtained by fitting to experimental mean ionic activity coefficient data corresponding to the highest available weight fraction of water within a given mixed-solvent electrolyte solution. It was observed during the fitting procedure that the anion-solvent dispersion energy has a weaker influence on the mean ionic activity coefficient data, which is consistent with our previous SAFT-VR+DE study of aqueous electrolyte systems [42] and hence no anion-solvent dispersion interactions are considered. The cross-interaction range parameters between the cations and solvent alcohol molecules were obtained using Lorentz-Berthelot like combining rule given by equation (4), i.e.,

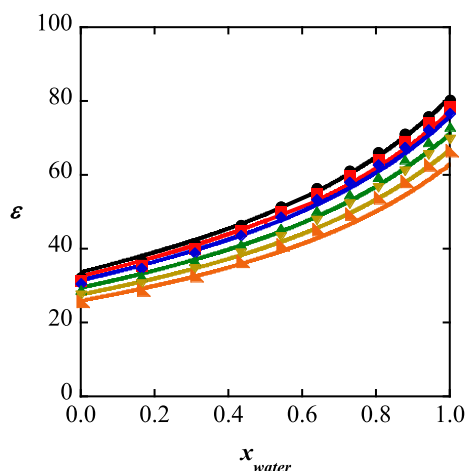
$$\lambda^{\text{cation-alcohol}} = \frac{\sigma^{\text{cation}} \lambda^{\text{cation}} + \sigma^{\text{alcohol}} \lambda^{\text{alcohol}}}{\sigma^{\text{cation}} + \sigma^{\text{alcohol}}} \quad (18)$$

The binary salt-specific cation-alcohol dispersion interaction parameters obtained from fitting to experimental mean ionic activity coefficient data of different mixed-solvent electrolyte solutions at 298.15 K and 1.01325 bar along with percentage average absolute deviations (% AAD) are reported in Table 2. Simulated annealing [63,64] was again used in the fitting process. Table 2 also contains the average absolute deviations from the experimental data for each system studied. In general, values of the  $\epsilon_{\text{cation-alcohol}}$  indicate that cations with smaller radii and higher charge densities, such as  $\text{Li}^+$ ,  $\text{Na}^+$  exhibit higher induced ordering effects on the surrounding water molecules compared to larger cations such as  $\text{Cs}^+$ , as values of the cation-solvent dispersive energy parameters are relatively higher.

We now consider the prediction of the mean ionic activity coefficients of several mixed-solvent electrolyte systems over a wide range of ionic and solvent compositions using the cation-alcohol dispersive energy parameters reported in Table 2.

### 3.4. RbCl/water/methanol

The SAFT-VR+DE approach with the one-fluid-like approximation gives a good description of the experimental mean ionic activity coefficient data [76] for the ternary mixture of RbCl + water + methanol at 20 and 40 wt % of alcohol at 298.15 K and 1.01325 bar as presented in Fig. 6. Using the cation-alcohol dispersive interaction energy parameter fitted at 20 wt %, the mean ionic activity coefficient of the ternary solution is then predicted at the higher alcohol concentration. The theory predicts the trend in the experimental data well at 40-wt % of alcohol, especially



**Fig. 5.** Dielectric constant of salt free methanol + water mixture at 293.15 K (black), 298.15 K (red), 303.15 K (blue), 313.15 K (green), 323.15 K (yellow), 333.15 K (orange). The solid lines correspond to the theoretical predictions from the SAFT-VR+D approach and the symbols to the experimental data [65]. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

**Table 2**

Salt specific dispersion energy parameters for the cation-alcohol ( $\epsilon_{\text{cation-alcohol}}$ ) interaction for the different mixed-solvent electrolytes studied and the percentage average absolute deviation for the mean ionic activity coefficient (% AAD  $\gamma_{\pm}$ ) obtained using the SAFT-VR+DE approach as compared to experimental data at 298.15 K and 1.01325 bar.

System	Alcohol weight fraction (wt %)	$\epsilon_{\text{cation-alcohol}}$	% AAD $\gamma_{\pm}$
CsCl/water/ethanol	10%	344.39	2.95
NaBr/water/ethanol	10%	2512.74	4.53
NaF/water/ethanol	10%	1923.89	2.77
CsCl/water/methanol	10%	894.87	1.40
KCl/water/methanol	20%	2052.31	1.65
LiCl/water/methanol	10%	2349.11	5.37
NaBr/water/methanol	10%	1915.47	3.11
NaCl/water/methanol	20%	2359.89	4.29
RbCl/water/methanol	20%	1080.15	2.92

at lower ionic concentrations where the bulk of the experimental data is available as can be seen in Fig. 6. The experimental results show a gradual decrease in mean ionic activity coefficient with the increase in alcohol concentration. Moreover, the theory predicts the existence of a minima in the mean ionic activity coefficient at a higher salt concentration. The increase in alcohol concentration decreases the overall solution dielectric constant, as seen earlier in Fig. 5, and subsequently the ions move into the water rich phase of the solution. The theory captures this phenomenon well with 2.92% and 7.49% in deviations of the mean ionic activity at 20 and 40 alcohol weight fraction, respectively. However, some deviations in the theoretical prediction are seen at higher salt concentrations near the saturation limit. These values are reported in table A1 of the appendix for the RbCl-water-methanol system.

### 3.5. CsCl/water/alcohol system

Considering systems containing CsCl, water, and alcohol (ethanol or methanol), the theory provides a good correlation of the experimental data [77] (1.40 and 2.95% AAD respectively) at 298.15 K, 1.01325 bar and 10 wt % of alcohol, as can be seen from Fig. 7. Using the fitted cation-alcohol unlike dispersive energy parameter, mean ionic activity coefficients at higher weight fractions up to 40% of alcohol are then predicted. As can be seen from Fig. 7, the theory gives a good qualitative as well as quantitative representation of the experimental data for most weight fractions of alcohol. With increasing alcohol weight fraction in solution, the

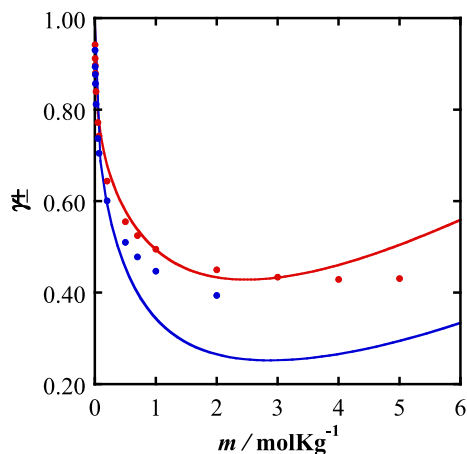
experimental mean ionic activity coefficient decreases, which is captured by the theoretical predictions. The predicted SAFT-VR+DE results are within approximately a 7% deviation of the experimental data for all weight percentages of alcohols studied except at 40 wt %, for which the SAFT-VR+DE equation over predicts the mean ionic activity coefficient for both methanol and ethanol based mixed-solvent electrolyte systems, although in general the theory tends to under predict the experimental results. This inconsistency could be due to a failure in the theory or errors present in the experimental data.

### 3.6. KCl/water/methanol

Experimental data [76] for the mean ionic activity coefficient data of KCl mixed-solvent systems are available for three alcohol weight fractions: 20%, 40% and 60%. The cation-alcohol dispersive interaction parameter was obtained by fitting to the lowest available weight fraction of alcohol (i.e. 20%). The SAFT-VR+DE equation provides a good correlation of the mean ionic activity at 298.15 K, 1.01325 bar and 20 wt % of alcohol with 1.65% AAD as can be seen in Fig. 8. At higher alcohol weight fractions the theory gives a good prediction of the experimental data, particularly at dilute salt concentrations where most of the experimental data exists. However, we note that the theoretical predictions show some deviations from experimental data near the saturation limit. The theoretical predictions for 40% and 60% weight fractions of alcohol give an average deviation of 3.4 and 7.6% respectively.

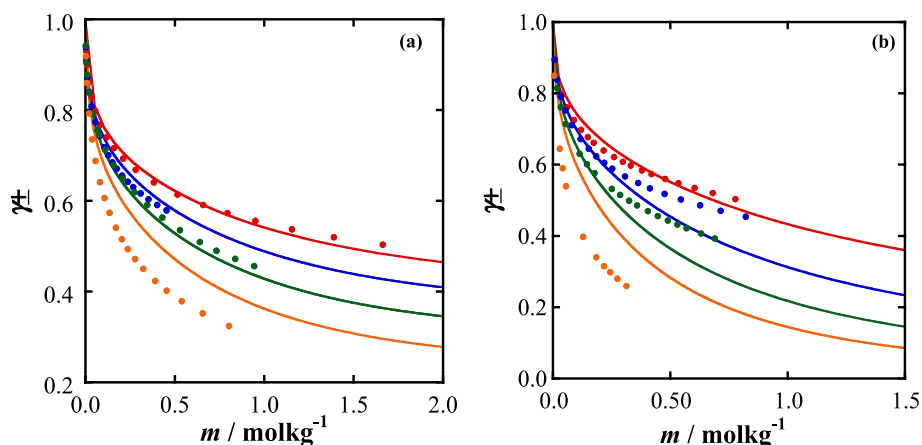
### 3.7. NaF/water/ethanol

We now consider the mixed-solvent solutions with NaF. The main difference between this system and the previously studied ones is the nature of ionic radii used for the  $\text{Na}^+$  and  $\text{F}^-$  ions. In previous work [42], an effective ionic radii for  $\text{Na}^+$  and  $\text{F}^-$  ions was proposed based upon each ions structure making/breaking effects in water; here we test how transferable these effective ionic radii are to mixed-solvent electrolyte systems in which additional interactions are present. Moreover, the introduction of alcohol into water has been shown to distort the existing solvent structure [78] and as such might have an effect on the transferability of the parameters. As can be seen from Fig. 9, the theory is able to both accurately correlate at 10 wt % of alcohol (with an average deviation of 2.85%) system and predict the experimental [79] mean ionic activity coefficient at 20–80% weight fractions of ethanol. Even at higher alcohol concentration (80 wt % of alcohol), the theory gives an accurate prediction with %AAD of 4.2, demonstrating the good transferability of the effective parameters. In the case of NaF, the experimental data is available only for dilute salt concentrations, less than  $0.2m$ , where even at high alcohol concentrations enough water molecules are present to form multiple shells to solvate the



**Fig. 6.** Mean ionic activity coefficients of RbCl in water/methanol mixtures at 298.15 K and 1.01325 bar with salt-free alcohol weight fractions at 20% (red) and 40% (blue). The symbols represent experimental data [76] and solid lines are theoretical correlations/predictions by the SAFT-VR+DE equation. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)





**Fig. 7.** Mean ionic activity coefficients of CsCl in water + (a) methanol and (b) ethanol mixtures at 298.15 K and 1.01325 bar with salt-free alcohol weight fractions at 10% (red), 20% (blue), 30% (green), 40% (orange). The symbols represent experimental data [77] and solid lines are theoretical correlations/predictions by the SAFT-VR+DE equation. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

$\text{Na}^+$  and  $\text{F}^-$  ions. This allows the effective ionic radii of Na developed by fitting to the experimental binary aqueous electrolyte solution data to work well.

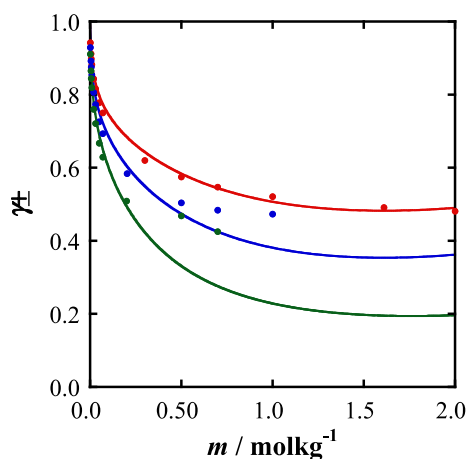
### 3.8. LiCl/water/methanol

In the case of LiCl, an effective ionic radii for  $\text{Li}^+$  ion was also defined in previous work [42] as it is a structure making/breaking ion. As can be seen from Fig. 10, the SAFT-VR+DE theoretical approach is able to give a good correlation of the mean ionic activity coefficient at 10 wt% of alcohol with 5.3% average deviation. In predicting the mean ionic activity coefficients at higher weight fraction of alcohol in solution, the theory shows the correct experimental trend, with the mean ionic activity coefficient decreasing with increasing alcohol fraction in solution. Although the data is very limited, we note that the theory predicts the mean ionic activity coefficient well, with an average deviation of ~8% at 20 wt % of alcohol. The fitted cation-alcohol unlike dispersive energy parameter demonstrates transferability, as it gives a good

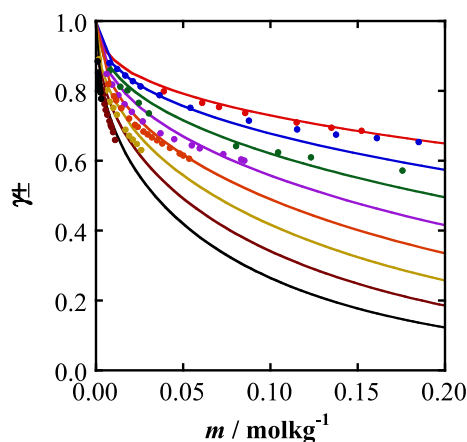
theoretical representation of the activity coefficient even at high (8 m) ionic concentration. The use of the effective ionic radii for the  $\text{Li}^+$  ion obtained from the binary aqueous solution works well for the mixed-solvent LiCl + water + methanol system, especially in the water rich solutions (10% and 20%), as there are enough water molecules present to form multiple solvation shells around the Li cation.

### 3.9. NaCl/water/methanol

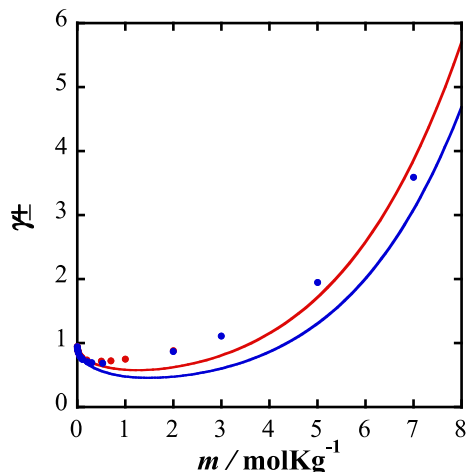
We now turn to the mean ionic activity coefficient of the NaCl + water + methanol mixture. From Fig. 11, it can be seen that although the theory gives a good correlation of the experimental mean ionic activity coefficient data [80] at 20% weight fraction of alcohol with an average deviation of 4.3% it fails to give an accurate quantitative prediction at higher weight fractions of alcohol and ionic concentrations. This is due to the use of an effective ionic radii for  $\text{Na}^+$  that was obtained by fitting to the water-Na-halide systems, where the cation has a greater influence on the solvent species. This results in a larger dielectric decrement at higher alcohol



**Fig. 8.** Mean ionic activity coefficients of KCl in water/methanol mixtures at 298.15 K and 1.01325 bar with salt-free alcohol weight fractions at 20% (red), 40% (blue), 60% (green). The symbols represent experimental data [76] and solid lines are theoretical correlations/predictions by the SAFT-VR+DE equation. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)



**Fig. 9.** Mean ionic activity coefficients of NaF in water/ethanol mixtures at 298.15 K and 1.01325 bar with salt-free alcohol weight fractions at 10% (red), 20% (blue), 30% (green), 40% (orange), 50% (purple), 60% (yellow), 70% (brown), 80% (black). The symbols represent experimental data [79] and solid lines are theoretical correlations/predictions by the SAFT-VR+DE equation. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

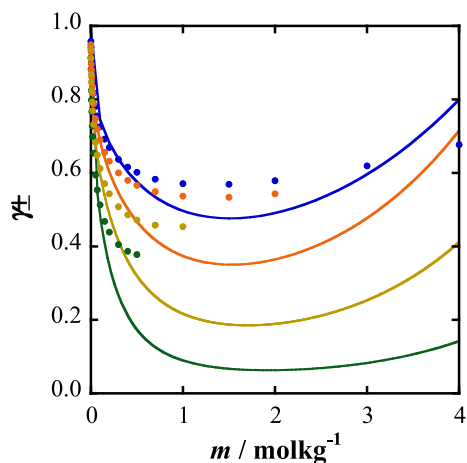


**Fig. 10.** Mean ionic activity coefficients of LiCl in water/methanol mixtures at 298.15 K and 1.01325 bar with salt-free alcohol weight fractions at 10% (red), 20% (blue). The symbols represent experimental data [76] and solid lines are theoretical correlations/predictions by the SAFT-VR+DE equation. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

concentrations and the under prediction of the activity coefficient. This influence of the effective radii on the mean ionic activity coefficient was not observed in the previously discussed LiCl and NaF salt systems, as the bulk of the experimental data for these systems is available only at low alcohol concentrations. At a higher salt concentration and higher alcohol fraction for the NaCl solution, there is a smaller (in some cases only trace amount) number of water molecules available to form multiple shells around the cation. Other Na ion containing systems are now investigated to determine whether the trend of under predicting the mean ionic activity coefficient with increasing salt and alcohol fraction in solution exists for all Na based systems.

### 3.10. NaBr/water/alcohol

In the study of NaBr + water + alcohol (methanol/ethanol) mixture system although the theory gives a good correlation at



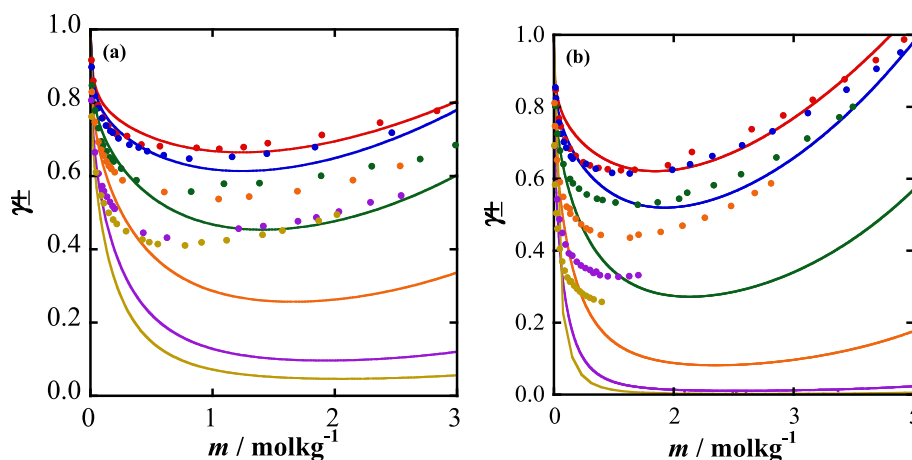
**Fig. 11.** Mean ionic activity coefficients of NaCl in water/methanol mixtures at 298.15 K and 1.01325 bar with salt-free alcohol weight fractions at 20% (blue), 40% (orange), 60% (yellow), 80% (green). The symbols represent experimental data [80] and solid lines are theoretical correlations/predictions by SAFT-VR+DE. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

10 wt % of alcohol (average deviations of 4.53% and 3.11% for ethanol and methanol containing systems respectively), it however fails to provide an accurate quantitative prediction of the mean ionic activity coefficient at higher concentrations of alcohol in solution, as can be observed from Fig. 12a and b for the methanol and ethanol systems, respectively.

Again the theory fails to accurately capture the influence of the cations on the surrounding alcohol molecules, which results in a substantial under prediction of the mean ionic activity coefficient. From Table 1A, it can be concluded that only the NaBr + water + alcohol systems show a substantial deviation from experimental mean ionic activity coefficient data compared to other systems, and in particular at higher alcohol content of the solution. The concept of ionic radius in electrolyte solutions is very fundamental in describing the ion-dipolar solvent interactions. The effective ionic radius used for Na<sup>+</sup> was obtained by fitting to experimental mean ionic activity coefficient data for binary Na-halide + water systems. The revised ionic radius used in prior work [42] was incorporated in order to capture the structure-making or breaking property of the Na ion in water. But with increasing alcohol concentrations in the system, the solvent structure changes and thus the ionic effect on the surrounding solvent molecule changes; especially in alcohol rich solutions. In the work of Abraham et al. [82] it is discussed that Na<sup>+</sup> is a net structure-making ion in any solvent, be it alcohol or water; the Na ion influences the surrounding alcohol molecules and creates a different structure compared to the water solution. The effective radius of Na<sup>+</sup> in alcohol should therefore be different to that used previously in the presence of water. An effective system specific ionic radius for Na<sup>+</sup> in alcohol systems has therefore been obtained by fitting to experimental mean ionic activity data at the highest available weight fraction of alcohol (i.e., 90 wt%). The effective ionic radii of Na<sup>+</sup> in methanol and ethanol are  $\sigma_{Na}^{90\%methanol} = 3.18$  and  $\sigma_{Na}^{90\%ethanol} = 3.52$ , respectively. The effective radii of Na<sup>+</sup> obtained for the alcohol systems is bigger than the one obtained in previous work for the water system [42]. This size difference could be due to the larger size of the surrounding alcohol molecules. This would also explain the larger value of the effective ionic radius of the Na<sup>+</sup> ion in ethanol compared to the radius in methanol. To consider the change in alcohol weight fraction in solution, the effective ionic radii of Na<sup>+</sup> also has been adjusted using the following expression,

$$\sigma_{Na}^{alcohol} = \sigma_{Na}^{0\%alcohol} + \frac{\sigma_{Na}^{90\%alcohol} - \sigma_{Na}^{0\%alcohol}}{90 - 0} \quad (19)$$

Fig. 13 presents the mean ionic activity coefficients using the revised Na<sup>+</sup> effective ionic radius for the NaBr + water + alcohol systems and the corresponding % AAD  $\gamma_{\pm}$  values are presented in Table 2A. As can be seen from the figure, an improvement in the theoretical representation of the mean ionic activity coefficient at higher alcohol weight fractions is observed. From Fig. 13a, we note that although the theory shows an improvement for 90 and 80 wt % of methanol, at the lower weight % system (i.e., 60 wt % methanol) the theory predicts the experimental data quantitatively only at very low concentrations of NaBr. This may be caused by the presence of enough water molecules in the vicinity of the ion, which preferably form a shell around the Na<sup>+</sup> ion instead of alcohol molecules, thus the ionic radius of Na<sup>+</sup> does not increase as much as given by equation (19). A similar explanation holds for the NaBr + ethanol + water system as presented in Fig. 13b. Perhaps it can be inferred that the estimation of mean ionic activity is very sensitive to the cation-solvent interaction, and particularly for cations with high charge density where the ionic radius plays a critical role in the arrangement of the surrounding solvent



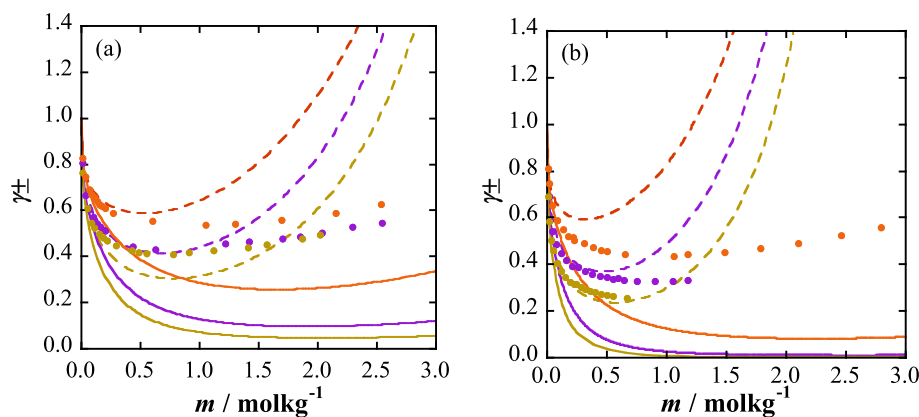
**Fig. 12.** Mean ionic activity coefficients of NaBr in water/(a) methanol and (b) ethanol mixtures at 298.15 K and 1.01325 bar with salt-free alcohol weight fractions at 10% (red), 20% (blue), 40% (green), 60% (orange), 80% (purple), 90% (yellow). The symbols represent experimental data [81] and solid lines are theoretical correlations/predictions by the SAFT-VR+DE equation. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

molecules. The use of a correct effective ionic radii based upon solvent compositions is therefore key for the accurate representation of thermodynamic properties, such as the activity coefficient. For the NaBr + alcohol + water systems presented in this study,  $\sigma_{Na}^{0\%alcohol}$  can be used up to 20 wt % of alcohol and there after a solvent composition based fitted effective radius is preferable in order to obtain an accurate quantitative representation of the experimental mean ionic activity coefficient data.

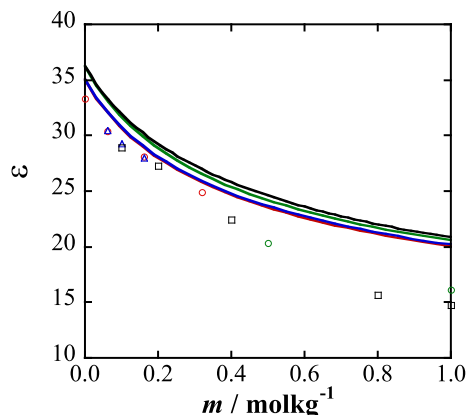
### 3.11. Dielectric decrement of non-aqueous solvent in the presence of salt

Finally, the effect of salt concentration on the solution dielectric constant has been investigated. The presence of an ionic species in the dielectric medium decreases the static permittivity as it restricts the free rotation of water/solvent molecules occupying the hydration shell [83–86]. In the primitive model, the theory cannot capture this phenomena as the dielectric constant is a required input and hence data for pure salt-free solvent (alcohol in this case) is used. However, the

non-primitive model provides the opportunity to capture the salt effect on the solution dielectric constant as it can be computed directly from the ion-dipolar interaction term that is embedded in the theoretical framework (equation (15)). Moreover, this provides a test of the theoretical accuracy in capturing the ion-dipolar interactions. While experimental data on the dielectric decrement of mixed-solvent systems in the presence of salt are not available to our best of knowledge, experimental dielectric constant data for several salt + alcohol systems is available and has been compared to the predictions from the SAFT-VR+DE approach. In Fig. 14, a comparison between theoretical and experimental [87,88] dielectric constant data for three different electrolyte systems, LiCl + methanol (20 and 25 °C), NaCl + methanol (25 °C) and NaBr + methanol (20 °C), are presented. From the figure, we note that the SAFT-VR+DE theoretical framework is able to predict the decrement in dielectric constant with increasing salt concentrations and quantitatively agrees with experimental data at lower concentrations. In particular, at 25 °C, the theory is able to accurately predict the dielectric constants of LiCl and NaCl + methanol systems over the entire range of available experimental data;



**Fig. 13.** Mean ionic activity coefficients of NaBr in water for (a) methanol and (b) ethanol mixtures at 298.15 K and 1.01325 bar with salt-free alcohol weight fractions at 60% (orange), 80% (purple), 90% (yellow). The symbols represent experimental data [81], solid lines are theoretical predictions by the SAFT-VR+DE equation using the original Na ionic radius and dashed lines represent theoretical predictions (orange and purple dashed lines)/correlations (yellow dashed line) using the revised Na ionic radius. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)



**Fig. 14.** Salt effect on the dielectric constant of methanol at 20 and 25 °C as predicted by the SAFT-VR+DE equation. Symbols represent experimental data [87,88]: LiCl at 25 °C (red circles), LiCl at 20 °C (green diamonds), NaCl at 25 °C (blue triangles) and NaBr at 20 °C (black squares). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

however, the SAFT-VR+DE prediction of the dielectric constant deviates from the experimental data at higher salt concentrations (where data is available). This might be due to inaccuracy in experimental measurement [87], which contains an error margin of  $\pm 1.5D$ . Overall, the theory is able to provide a realistic representation of the dielectric decrement of methanol in the presence of salt.

#### 4. Conclusion

The SAFT-VR+DE approach with a one-fluid-like approximation has been used to study experimental mixed-solvent electrolyte systems ranging across different ionic concentrations and solvent compositions. As such, a non-primitive model based equation of state has been used for the first time to study mixed-solvent electrolyte systems. The solvent molecules are modeled as dipolar square-well dispersive chains and spheres with association sites for the representation of alcohol and water molecules respectively. The SAFT-VR+D theoretical framework is found to be able to capture the vapor-liquid equilibrium behavior of the solvent methanol-water system from ambient temperature to 333.15 K as well as the composition dependent dielectric constant without fitting to experimental mixture data. However, for the ethanol-water system a binary unlike dispersive interaction energy parameter is needed for the accurate representation of the phase behavior. For, alcohol-water-salt systems, a predictive approach has been taken; based upon a single alcohol-salt fitted parameter obtained from ternary mean ionic activity coefficient data, mean ionic activity coefficients of nine different electrolyte systems have been predicted. The theory in general provides a good qualitative representation of the experimental data for most of the systems but lacks quantitative accuracy in some cases. Since the main objective of this work is to determine the predictive ability of the non-primitive model based SAFT-VR+DE theory, a minimum number of fitted model parameters for real electrolyte systems was used and less emphasis given to quantitative accuracy. Using this approach, it is observed that in order to achieve a good quantitative description of the experimental data, the effect of the ions on the surrounding solvent molecules needs to be accurately captured, especially for ions with small radii and high charge density. In the case of NaBr based ternary systems, the use of an effective ionic radii for the Na cation, which was fitted to Na-halide + water-based mean ionic activity data, fails to provide a good quantitative agreement with

experimental data at higher alcohol weight fractions as it fails to capture the effect of  $\text{Na}^+$  on the surrounding alcohol molecules. In this scenario, a system specific revised effective  $\text{Na}^+$  ionic radius has been proposed that is only applicable at higher alcohol weight fractions. The use of the fitted effective ionic radius improves both the theoretical correlation as well as prediction. Finally, dielectric constants of several methanol-salt solutions have been predicted and compared to experimental data at 20 and 25 °C. The non-primitive model based SAFT-VR+DE equation of state is overall found to capture the salt effect on the solution dielectric constant well.

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#### Appendix

The SAFT-VR+DE cation-alcohol interaction energy parameters for mixed-solvent electrolyte solution systems are obtained by optimizing the following objective function,

$$obj(\gamma_{\pm}) = \frac{1}{N_{pt}} \sum_{i=1}^{N_{pt}} \left| \frac{\gamma_{\pm}^{\text{exp}} - \gamma_{\pm}^{\text{theo}}}{\gamma_{\pm}^{\text{exp}}} \right| \times 100\% \quad (20)$$

where  $N_{pt}$ ,  $\gamma_{\pm}$ , AAD represents number of experimental data points, mean ionic activity coefficient and average absolute deviations respectively. In Table 1A, we report the calculated %AAD of the mean ionic activity coefficient.

**Table 1A**

Comparison between experimental mean ionic activity coefficient ( $\gamma_{\pm}$ ) and theoretical predictions obtained by SAFT-VR+DE equation of state for the different electrolytes.

System	Alcohol weight fraction (% wt)	% AAD $\gamma_{\pm}$	
RbCl + Methanol + Water	40	7.49	
	CsCl + Methanol + Water	20	2.23
	30	5.55	
CsCl + Ethanol + Water	40	15.29	
	20	6.13	
	30	9.92	
KCl + Methanol + Water	40	34.36	
	40	3.44	
	60	7.63	
NaF + Methanol + Water	20	2.85	
	30	3.29	
	40	3.00	
	50	2.13	
	60	4.19	
	70	7.43	
LiCl + Methanol + Water	80	4.22	
	20	9.43	
	40	8.71	
NaCl + Methanol + Water	60	10.97	
	80	12.02	
	80	12.02	
NaBr + Methanol + Water	20	2.89	
	40	8.64	
	60	5.42	
NaBr + Ethanol + Water	80	31.24	
	90	53.97	
	20	8.02	
	40	30.54	
	60	48.39	
	80	50.46	
90	52.59		



**Table 2A**Comparison between %AADs of mean ionic activity coefficient ( $\gamma_{\pm}$ ) at different alcohol concentrations using old and modified Na<sup>+</sup> ionic radius.

	Alcohol weight fraction (% wt)	%AAD $\gamma_{\pm}$ with original Na <sup>+</sup> ionic radii	%AAD $\gamma_{\pm}$ with revised Na <sup>+</sup> ionic radii
NaBr + Methanol + Water	80	31.24	20.24
	90	53.97	13.40*
NaBr + Ethanol + Water	80	50.46	12.75
	90	52.59	10.71*

\*Indicates fitted values.

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