A SAFT-VR+DE equation of state based approach for the study of mixed dipolar solvent electrolytes

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Article info
Article history:
Received 6 July 2015
Received in revised form 21 October 2015
Accepted 23 November 2015
Available online 26 November 2015

Keywords:
Ions
Dipoles
Electrostatics
Molecular model
Theory
Salt

Abstract
The SAFT-VR+DE approach was developed by combining the statistical associating fluid theory for potentials of variable range (SAFT-VR) with integral equation theory and the generalized mean spherical approximation using a non-primitive model, in order to explicitly describe the solvent in electrolyte solutions. Subsequently, the theory was applied to study nineteen different aqueous electrolyte solutions and a range of thermodynamic properties across different temperatures and salt concentrations were successfully predicted. Here, the theory is applied to study several model mixed dipolar solvent electrolytes in order to validate a simple one-fluid-like approximation that is proposed to describe the interactions between ions and dipolar solvents of arbitrary size and dipole moment. Before application to real fluids the approach is extensively tested through comparison with isothermal-isobaric ensemble (NPT) Monte Carlo simulations for a number of model mixed dipolar solvent electrolyte systems. Simulations have been performed for different ionic concentrations, solvent compositions, cation, anion, and solvent segment diameters, and solvent polarity. The results show that the SAFT-VR+DE equation provides a good description of the PVT behavior of the model mixed solvent electrolyte systems studied, with some over-prediction of the PVT behavior observed only at higher ionic concentrations. Additionally, comparisons are made between predictions from the non-primitive and primitive models for electrolytes and the importance of capturing the effect of ions on the solvent dielectric is demonstrated.

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1. Introduction

Mixed solvent electrolyte solutions are of significant industrial interest due to their application in several chemical processes, such as wastewater treatment, crystallization, liquid–liquid extraction, extractive distillation, and seawater desalination [1]; however, only limited experimental data on the thermodynamic properties of these fluids compared to aqueous electrolyte systems are available [2]. An attractive approach to explore such systems is therefore to develop theoretical tools that can predict the phase behavior and thermodynamic properties of mixed solvent electrolytes as a means of generating “pseudo” experimental data. Though, this is made more difficult by the fact that these fluids are highly non-ideal systems because of the dominant long-range electrostatic interactions, which makes their theoretical study challenging.

Theoretical developments for electrolyte solutions can be broadly divided into two approaches: those in which the solvent is described implicitly by a dielectric constant (known as primitive models) [3] and those in which the ions and solvent species are both treated explicitly (known as non-primitive models). The primitive model is a McMillan-Mayer level of theory [4], developed with the notion that an explicit representation of the solvent is not necessary and can be treated implicitly within the theory. This approximation is likely to be valid at low ionic concentrations. In contrast, the non-primitive model allows for the explicit description of solvent species within the theoretical framework and is in the general class of Born-Oppenheimer models [4]. In the simplest Born-Oppenheimer models of electrolytes, the electrolyte solution is described as a mixture of charged hard spheres in a solvent of spherical hard dipolar molecules. We note that to date, only the primitive model has been applied to the study of mixed solvent electrolytes.

In the context of the development of theoretical approaches for the calculation of the thermodynamic properties of mixed solvent electrolytes, the primitive-model-based semi-empirical
A comprehensive approach to the development of equations of state can be adopted through the use of classical statistical mechanics, which relates intermolecular forces to the thermodynamic functions of fluids. In this regard, the rigorous conversion required between the Lewis–Randall and McMillan–Mayer frameworks is typically ignored; however, the inconsistent treatment of the solvent chemical potential (i.e., as an independent variable in the Lewis–Randall framework) gives rise to thermodynamic inconsistencies and introduces errors.

In order to rectify this inconsistency, several authors have developed an extended DH formalism that is suitable for use in the Lewis–Randall framework. A more comprehensive approach to the development of equations of state can be adopted through the use of classical statistical mechanics, which relates intermolecular forces to the thermodynamic functions of fluids. In this regard, the rigorous conversion required between the Lewis–Randall and McMillan–Mayer frameworks is typically ignored; however, the inconsistent treatment of the solvent chemical potential (i.e., as an independent variable in the Lewis–Randall framework) gives rise to thermodynamic inconsistencies and introduces errors. In order to rectify this inconsistency, several authors have developed an extended DH formalism that is suitable for use in the Lewis–Randall framework.
describe the long-range ion–ion, ion-dipole, and dipole–dipole interactions to develop the SAFT-VR + DE equation, a non-primitive-model-based electrolyte version of the SAFT-VR equation. The predictions of PVT behavior for several model electrolyte fluids were compared against NPT Monte Carlo simulation data for systems of different ionic concentrations and different ratio of the cation, anion, and solvent segment diameters to test the accuracy of the approach. Comparisons were also made with the DH and primitive models, illustrating that the full non-primitive model better captures the electrostatic interactions due to the explicit consideration of solvent. The importance of properly accounting for the difference in size between the ions and solvent and providing an accurate description of the dielectric constant was also shown. In subsequent work, the SAFT-VR + DE equation of state was applied to study nineteen aqueous alkali halide electrolyte systems and evaluate a range of thermodynamic properties, including the mean ionic activity coefficient, osmotic coefficient, water activity coefficient, density, Gibbs free energy of hydration, and the dielectric decay [43]. The results demonstrated that when developing a predictive equation of state for a family of electrolyte solutions, a uniform model is not appropriate and the nature of the salt and the concentration range being studied should be taken into account and the model tailored to capture the correct interactions. Specifically when studying electrolyte solutions from infinite dilution to the fused salt limit, while a fully dissociated model of electrolytes can be expected to capture the thermodynamic behavior at low to moderate concentrations, at higher concentrations, with the changes in intermolecular/ionic interactions, the underlying theoretical considerations should also change and depending upon the nature of the ions, ion association or enhanced anion–solvent interactions should be considered.

Since statistical-mechanics-based equations of state like SAFT are formulated upon a well-defined molecular model, they have an inherent advantage over more empirical approaches as the approximations made in the development of the theory can be rigorously tested through comparison with computer simulation results for the exact same model. This allows the accuracy of the theory to be determined before comparison with experimental data and parameters are fitted [29]. This approach has been used heavily in the development and testing of new versions of the SAFT equation of state. For example, in the development of the SAFT-VR + D approach, which describes dipolar associating fluids and explicitly considers the effect of dipolar interactions on both the thermodynamics and structure of the fluid, the theoretical framework was extensively tested against isothermal-isobaric (NPT) and Gibbs ensemble Monte Carlo simulation data for the thermodynamic properties and phase behavior of several model dipolar square-well monomer and chain fluids before application to experimental fluids. Similarly, as described above, the SAFT-VR + DE equation was first validated using computer simulation results [42] before being applied to study experimental systems [43]. In this work, the SAFT-VR + DE equation of state has been applied to the study of mixed dipolar solvent electrolyte systems, i.e., ions solvated by at least two distinct dipolar solvent species and therefore computer simulations have been performed for a series of different molecular models in order to test the theory before experimental mixed dipolar solvent electrolyte systems are studied. Specifically simulations have been performed in which, the size of the cation, anion, and solvents are assumed to be equal (known as the semi-non-primitive model), the ions and solvents are of different sizes while the cation and anion have equal and also different diameters (known as the restricted non-primitive model). The effect of the dipole moment of each solvent and ion concentration is also investigated and a comparison with the primitive model of electrolytes included to examine the effect of using a salt-concentration-dependent dielectric constant on the theoretical predictions.

The remainder of the paper is organized as follows: In section 2 we present the SAFT-VR + DE model as applied to mixed dipolar solvent electrolyte solutions, along with the primitive model approach. In section 3, details of the molecular simulations performed are presented. A comparison of the theoretical predictions and simulation results are then reported and discussed in section 4 and concluding remarks made in section 5.

2. Molecular model and theory

Mixed dipolar solvent electrolyte solutions are modeled as a mixture of charged ions of arbitrary size within dipolar associating solvents composed of molecules of arbitrary size and polarity as illustrated in Fig. 1. The ions are described as hard spheres, half with charge +q and diameter σ⁺, and half with charge −q and diameter σ⁻. Two types of dipolar solvent molecules are considered: a monomer fluid that mimics water molecules and a dimer fluid that represents a second solvent such as an alcohol. The monomer solvent is described by diameter σ₁ and dipole moment μ₁ and contains four association sites, two each of different kinds that represent hydrogen bonding sites (i.e., mimicking H and O atoms in water). The dimer solvent molecules are described by segments of diameter σ₂ and embedded dipole moment of μ₂ with two association sites.

The potential model for interaction between dipolar solvents and ionic species is given by,

\[
 u(r) = u_{SW}(r) + u_{CC}(r) + u_{CD}(r) + u_{DD}(r)
\]

(1)

where the square-well, coulombic charge–charge, charge-dipole, and dipole–dipole interactions are represented by \( u_{SW}(r) \), \( u_{CC}(r) \), \( u_{CD}(r) \), and \( u_{DD}(r) \) potentials, respectively and are defined as follows:

\[
 u_{SW}(r) = \begin{cases} 
 +\infty & r < \sigma_{ij} \\
 -\epsilon_{ij} & \sigma_{ij} \leq r < \lambda_{ij}\sigma_{ij} \\
 0 & r \geq \lambda_{ij}\sigma_{ij}
\end{cases}
\]

(2)

Here the cross interaction square well depth (\( \epsilon_{ij} \)), range (\( \lambda_{ij} \)) and diameter (\( \sigma_{ij} \)) parameters between molecules \( i \) and \( j \) are

![Fig. 1. Schematic representation of the molecular model used in the SAFT-VR + DE equation to describe mixed dipolar solvent electrolyte solutions containing ions and two types of associating dipolar solvent.](image-url)
determined using the following combining rules,

\[ \xi_{ij} = \sqrt{\xi_{ii}\xi_{jj}} \quad (3) \]

\[ \lambda_{ij} = \frac{\lambda_i\sigma_j + \lambda_j\sigma_i}{\sigma_i + \sigma_j} \quad (4) \]

\[ \sigma_{ij} = \frac{(\sigma_i + \sigma_j)}{2} \quad (5) \]

The Coulombic charge–charge interaction between ions is given by,

\[ u_{ij}^{CC}(r) = \frac{1}{4\pi\varepsilon_0 r} \left\{ \begin{array}{ll}
+\infty & \text{if } r \leq \sigma_{ij} \\
\frac{z_i z_j e^2}{4\pi\varepsilon_0 r^3} & \text{if } r > \sigma_{ij}
\end{array} \right. \quad (6) \]

and the charge–dipole interaction between ions is represented by,

\[ u_{ij}^{CD}(r) = \frac{1}{4\pi\varepsilon_0 r^2} D(n_1, n_2) \left\{ \begin{array}{ll}
+\infty & \text{if } r \leq \sigma_{ij} \\
-\frac{\mu_i^2}{4\pi\varepsilon_0 r} D(n_1, n_2) & \text{if } r > \sigma_{ij}
\end{array} \right. \quad (7) \]

where \( z_i \) and \( \mu \) are the charge on ion \( i \) and the dipole moment of solvent respectively. The dipole–dipole potential between dipolar solvent species is represented by

\[ u_{ij}^{DD}(r) = \frac{1}{4\pi\varepsilon_0 r^3} D(n_1, n_2) \left\{ \begin{array}{ll}
+\infty & \text{if } r \leq \sigma_{ij} \\
-\frac{\mu_i^2}{4\pi\varepsilon_0 r^3} D(n_1, n_2) & \text{if } r > \sigma_{ij}
\end{array} \right. \quad (8) \]

where

\[ D(n_1, n_2) = 3(n_1 \cdot \hat{r})(n_2 \cdot \hat{r}) - n_1 \cdot n_2 \quad (9) \]

Here \( \hat{r} \) is the unit vector in the direction of \( r \) joining the center of the segments and \( n_i \) is a unit vector parallel to the dipole moment of segment \( i \).

The solution of the Ornstein–Zernike equation with the NPMSA closure proposed by Blum et al. [44] is for ions of arbitrary sizes in a dipolar solvent with a separate segment diameter. No solution of the NPMSA has been developed to date for ions of arbitrary size in a solvent composed of more than one type of dipolar species. It is proposed in this work to circumvent this limitation by the application of the NPMSA for mixed dipolar solvent electrolytes by using a one-fluid type approximation in the ion–dipole and dipole–dipole terms within the SAFT-VR+DE equation of state. It is therefore assumed that the properties of the solvent can be described by those of a hypothetical or effective fluid that is represented through an effective segment diameter \( (\sigma_{eff}) \) and dipole moment \( (\mu_{eff}) \) with parameters determined via [45–47]:

\[ \sigma_{eff} = \sum_{i=1}^{N_{\text{poly}}} \sum_{j=1}^{N_{\text{poly}}} x_i x_j \sigma_{ij} \]

\[ \mu_{eff} = \left( \sum_{i=1}^{N_{\text{poly}}} x_i m_i \right)^2 \left( \sum_{i=1}^{N_{\text{poly}}} x_i m_i \right) \]

Even though, an effective fluid has been utilized in this study, the proposed mixing rules in Eq. (10)–(11) implicitly include the effect of solvent composition. Equation (10) represents the van der Waals one fluid mixing rule for size [45], while Equation (11) for the effective dipole moment is based upon the work of Karakatsani et al. [47]. These approximations were chosen as they were found to yield better results for the thermodynamic properties of interest compared to other approximations based on the concept of random mixing [48].

To describe the model electrolyte fluids being studied within the SAFT-VR+DE theoretical framework the Helmholtz free energy per molecule is given by

\[ \frac{A_{\text{sol}}}{N k_B T} = \frac{A_{\text{ideal}}}{N k_B T} + \frac{A_{\text{mono}}}{N k_B T} + \frac{A_{\text{chain}}}{N k_B T} + \frac{A_{\text{assoc}}}{N k_B T} \quad (13) \]

where \( A_{\text{sol}} \) and \( A_{\text{ideal}} \) are the free energy contributions due to the ideal, monomer, and association interactions, respectively. The theory has been presented in previous work [43] and so only an overview of the approach is described below.

The contribution to the Helmholtz free energy due to the monomer fluid is given as a combination of the dispersion and electrostatic interactions between the segments as:

\[ \frac{A_{\text{mono}}}{N k_B T} = \frac{A_{\text{sw}}}{N k_B T} + \frac{A_{\text{el}}}{N k_B T} \quad (14) \]

where \( A_{\text{sw}} \) and \( A_{\text{el}} \) are the free energy contributions due to square-well dispersion interaction and electrostatic interactions, respectively.

\[ \frac{A_{\text{sw}}}{N k_B T} = \sum_{i=1}^{n} \frac{x_i m_i}{N k_B T} \frac{A_{\text{sw}}}{N k_B T} = \left( \sum_{i=1}^{n} x_i m_i \right) a_{\text{sw}} \quad (15) \]

\( a_{\text{sw}} \) is the contribution to free energy due to the attractive square-well dispersive interactions between monomer segments and is obtained as in the original SAFF-VR approach from a second order high temperature perturbation expansion [34]. The contribution to the Helmholtz free energy from the electrostatic interactions, \( A_{\text{el}} \), is obtained from Blum and Wei [41] solution to the Ornstein-Zernike equation using integral theory within the NPMSA closure for a mixture of ions and dipole of arbitrary size, and is given by,

\[ \frac{A_{\text{el}}}{N k_B T} = \frac{E_{\text{el}}}{V k_B T} - J - \dot{J} \quad (16) \]

where, \( V \) is the total volume of the solution, \( J \) and \( \dot{J} \) are the virial integral terms and \( E_{\text{el}}/V k_B T \) is the internal energy per unit volume defined as,

\[ \frac{E_{\text{el}}}{V k_B T} = \frac{1}{4\pi} \left\{ \alpha_0^2 \sum_{k=1}^{2} \rho_k z_k N_k - 2\alpha_2 \alpha_0 \rho_b B^{10} - \frac{2\alpha_2^2 \rho_b B^{10}}{\sigma_2^2} \right\} \quad (17) \]

with the virial integral terms \( J \) and \( \dot{J} \) defined as [50],

\[ J = \frac{1}{12\pi} \left\{ \alpha_0^2 \sum_{k=1}^{2} \rho_k z_k N_k - 2\alpha_2 \alpha_0 \rho_b B^{10} - \frac{6\alpha_2^2 \rho_b B^{10}}{\sigma_2^2} \right\} \quad (18) \]

\[ \dot{J} = \frac{\alpha_0 \rho_b}{\sigma_2} \sum_{j=1}^{2} \rho_j \sigma_{ij} \left\{ \sum_{m,n} \frac{\sigma_{mn} \sigma_{j}}{2T + 1} \left[ \sigma_{mn} \sigma_{j} \right]^2 - \left[ \sigma_{mn} \sigma_{j} \right]^2 \right\} \quad (19) \]

Here \( \alpha_0 \) and \( \alpha_2 \) are the ion–ion coupling and dipole–dipole
interaction energy strength parameters, \( g_{\text{SW}}(\sigma_A) \) is the radial distribution function (RDF) of ion/dipolar species at contact and \( g_{\text{SW}}(\sigma_B) \) is the hard-sphere RDF at contact. The parameters \( B^{\text{SW}} \) and \( b_{\text{SW}} \) correspond 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 [41]. The detailed description of each term in the expression for \( A^{\text{SW}} \) has been reported in previous works [42,43].

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

\[
\frac{A_{\text{chain}}}{Nk_B T} = \frac{\mu_{\text{cont}}}{4} \sum_{i=1}^{m_i} x_i (1 - m_i) \ln g_{\text{SW}}(\sigma_i) \tag{19}
\]

where, the sum is over all solvent compounds in the mixture and \( g_{\text{SW}}^M \) represents the contact value of the RDF of monomer segments. Since solvent molecules are described as dipolar SW molecules, the required \( g_{\text{SW}}^M \) is that of the dipolar square well fluid, i.e., \( g_{\text{SW}}^{D\text{SW}} \) and is obtained from the linearized version of the exponential (LEXP) approximation [51]. As shown in previous work [51], the LEXP approximation for the RDF is more accurate than the MSA, as it provides a better description of PVT and VLE properties of dipolar dispersive square well chain fluids.

The contribution to the free energy due to short-ranged attractive association interactions between solvent molecules is given by the usual SAFT expressions [52].

3. Simulation

Monte Carlo simulations in the isothermal-isobaric (NPT) ensemble have been performed to study the PVT behavior of several model mixed dipolar solvent electrolyte systems. Each simulation was started from an initial configuration in which 256 molecules were placed in random orientations on the sites of a face centered cubic lattice in a simulation box with periodic boundary conditions. The long-range charge–charge, charge-dipole, and dipole–dipole interactions between polar solvents and charged ions were captured through the reaction field method [53–56]. The reaction field method has shown to be as accurate as the Ewald sum for calculating long-range dipolar and electrostatic forces [57–60]. In the reaction field method, the long-range interactions are truncated at a finite cut-off distance from each ion and dipolar molecule and replaced by a dielectric continuum. The effect of the dielectric continuum is taken into account by including an additional term into the long-range charge–charge, charge-dipole, and dipole–dipole interaction potentials. In this work, the cut-off distance \( r_c \) was set to 3\( \sigma \), beyond which the pair potential is zero and a dielectric continuum \( \varepsilon_F \) applied.

In the systems included in this study, the solvent molecules are highly associative. This kind of strong association interaction between molecules can promote the formation of stable clusters, making the complete sampling of phase space challenging [61–63]. To avoid poor sampling, several biasing schemes have been proposed in the literature [61,62,64–66]. For example, the association-biased Monte Carlo (ABMC) [67] method, which strategically biases the configuration site where association is likely to occur, was the first biasing scheme to be proposed: however, it requires the determination of bonding regions, making the algorithm rather complex. Subsequently, Tsangaris et al. developed the bond bias Monte Carlo method for the sampling of dimer clusters [61] and Visco et al. [62] proposed the monomer-addition-subtraction algorithm for the study of linear and ring aggregates. More recently, Chen et al. [63] proposed the aggregation volume bias Monte Carlo (AVBMC) scheme, which can be applied to any cluster architecture (i.e., it is not restricted to the sampling of dimers, chains or rings) and is computationally more efficient as the identification of clusters is not required. In the simulations reported here, although systems with low association energy (i.e., \( \varepsilon_{\text{HB}} < 10 \varepsilon \)) are studied and so are outside of the range in which regular GEMC simulations are expected to fail [61], we have used the AVBMC biasing scheme developed by Chen et al. [63], to avoid potential issues of poor sampling and increase the reliability of the PVT data.

In the simulations the potential model for the association interactions is given by,

\[
u(r_{ij}; \theta_i, \theta_j) = \begin{cases} \varepsilon_{\text{HB}} & \sigma < r_{ij} < r_{ij}^* \text{ and } |\theta_i| < \theta_c \text{ and } |\pi - |\theta_i|| < \theta_c \\ 0 & \text{otherwise.} \end{cases} \tag{20}
\]

where, \( \theta_i \) and \( \theta_j \) are the angles between the direction vectors and the center-to-center vector of atoms \( i \) and \( j \) respectively. Different association sites residing upon the same or different molecules can interact with a short-ranged associating energy of magnitude \( \varepsilon_{\text{HB}} \). Although in Wertheim’s theory bonding is limited at each association site to dimers, higher order cluster formation is possible depending upon the size of the association site, strength of the site–site interactions, and the state conditions as illustrated by Docherty and Galindo [68]. In this work, the angular cut-off \( \theta_c \) is set to 27° in order to restrict bonding to dimer formation [22].

The AVBMC move has been used in conjunction with traditional Monte Carlo displacement, rotation and volume moves. In a single simulation cycle, N trial displacement, rotations, and AVBMC moves along with one volume change move have been employed. The extent of displacement, reorientation, AVBMC and volume trial moves has been adjusted so that individual acceptance probabilities are between 20 and 30%. An initial simulation of 500,000–1,000,000 cycles was performed to equilibrate the system before averaging for between 1,000,000 and 2,000,000 cycles. In order to examine whether equilibrium had been reached, several simulations from different initial configurations were performed and results for the thermodynamic properties compared. For each system studied, the packing fraction and system energy at a given reduced pressure are reported and were obtained as ensemble averages, with the errors estimated by taking the standard deviation, as given by the following equation.

\[
\text{Error} = \sqrt{\frac{1}{M} \sum_{n=1}^{M} \left( \frac{1}{M} \sum_{n=1}^{M} I' \right)^2 - \left( \frac{1}{M} \sum_{n=1}^{M} I' \right)^2} \tag{21}
\]

where, \( I' \) is the calculated packing fraction/energy and \( M \) the number of cycles.

4. Results and discussion

A complete list of systems studied by Monte Carlo simulation is provided in Table 1. In systems 1 and 2, the effect of solvent polarity on the PVT behavior is evaluated while systems 1, 3 and 4 enable the effect of different ionic concentrations on the PVT behavior to be examined. In order to take into account the effect of solvent composition, in systems 1, 5 and 6 we consider different ratios of monomer and dimer solvent molecules. We note that systems 1–6 are symmetric in nature as all the ions and molecules have the same segment diameter; however, in experimental mixed solvent electrolyte systems the ions and solvent molecules are of different sizes. Therefore the effect of ion and solvent molecule size on the thermodynamics of the fluid has been tested in systems 7 and 8. The results of the NPT Monte Carlo simulations are provided in Table 2.
In Fig. 2, a comparison has been made between the SAFT-VR + DE theoretical predictions and Monte Carlo NPT ensemble simulation results for the PVT behavior of systems 1 and 2. From the figure we can see that over the range of temperatures studied \((T^* = 1.2, 1.4, 1.6, 1.8)\), the theory is found to be in good agreement with the simulation results. In system 2, compared to system 1, the polarity of dimer molecules increases (from \(\mu_2^2 = 2\) to 4), which results in increased attractive interactions between the solvent molecules and an increase in the density at a fixed pressure. Although the theory correctly captures this trend, we note that at higher temperatures for system 2 the theory under predicts the density as shown in Fig. 2b; however, the deviations are well within the errors as reported in Table 2.

Systems 1 and 2 contain 8 ions (4 cations and 4 anions) along with 248 solvent (both monomer and dimer) molecules. In experimental electrolyte systems, thermodynamic properties vary as a function of ion concentration. In order to test whether the proposed theoretical approach can capture the effect of changes in ion concentration systems 3 and 4 in which the ion concentrations are 0.79\% (4/256) and 3.2\% (16/256) mol \% of salt respectively are considered in concentration systems 3 and 4 in which the ion concentrations are 0.79\% (4/256) and 3.2\% (16/256) mol \% of salt respectively are presented. As can be seen from the figure, the theory predicts a slight decrease in the density with increasing concentration in both systems.

In addition to the concentration of ions in electrolyte solutions, the composition of the solvent in mixed solvent electrolyte systems can play an important role in determining the thermodynamic properties \([69]\). For example, in the measurement of mean ionic activity coefficients for NaBr + ethanol + water the ionic activity was found to change from 0.6643 to 2.951 at 0.31 salt molality \((m)\) with a change in the solvent ratio between water and ethanol from 9:1 to 1:9 \([69]\). To examine this effect, in systems 5 and 6 the ratio of the dimer and monomer solvent is varied from the 50:50 mixture used in systems 1–4 (i.e., in systems 1–4, the solvent molecules are divided equally between the monomer and dimer molecule). In system 5200/248 and in system 6 4248 particles are considered monomers, whereas the number of ions is maintained at 8 in both cases. The polarity of the systems studied also increases as the number of dimers in the system increases, due to the higher dipole moment in the dimer molecules compared to the monomer molecules. As a result, as shown in Fig. 4, the density of system 6 is higher at a given temperature and pressure than for system 5. For system 1 with a 50:50 mixture of dimer and monomer solvent species the solution density lies as expected in between system 5 and 6 at a specific temperature and pressure. From Fig. 4, it can also be seen that the theory is able to capture this change in the PVT behavior and is in good agreement with the simulation results.

To more closely mimic experimental systems, we now consider systems (7 and 8) in which the ions and dipolar solvent molecules have different diameters. Experimentally, electrolyte solutions often contain highly asymmetric species, for example the LiBr + ethanol + water mixture in which Li\(^{+}\) has an ionic diameter of 1.2 compared to Br\(^{-}\) having an ionic diameter of 3.92 and solvents water and ethanol are of different sizes and polarities. It is therefore desirable to be able to capture the effect of asymmetry on the PVT behavior. In system 7, while the ions have the same diameter, the solvent molecules are asymmetric in nature, with a ratio of 3:4 between the monomer and dimer molecules. System 8 is composed of completely asymmetric species, with the ratio of monomer, dimer, cation and anion diameters being 3:4:2:5. The results for both systems are presented in Fig. 5, where again we see that the SAFT-VR + DE approach is in good agreement with the simulation data. Comparison between systems 1, 7, and 8 (Figs. 2a, 5a and 5b) show that the asymmetric system (system 8) exhibits the highest density at a given pressure and temperature, while the symmetric system (system 1) has the lowest density.

Having seen that the non primitive model based SAFT-VR + DE equation of state is able to accurately predict the effect of long-range electrostatic interactions on the thermodynamics of mixed dipolar solvent electrolyte solutions for both symmetric (semi-non primitive model) and asymmetric (unrestricted-non primitive model) model systems, a comparison is now made with the primitive model of electrolytes to highlight the improved accuracy obtained through an implicit representation of solvent species as in the SAFT-VR + DE equation. Since the primitive model employs an implicit solvent the dielectric constant is an input to the calculations and therefore dependent on available experimental data. Although ion concentration in the solution is known to have a significant influence on the solution dielectric \([70]\), with the dielectric constant decreasing as the salt concentration increases, experimental dielectric data as a function of ion concentration is not available for mixed solvent electrolyte systems and so primitive model approaches must use solvent composition based experimental dielectric constant data that is independent of salt concentration. In Fig. 6, the SAFT-VR + DE prediction for the influence of the ion concentration on the dielectric constant for the NaBr + methanol + water system is presented. As can be seen from the figure, the theory predicts a significant reduction in the dielectric constant with increasing

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### Table 1

Model parameters for the electrolyte fluids studied. \(\sigma_{qV}, \sigma_{qD}, \sigma^+\) and \(\sigma^-\) are the reduced diameter of the solvent 1 (monomer), solvent 2 (dimer), cation and anion respectively, where reduced diameters are defined as \(\sigma_{q_i} = \sigma_{q_i}/(s_{q_i} \sqrt{3})\) and \(s_{q_i}\) are the reduced squared dipole moments of solvent 1 and solvent 2, where \(\mu^2 = \mu^2/k_BT\) is the reduced association energy, \(\epsilon^*\) the reduced association cutoff radius, \(N_{\text{ion}}\) the number of ions, and \(N_{\text{solvent}}\) the number of monomer and dimer solvent molecules.

<table>
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<th>System</th>
<th>(\sigma_{qV}^1)</th>
<th>(\sigma_{qD}^1)</th>
<th>(\sigma^+)</th>
<th>(\sigma^-)</th>
<th>(\nu_{qV}^2)</th>
<th>(\nu_{qD}^2)</th>
<th>(\epsilon^*)</th>
<th>(\epsilon^l)</th>
<th>(\epsilon^r)</th>
<th>(N_{\text{ion}})</th>
<th>(N_{\text{solvent}_1})</th>
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\(T^* = 1.2, 1.4, 1.6, 1.8\)
salt molality at 50 weight % composition of methanol-water. Although no experimental data is available for verification, the trend predicted by the SAFT-VR + DE equation is consistent with that observed in experimental studies of aqueous (i.e., single solvent) electrolyte systems [70].

To quantify the effect of an ionic concentration based dielectric constant on the predictive ability of an equation of state, a comparison has been made between the non-primitive and primitive models, both with and with out the salt concentration dependent dielectric constant in Fig. 7 for system 1 at $T^* = 1.8$. From the figure we can see that the primitive model with a salt concentration independent dielectric constant shows significant deviations from the simulated PVT results, whereas the non-primitive model provides an accurate prediction. We note that, when the input dielectric constant of the primitive model is changed to a salt concentration dependent one (obtained as an output from the non-primitive model), the primitive model shows immediate improvement in predictive ability and the result is comparable in accuracy with the non-primitive model. Similar trends are observed for the asymmetric system (system 8) as presented in Fig. 8, i.e., the theoretical predictions of the PVT behavior from the primitive model significantly improve with the use of a salt concentration dependent dielectric constant, with the resulting accuracy being comparable to that of the non-primitive model. The use of the non-primitive model in the development of equations of state for mixed solvent electrolytes is therefore advantageous as it requires no prior knowledge of the appropriate dielectric constant in order to capture changes in the dielectric constant with salt concentration; such information can be hard to obtain for mixed solvent electrolyte systems.
Table 3
SAFT-VR + DE parameters for methanol, Na and Br determined in this work. The reported parameters for water were taken from Ref. [43].

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<th>(\sigma) (Å)</th>
<th>(\epsilon/\kappa_b) (K)</th>
<th>(\lambda)</th>
<th>(\psi)</th>
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Fig. 2. Comparison of predictions from the SAFT-VR + DE equation and NPT Monte Carlo simulation results for symmetric electrolyte solutions with \(\epsilon^\prime = 1.0, \lambda = 1.5, \sigma^\prime = \sigma^\prime \_\text{H}_2\text{O} - \sigma^\prime \_\text{CH}_3\text{OH} = 10, \psi^\prime = 5.0, \psi^\prime = 1.05\), charge \(q = 1\), ion concentration of \(8/256\), and (a) dipole moment \(\mu_{\text{H}_2\text{O}}^\prime = 1.0\) and \(\mu_{\text{CH}_3\text{OH}}^\prime = 2.0\) at \(T^\prime = k_bT/\epsilon = 1.2, 1.4, 1.6\) and 1.8 for system 1 and (b) dipole moment \(\mu_{\text{H}_2\text{O}}^\prime = 1.0\) and \(\mu_{\text{CH}_3\text{OH}}^\prime = 4.0\) at \(T^\prime = k_bT/\epsilon = 1.2, 1.4, 1.6,\) and 1.8 for system 2. The solid lines represent predictions from the SAFT-VR + DE equation and the squares represent NPT Monte Carlo simulation data.

Fig. 3. Comparison of predictions from the SAFT-VR + DE equation and NPT Monte Carlo simulation results for symmetric electrolyte solutions with \(\epsilon^\prime = 1.0, \lambda = 1.5, \sigma^\prime = \sigma^\prime \_\text{H}_2\text{O} - \sigma^\prime \_\text{CH}_3\text{OH} = 10, \psi^\prime = 5.0, \psi^\prime = 1.05\), charge \(q = 1\), and dipole moments \(\mu_{\text{H}_2\text{O}}^\prime = 1.0\) and \(\mu_{\text{CH}_3\text{OH}}^\prime = 2.0\) at \(T^\prime = k_bT/\epsilon = 1.2, 1.4, 1.6,\) and 1.8 for ion concentrations of (a) \(4/256\) and (b) \(16/256\), with \(N_{\text{solvent}} = N_{\text{solvent}}^\prime\). The solid lines represent predictions from the SAFT-VR + DE equation and the squares represent NPT Monte Carlo simulation data.

Fig. 4. Comparison of predictions from the SAFT-VR + DE equation and NPT Monte Carlo simulation results for symmetric electrolyte solutions with \(\epsilon^\prime = 1.0, \lambda = 1.5, \sigma^\prime = \sigma^\prime \_\text{H}_2\text{O} - \sigma^\prime \_\text{CH}_3\text{OH} = 10, \psi^\prime = 5.0, \psi^\prime = 1.05\), charge \(q = 1\), and dipole moments \(\mu_{\text{H}_2\text{O}}^\prime = 1.0\) and \(\mu_{\text{CH}_3\text{OH}}^\prime = 2.0\). For ion concentrations of (a) \(8/256\) at \(T^\prime = k_bT/\epsilon = 1.2, 1.4, 1.6,\) and 1.8 for different solvent ratios of (a) 200 particles of monomers and 48 of dimers and (b) 4 particles of monomers and 244 of dimers. The solid lines represent predictions from the SAFT-VR + DE equation and the squares represent NPT Monte Carlo simulation data.
and represent NPT Monte Carlo simulation data.

Fig. 7. Comparison of predictions from the SAFT-VR + DE equation and NPT Monte Carlo simulation results for asymmetric electrolyte solutions with \( r^* = 1.0, \lambda = 1.5, \phi^* = 5.0, r^*_s = 1.05, \) charge \( q = 1, \) dipole moments \( d^s_1 = 1.0 \) and \( d^s_2 = 2.0, \) and ion concentration of 8/256 at \( T^* = k_b T / \epsilon = 1.2, 1.4, 1.6 \) and 1.8 for different solvent and ion sizes of (a) \( \sigma^* = \sigma^{-} = \sigma^+_d = 1.0, \sigma^*_s = 1.333 \) and (b) \( \sigma^* = 0.667 \sigma^+ = 1.667 \sigma^*_d = 1.0, \sigma^*_s = 1.333. \) The solid lines represent predictions from the SAFT-VR + DE equation and the squares represent NPT Monte Carlo simulation data.

Fig. 6. Comparison of the ion concentration and solvent composition dependent dielectric constant (solid line) with the solvent concentration dependent dielectric constant, the dash-dotted line represents predictions from the primitive model based SAFT-VR (dotted line) for NaBr + water + (50 weight%) methanol mixed solvent electrolyte systems at 298.15 K and 1.01325 bar. The system parameters are given in Table 3.

Fig. 8. Comparison of predictions from the SAFT-VR + DE equation and NPT Monte Carlo simulation data for asymmetric electrolyte solutions with \( r^* = 1.0, \lambda = 1.5, \phi^* = 5.0, r^*_s = 1.05, \) charge \( q = 1, \) dipole moment \( d^s_1 = 1.0 \) and \( d^s_2 = 2.0, \) and an ion concentration of 8/256 (124 monomers and 124 dimers) at \( T^* = k_b T / \epsilon = 1.8. \) The solid line represents predictions from the non-primitive model based SAFT-VR + DE, the dotted line represents predictions from the primitive model + SAFT-VR using a solvent composition based (and salt concentration independent) dielectric constant, the dash-dotted line represents predictions form the primitive model + SAFT-VR using a salt concentration and solvent composition dependent dielectric constant, and the squares are NPT Monte Carlo simulation results.

5. Conclusion

In this work the SAFT-VR + DE approach, which was developed by combining the SAFT-VR equation of state with the solution of the MSA within the non-primitive model, to provide an accurate representation of the free energy contribution due to electrostatic interactions in mixtures of ions and dipolar species, has been extended to the study of mixed dipolar solvent electrolytes. This is achieved using a one-fluid-like approximation in the ion-dipole and dipole-dipole terms. The approach has been extensively tested against PVT data obtained from NPT Monte Carlo simulations for a wide range of model mixed dipolar solvent electrolyte systems that vary in terms of the size of the ions and solvent molecules, polarity of solvent molecules, and salt and solvent composition. The theoretical approach is found to be in excellent agreement with the simulated PVT data illustrating that the effects of solvent and ionic size, polarity and composition on the thermodynamics of electrolyte solution are well captured by the theory. Comparisons were also made to predictions from the non-primitive model to demonstrate that capturing the salt concentration dependence of...
the solvent dielectric is important in order to accurately predict the PVT behavior of mixed solvent electrolyte solutions.

Acknowledgments

We gratefully acknowledge financial support from the National Science Foundation under Grant CBET-1067642 and the U.S. Department of Energy (DOE), Office of Basic Energy Sciences, Geoscience Research Program, through Grant No. ERCC72 of Oak Ridge National Laboratory, which is managed for DOE by UT Battelle, LLC under Contract No. DE-AC05-00OR22725.

References


