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Modeling Tetra-n-butyl Ammonium Halides Aqueous Solutions with the Electrolyte CPA
Equation of State

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Keywords: e-CPA; TBAB; Semi-clathrate Hydrate; Relative Static Permittivity;
Thermodynamic Properties

Abstract

This work presents the thermodynamic modeling of the fluid phases of Tetra-n-butyl ammonium halides aqueous solutions with the electrolyte Cubic-Plus-Association (e-CPA) Equation of State (EOS). The adjustable model parameters are obtained by fitting the experimental data of mean ionic activity coefficients and osmotic coefficients. Several other thermodynamic properties of the aqueous solutions, such as relative static permittivity, liquid density and saturation pressure, are subsequently predicted by the e-CPA EOS. The results of Tetra-n-butyl ammonium bromide aqueous solution show that the model can satisfactorily correlate the mean ionic activity coefficients and osmotic coefficients with the percentage average absolute deviations being 7.2% and 5.9%. The model overpredicts the liquid density with a deviation of 9.2%, while it can correlate the liquid density within 0.2% with a volume translation parameter. In order to have a more complete picture of the capabilities and limitations of the model, the consistencies of experimental data, parameter estimation approaches and the ion sizes are extensively analyzed and discussed.

1. Introduction

Semi-clathrate hydrates (SCH) have attracted attention in recent years, because of application possibilities such as gas separation, thermal storage, CO₂ sequestration and CH₄ transportation [1, 2, 3]. In 1940, Fowler and coworkers [4] discovered that the addition of some quaternary ammonium salts, such as Tetra-n-butyl ammonium fluoride in water, could result in the formation of crystals at room temperature. McMullan and Jeffrey [5] used X-ray diffraction to report dimensions of the unit cells, hydration numbers, and crystal symmetry in 1959. Jeffrey and coworkers [6] studied the structure of these crystals using crystallographic and X-ray structural analysis, and they proposed to call them semi-clathrates in 1969. In the structure of SCH, the anions of salts coupled with water molecules build a clathrate framework (formed by hydrophilic beads), and the cation is embedded in framework cavities (formed by hydrophobic beads), while the small guest gas molecules could be contained in empty pentagonal dodecahedron cages. This special structure makes SCH more stable than usual hydrates. Since there is a wide range of anions and cations that can compose semi-clathrates, many different crystalline structures can be formed. Dyadin and Udachin [7] provided comparative analysis of structures and characteristics between SCH and normal gas hydrates. Dyadin et al. [8] discussed the structural stability of SCH with respect to their stoichiometry. Nowadays, Tetra-n-butyl ammonium halides (in short, TBAX, with X being bromide: B, chloride: C, fluoride: F, nitrate: NO₃ etc.) and Tetra-n-butyl phosphonium halides (in short, TBPX) receive most attention as SCH additives [7, 8, 9, 10].

The fluid phase modeling is an important step for the thermodynamic modeling of TBAX containing SCH systems. Different approaches have been proposed for TBAX aqueous solutions. One typical approach is the so-called $\varphi - \varphi$ approach, which uses an electrolyte equation of state (EOS) for all phases. Paricaud [11] used the statistical associating fluid theory with variable range for electrolytes (SAFT-VRE) to describe the fluid phases. Following Paricaud's approach, Fukumoto et al. [12, 13, 14] adjusted the temperature dependency parameter in the SAFT-VRE EOS by using solid-liquid equilibrium data of

salt-water binary systems, and applied the approach to TBAB, TBAC, TBAF, TBPB, and TBANO₃ SCH systems. Babu et al. [15] re-adjusted the depth of the square-well cell potential, enthalpic and melting point parameters, and applied the approach to TBANO₃ system. The SAFT-VRE EOS is shown to give a satisfactory agreement with experimental data for the mean ionic activity coefficients and osmotic coefficients of TBAX aqueous solutions [11, 12]. For other TBAX systems, Fukumoto et al. [12] stated that good description of mean ionic activity coefficients and osmotic coefficients of electrolyte solution can be obtained by using SAFT-VRE. Ma et al. [16] applied the Modified Patel-Teja (MPT) EOS [17] to the fluid phase equilibrium calculations for the TBAB aqueous solution and TBAF aqueous solution. The MPT EOS uses a Debye-Hückel term for the electrostatic contributions, while the authors [16] give few details of fluid modeling performance for TBAX related systems.

Another typical approach is the so-called $\varphi - \gamma$ approach, which uses a non-electrolyte EOS for the vapor phase and an electrolyte activity coefficient model for the liquid phase. The electrolyte non-random two-liquid (e-NRTL) model proposed by Chen et al. [18] is a common model for the activity coefficient in this approach. e-NRTL performs very well in modeling activity coefficients of quaternary ammonium salts in water at 298.15 K [19]. Based on the mean spherical approximation for aqueous electrolytes (MSA-NRTL) model, AMSA-NRTL [20] takes the ionic hydration and association into account. Kwaterski and Herri [21] used the Soave-Redlich-Kwong (SRK) EOS plus e-NRTL for the TBAB aqueous solution. Verrett et al. [22] used the Trebble-Bishnoi (TB) EOS plus e-NRTL for the TBAB aqueous solution, Shi and Liang [23] applied the Peng-Robinson (PR) EOS plus e-NRTL for TBAB, TBAC, and TBAF aqueous solutions, Najibi et al. [24] utilized the PR EOS plus AMSA-NRTL for TBAB aqueous solutions. Both e-NRTL and AMSA-NRTL provide good agreement with experimental data of mean ionic activity coefficients (the performance can be seen in the discussion section). Eslamimanesh et al. [25] used the PR EOS for the vapor phase, plus NRTL for non-electrolyte compounds in the liquid phase, and they used a correlation based on the experimental data for the mean ionic activity

coefficients of the electrolyte part. These authors did not investigate the predictive ability of the model for TBAB related fluid systems. Other researchers [26, 27, 28] applied non-electrolyte EOS plus empirical correlations for water activity.

It is of interest to investigate a new modeling approach, and the predictive capability and flexibility of the approach over a wide range of properties. In this work, the electrolyte Cubic-Plus-Association (e-CPA) EOS proposed by Maribo-Mogensen et al. [29, 30] is used. The adjustable parameters will be obtained by fitting the mean ionic activity coefficients and osmotic coefficients, and other thermodynamic properties will be predicted by e-CPA. The parameter estimation procedure and modeling approaches will be analyzed and discussed.

The rest of the paper is organized as follows: firstly, thermodynamic properties of TBAX aqueous solutions will be shortly introduced. Then, e-CPA will be presented, and the parameter estimation results of modeling will be proposed. Finally, analysis of the parameter estimation will be presented, followed by our conclusions.

2. Thermodynamic Properties of TBAX Aqueous Solutions

TBAX are common additives for SCH, and TBAX aqueous solutions have been extensively studied because of potential industrial applications, such as intermediate reactants and as phase transfer catalysts [11]. Tetra-n-butyl ammonium cation (TBA^+) is a hydrophobic organic cation, with a molecular formula $[\text{CH}_3(\text{CH}_2)_3]_4\text{N}^+$.

Figure 1. Structural formula of TBA^+ [31].

It can be seen from Figure 1 that TBA^+ has four long and soft hydrophobic alkyl side chains, and the positive charge, which comes from the center nitrogen atom, is sterically hindered by the alkyl substituents. Thermodynamic properties of the TBAX aqueous solutions are influenced by the interactions that occur between the hydrophobic alkyl groups of the ions and the water molecules [32]. Table 1 summarizes experimental studies of mean ionic activity coefficients and osmotic coefficients for TBAX aqueous solutions at atmospheric pressure.

Table 1. Experimental studies of mean ionic activity coefficients and osmotic coefficients for TBAX aqueous solutions at atmospheric pressure

TBAX	Molality [mol/kg water]	Temperature [K]	N*	Ref.
	0.1~27	298.15	38	[33]
TBAB	0.0912~1.0060	298.15	10	[34]
	0.1~9.5	298.15, 373.15, 423.15	27 ⁺	[35]
TBAC	0.1~15	298.15	32	[33]
TBAF	0.1~1.6	298.15	13	[36]

* N represents the number of data points. ⁺ The authors gave the changes in osmotic coefficients and in activity coefficients.

The mean ionic activity coefficients and osmotic coefficients are important for electrolyte solutions. It can be seen from Figure 2 that these two properties of TBAX aqueous solutions are complex functions of molality. For the TBAB system, at low to medium salt concentration, both the mean ionic activity coefficients and osmotic coefficients decrease with increasing salt concentration. At higher salt concentration, both activity coefficients show a slight increase. For the TBAC system, at low molality, the values of mean ionic activity coefficients and osmotic coefficients first decrease, and then increase to reach maxima at around 2 mol/kg water. After the maxima, the values first decrease, and then rise again. The mean ionic activity coefficients and osmotic coefficients of TBAF solution

increase sharply with increasing salt concentration. Wen et al. [36] stated that the large values for these fluorides could be attributed to the ‘structural repulsion’: F^- anion is small and may tend to immobilize water in a more or less radial pattern around it due to its specific size and surface charge density [36]. The TBA^+ is large and tends to enhance the ‘cage-like’ structure of water due to its hydrophobic properties. The cation and anion compete against each other to influence the structure of water in different ways.

(a) Mean ionic activity coefficients.

(b) Osmotic coefficients.

Figure 2. Experimental data of (a) mean ionic activity coefficients and (b) osmotic coefficients of TBAX aqueous solution at 298.15 K. $\circ$, TBAB aqueous solution (Amado

and Blanco, 2005 [34]); +, TBAB aqueous solution (Lindenbaum and Boyd, 1964 [33]);
 , TBAC aqueous solution (Lindenbaum and Boyd, 1964 [33]); □, TBAF aqueous
 solution (Wen et al., 1965 [36]).

Ion radius is a very important physical parameter in electrostatic calculations. Pauling [37] stated that there is no specified size which can be assigned to an ion, because of the indefinite extent of the electron distribution function. Pauling [37] also pointed that the apparent ionic radius will depend on the physical properties.

Different type of ion sizes for TBA^+ are published. Pauling radius is calculated from the nuclear charge and the shielding constant based on Pauling rules. van der Waals radius is the radius of an imaginary hard sphere representing the distance of closest approach for another atom. Hard-sphere radius is calculated from the rigid sphere model. Hydrated radius is the radius of ion and closely bounded water molecules. Stokes radius (or hydrodynamic radius) is the radius of a hard sphere that diffuses at the same rate as the solute. McGowan radius is calculated from the McGowan characteristic volume, which is the actual volume of a mole when the molecules are not in motion. Table 2 summarizes some published ion size of TBA^+ , from which it can be seen that the radii of TBA^+ vary from 3.81 Å to 4.94 Å, a difference (highest to lowest value) of 1.13 Å. The TBA^+ is a soft and irregular organic cation, and it is not entirely clear which radius approximately reflects the physics of the electrostatic interactions. For this reason, the effect of ion radius on the thermodynamic modeling will be investigated in this work.

Table 2. Summary of literature values proposed for the radius of TBA^+

Size Type	Ion Radius r (Å)	Reference
Pauling crystal radius	4.94	[38]
van der Waals radius	3.87	[39]
	4.13	[32,40]
hard-sphere radius	3.81	[41]
hydrated radius	4.94	[42]
hydrodynamic radius	3.84	[43]

	4.73	[44]
	4.72	[38]
McGowan radius	4.62	[45]

3. The e-CPA EOS

Maribo-Mogensen et al. [29, 30] extended the CPA EOS, proposed by Kontogeorgis et al. [46], to mixtures containing electrolytes. It includes the electrostatic contributions from the Debye–Hückel theory [47] (which accounts for the long-range interaction of the ions), and the Born equation [48] (which accounts for ion solvation).

In the e-CPA EOS, the residual Helmholtz energy is given by

$$A^r = A^{SRK} + A^{ASSOC} + A^{DH} + A^{Born} \quad (1)$$

In the right-hand side of Eq. (1), the first two terms are the contributions from CPA, and the remaining two contributions are from the Debye–Hückel theory [49] and Born equation [48], respectively.

The residual Helmholtz energy for the cubic Soave–Redlich–Kwong EOS [50] is calculated from

$$A^{SRK} = nRT \left[-\ln \left(1 - \frac{b}{v} \right) - \frac{a(T)}{bRT} \ln \left(1 + \frac{b}{v} \right) \right] \quad (2)$$

Where n is the total number of moles, T is the temperature, R is the gas constant, v is the molar volume, b is the CPA co-volume parameter of the mixture, calculated from the pure component co-volume parameter b_i ,

$$b = \sum_i x_i b_i \quad (3)$$

And $a(T)$ is the temperature dependent energy parameter of the mixture, obtained via the Huron-Vidal/NRTL (HV-NRTL) infinite pressure mixing rule [29, 51],

$$\frac{a}{b} = \sum_i x_i \frac{a_i}{b_i} - \frac{g^{E,\infty}}{\ln 2} \quad (4)$$

$$\frac{g^{E,\infty}}{RT} = \sum_i x_i \frac{\sum_j x_j b_j \exp \left(-\alpha_{ji} \frac{\Delta U_{ji}}{RT} \right) \frac{\Delta U_{ji}}{RT}}{\sum_j x_j b_j \exp \left(-\alpha_{ji} \frac{\Delta U_{ji}}{RT} \right)} \quad (5)$$

Where x_i is the mole fractions of component i (solvent, cation, anion), $g^{E,\infty}$ is the excess Gibbs energy at infinite pressure calculated with the NRTL equation, α_{ji} is the NRTL non-randomness parameter, ΔU_{ji} is the change in interaction energy between like and unlike interactions ($\Delta U_{ji} = \Delta U_{ij} - \Delta U_{jj}$), and the temperature dependent component specific parameter a_i is given by

$$a_i = a_{0i} \left(1 + c_{1i} (1 - \sqrt{T_{ri}}) \right)^2 \quad (6)$$

Where T_{ri} is the reduced temperature of component i , defined as $T_{ri} = T/T_{ci}$, with T_{ci} the critical temperature of component i . Therefore, b_i , a_{0i} and c_{1i} are adjustable pure component CPA parameters. In this work, the CPA reduced energy parameter $\Gamma_i = a_{0i}/Rb_i$ is used.

It is worth pointing out that the HV-NRTL infinite pressure mixing rule has the flexibility to reduce to the classical one-fluid mixing rule if α_{ji} is set to zero and ΔU_{ji} is appropriately chosen. In order to apply the model over a wide range of temperature, a quadratic temperature dependence for the interaction parameter was proposed [29]

$$\frac{\Delta U_{ij}}{R} = \frac{\Delta U_{ij}^{ref}}{R} + \omega_{\Delta U_{ij}} \left[\left(1 - \frac{T}{T_{\Delta U_{ij}}} \right)^2 - \left(1 - \frac{T_{ref}}{T_{\Delta U_{ij}}} \right)^2 \right] \quad (7)$$

Where T_{ref} is the reference temperature and set to 298.15 K, and ΔU_{ij}^{ref} , $\omega_{\Delta U_{ij}}$ and $T_{\Delta U_{ij}}$ are adjustable parameters.

The residual Helmholtz energy for association A^{ASSOC} is similar to SAFT [52]: based on the formulation of Wertheim's association theory [53, 54, 55, 56] and can be found from the solution of the constrained optimization problem [57] given by

$$A^{assoc} = RT \left[\sum_i n_i \sum_{A_i} \left(\ln X_{A_i} - \frac{1}{2} X_{A_i} + \frac{1}{2} \right) \right] \quad (8)$$

$$\frac{1}{X_{A_i}} = 1 + \sum_j \rho_j \sum_{B_j} X_{B_j} \Delta_{A_i B_j} \quad (9)$$

In Eqs. (8) and (9), X_{A_i} is the fraction of site A on component i that is not bonded to any other site, ρ_j is the density of component j , and $\Delta_{A_i B_j}$ is the association strength, which is

calculated from

$$\Delta_{A_i B_j} = g(\rho) \left[\exp\left(\frac{\varepsilon^{A_i B_j}}{k_B T}\right) - 1 \right] b_{ij} \beta^{A_i B_j} \quad (10)$$

Where, the two association parameters are the association volume, $\beta^{A_i B_j}$, and the association energy, $\varepsilon^{A_i B_j}$, while b_{ij} is given as $b_{ij} = (b_i + b_j)/2$. The simplified radial distribution function $g(\rho) = (1 - 1.9\eta)^{-1}$, and the packing fraction η is equal to $b/4v$.

The contribution to the Helmholtz energy from ion-ion interactions is calculated from the Debye-Hückel theory [47], as shown in the following equation

$$A^{DH} = -\frac{k_B T V}{4\pi N_A \sum_i n_i z_i^2} \sum_i n_i z_i^2 \chi_i \quad (11)$$

Where, V is the total volume, n_i is the mole number of component i , k_B is Boltzmann constant, N_A is the Avogadro constant, Z_i is the charge of component i , and the function χ_i is given by

$$\chi_i = \frac{1}{d_i^3} \left[\ln(1 + \kappa d_i) - \kappa d_i + \frac{1}{2} (\kappa d_i)^2 \right] \quad (12)$$

Where, κ is the inverse Debye screening length, and d_i is the hard-sphere diameter of the ion. Maribo-Mogensen et al. [29, 30] assumed that in the Eq. (12) the same value of the ion diameter as in the physical part of the EOS can be used.

Finally, the contribution of ion-solvation is from the Born equation [48, 58]

$$A^{Born} = \frac{N_A e^2}{8\pi \varepsilon_0} \sum_i \frac{n_i z_i^2}{r_{Born,i}} \left(\frac{1}{\varepsilon_r} - 1 \right) \quad (13)$$

Where, $r_{Born,i}$ is the radius of the Born cavity caused by the transfer from vacuum to the fluid phase, and e is the elementary charge.

The relative static permittivity is of central importance in the thermodynamics of electrolyte solutions [59, 60]. In e-CPA, the model developed by Maribo-Mogensen [30, 61] for the relative static permittivity is used in both Debye-Hückel and Born terms. For more details, the reader is referred to the Support Information and Maribo-Mogensen et al. [30].

4. Results and Discussion

4.1 Parameter Setting and Discussion

As presented above, the framework of e-CPA is set up to account for each ion separately, and it is by nature ion specific. For a single salt/single solvent solution, there are in principle six pure component parameters (five CPA parameters and one Born term parameter) and twelve interaction parameters for the standard e-CPA EOS (as shown in Eqs. (4) and (5), the HV-NRTL mixing rule gives the possibility of having four additional adjustable parameters per interaction, which for a single salt in a solvent will be three interactions: cation-anion, cation-solvent, and anion-solvent). In order to minimize the number of parameters, a series of assumptions are made [29, 30, 61]: the temperature dependence parameter (c_{1i}) and the CPA reduced energy parameter (Γ_i) of ions are set to zero; the ions are assumed to be non-associating; the NRTL non-randomness factor and ion-ion interaction parameters are set to zero; the interaction parameters between ions and water are salt-specific, i.e. the cation-water and anion-water interaction parameters are equal.

It is also assumed that the Born radius may be estimated by using the following empirical equations, which were first proposed by Latimer et al. [62] and later supported by molecular simulation [63]

$$r_{Born,anion} = r_{anion} + 0.1 \text{ \AA} \quad (14)$$

$$r_{Born,cation} = r_{cation} + 0.85 \text{ \AA} \quad (15)$$

In Eqs. (14) and (15), r_{cation} and r_{anion} are the hard-sphere radii of cation and anion, respectively, which are equal to half of the ion diameters ($r_i = d_i/2$). $r_{Born,cation}$ and $r_{Born,anion}$ are the Born radii of cation and anion, respectively.

For simple monatomic ions such as Na^+ and Cl^- which can be assumed to be spherical, it is expected that the CPA co-volume parameter can be predicted to fair accuracy using the following equation [30, 46]

$$b = 2/3\pi N_A (2r_i)^3 \quad (16)$$

Where r_i is the hard-sphere radius of the ion i and N_A is the Avogadro constant.

As mentioned earlier, the TBA^+ is a relatively large, irregular organic cation with soft alkyl chains, and the negative charge is provided by the nitrogen atom. It is unclear which radius value reflects the physical facts more accurately. In this work, the same TBA^+ ion radius is used for all three TBAX aqueous solutions. Since the TBAB aqueous solution is the most widely studied system, and the one for which most experimental data is available, the TBA^+ ion radius is obtained by fitting the TBAB aqueous solution data.

With these assumptions, the estimation procedure is as follows: (1) the ion size of TBA^+ and HV-NRTL interaction parameters between ions and water are obtained by fitting the mean ionic activity coefficients and osmotic coefficients of TBAB aqueous solutions; (2) fixing the ion size of TBA^+ , the HV-NRTL interaction parameters between TBA^+ and water are obtained by fitting the mean ionic activity coefficients and osmotic coefficients simultaneously.

The objective function used for the regression is

$$F = \sum \left[\frac{\gamma_{\pm}^m(\text{cal}) - \gamma_{\pm}^m(\text{exp})}{\gamma_{\pm}^m(\text{exp})} \right]^2 + \sum \left[\frac{\Phi(\text{cal}) - \Phi(\text{exp})}{\Phi(\text{exp})} \right]^2 \quad (17)$$

Where, $\gamma_{\pm}^m$ represents the mean ionic activity coefficients, and Φ are the osmotic coefficients, 'cal' represents calculated values, and 'exp' are experimental data.

The results are typically listed as percentage average absolute deviations

$$AAD = \frac{1}{N} \sum_i^N \left| \frac{y_i^{\text{cal}} - y_i^{\text{exp}}}{y_i^{\text{exp}}} \right| \times 100\% \quad (18)$$

Where, N is the number of data points, y_i^{cal} represents the calculated results of any property, and y_i^{exp} represents the experimental data of a given property.

Mayrath and Wood [35] measured enthalpies of dilution of aqueous solutions of TBAB at 346.15 to 423.65 K, and they used these data to calculate the changes in osmotic coefficients and activity coefficients from 298.15 K to 373.15 K, which have been used to obtain the temperature dependent interaction parameters

The fitted parameters are presented in Table 3, and the related properties and parameters of water and anions taken from literature [30, 46, 64, 65, 66] are given in Tables S1 and

S2 in the Support Information. The anion radius used in this modeling work is the calculated ionic radius in solution from Marcus [66].

Table 3. Fitted, estimated and fixed e-CPA parameters and the regression performance

CPA	
Γ [K]	Set to 0
c_1	Set to 0
b [cm ³ /mol]	115.2*
$\beta^{A_i B_j}$	Set to 0
$\varepsilon^{A_i B_j} / R$ [K]	Set to 0
Debye-Hückel and Born terms	
r_i [Å]	2.25 (TBA ⁺ , Fit)
$r_{Born,i}$ [Å]	3.10* (TBA ⁺)
Interaction Parameter	
$\Delta U_{ij}^{ref} / R$ [K]	-114.9 (TBAB, Fit)
	-219.3 (TBAC, Fit)
	-450.1 (TBAF, Fit)
$T_{\Delta U_{ij}}$ [K]	192.4 (TBAB, Fit)
$\omega_{\Delta U_{ij}}$ [K]	137.3 (TBAB, Fit)
AAD at 298.15 K	
TBAB aqueous solution ($\gamma_{\pm}^m / \Phi$)	7.2% / 5.9% (0.0912~10.0 mol/kg)
TBAC aqueous solution ($\gamma_{\pm}^m / \Phi$)	6.6% / 4.5% (0.1~10.0 mol/kg)
TBAF aqueous solution ($\gamma_{\pm}^m / \Phi$)	4.8% / 2.6% (0.1~1.6 mol/kg)

* The Born radius $r_{Born,i}$ of cation is calculated from ion radius by using Eq. (15), the Born radius of anion is calculated from ion radius by using Eq. (14), the CPA co-volume b is calculated from ion radius by using Eq. (16).

Figure 3 presents the results of mean ionic activity coefficients and osmotic coefficients of TBAX aqueous solutions. It can be seen that, at the same molality, the order of values of osmotic coefficients and mean ionic activity coefficients are: TBAF > TBAC > TBAB. Combining this with pure component parameters and the parameters of Table 3, we observe that the order of the absolute value of the interaction parameter ΔU_{ij}^{ref} follows the opposite order of halide ion size. This can be explained by the fact that the smaller the radius of the halide ion is, the larger interaction with water molecules is expected.

The regressed value of the TBA^+ radius r is 2.25 Å, which is smaller than 3.81 Å [41] (smallest value listed in Table 2), and larger than the value of N_3^- (1.46 Å) [67]. Paricaud [11] reported the molecular radius of 1.927 Å for TBAB, and Ma et al. [16] obtained the ion radius of 1.4555 Å for TBA^+ . These researchers presented smaller radius of TBA^+ , one reason being that they did not take the Born term into account which may indicate that they incorporate the hydration effect into the long-range interaction. Moreover, it may indicate that all these electrolyte EOS might have not fully captured the physics of the TBAX aqueous solutions.

Figure 3. Calculated mean ionic activity coefficients and osmotic coefficients of TBAB, TBAC and TBAF aqueous solutions at 298.15 K using the e-CPA EOS against experimental data [33, 34, 36].

4.2 Modeling of Relative Static Permittivity

The relative static permittivity plays a very important role in thermodynamic modeling of electrolyte solutions when the primitive approach is employed. The predicted static permittivity from e-CPA is presented in Figure 4, in which calculation the polarizability of TBA^+ is $34.70 \times 10^{-40} \text{ C} \cdot \text{m}^2 \cdot \text{V}^{-1}$, taken from Gilkerson and Stewart's work [68]. The dot line represents an empirical equation reported by Buchner et al. [69], in which there are no experimental data reported. It has been stated that ion-pairs [69] and hydrophobic interactions [69, 70] exist in TBAX aqueous solution even at moderate concentrations, in which manner, the TBAX could be treated as a 'weak electrolyte' [71]. Both ion-pairs and hydrophobic effects can cause water structure making [72], and strengthen the hydrogen bonding around ions, thus increasing the relative static permittivity. According to Buchner et al. [69] and Kaatz [70], these effects may be responsible for the unusual behavior of the relative static permittivity of TBAB aqueous solution in Figure 4: dielectric saturation and the kinetic depolarization which both contribute to the decrease of the relative static permittivity, and the ion-pairs and hydrophobic hydration contribute to the increase of the relative static permittivity. More discussions are given in the Support Information.

Figure 4. Predicted relative static permittivity of the TBAB aqueous solution binary system at 298.15 K using the e-CPA EOS against the empirical correlation from Buchner et al. [69] and experimental data from Kaatz [69, 73].

It can be seen from Figure 4 that the values from e-CPA decrease monotonically with increasing solute molality as is the case for other electrolyte solutions. Under low to medium concentrations, e-CPA gives reasonable relative static permittivity for thermodynamic modeling, as e-CPA ignores the effect of kinetic depolarization which should not be included in thermodynamic modeling. On one hand, it needs to be pointed out that e-CPA does not take dissociation equilibrium into account for the fact that the electrolytes are not fully dissociated [74], so the current version of e-CPA cannot describe the possible ion-pairs and hydrophobic effects in TBAX aqueous solutions. On the other hand, there are very few experimental data of the relative static permittivity published for TBAX aqueous solutions, so more systematic measurements are recommended.

4.3 Modeling of other Properties

Volumetric properties are important thermodynamic properties. Unfortunately, only TBAB aqueous solution volumetric data are available [75, 76, 77, 78], and the molality range of experimental data is not as extended as those of the mean ionic activity coefficients and osmotic coefficients shown in Table 1. Few saturation pressure data for aqueous solutions

are available and only for TBAB aqueous solution [79]. The collected information of other properties is given in the Table S3 in the Support Information.

The liquid density experimental data [75, 76, 77, 78] are only available for the TBAB aqueous solution with the molality lower than 3.1 mol/kg water. The modeling results are shown in Figure 5, and it can be seen that e-CPA overestimates the liquid densities of TBAB solution, which may be because the model cannot represent the formation of low-density ice-like structures around the large hydrophobic TBA^+ [11].

Maribo-Mogensen et al. [29, 30] introduced a Peneloux volume translation, as shown in Eq. (19), to improve the description of density of salt solutions with e-CPA

$$v = v^{EoS} + \sum_i^{all\ ions} x_i C_i \quad (19)$$

Where v is the molar volume, v^{EoS} is the molar volume calculated from the e-CPA EOS, x_i is the mole fraction of ion i , and C_i is the Peneloux volume correction parameter of ion i . As the salt-specific approach is used in this work, the Peneloux parameters of cation and anion are the same.

The solid lines in Figure 5 show that e-CPA can give good agreement with experimental liquid density (AAD=0.2%) when using the Peneloux parameter of ions $C_i = 45.2 \text{ cm}^3/\text{mol}$.

Figure 5. Liquid densities of TBAB solutions at different temperatures from the e-CPA EOS (with parameters in Table 3) with and without using a Peneloux parameter against experimental data from Belandria et al. [76].

In addition to the calculations of activity coefficients, saturation pressure calculations are also important for hydrate modeling. Before calculating the saturation pressure of TBAB aqueous solution, the model was first used to predict the saturation pressure of NaCl solution under different molality and temperature conditions. The number of experimental data points [80, 81, 82, 83] is 327, the molality range is 0.5~7.2 mol/kg water, and the temperature range is 273.16~423.15 K. Excellent results are obtained for NaCl aqueous solution, as seen in Figure 6 (a). The AAD from the experimental data is 2.0%. It can be assumed that e-CPA can satisfactorily predict saturation pressure for single electrolyte systems.

When e-CPA is used for TBAB aqueous solution, much larger deviations are observed, with AAD=7.1% and 5.4% at the two temperatures, as presented in Figure 6 (b), which also shows the estimated saturation pressure from the experimental osmotic coefficients

$$P = P_w^{sat} a_w \quad (20)$$

Where P is the saturation pressure of the system, P_w^{sat} is the saturation pressure of pure water the same temperature, and a_w is the activity of water, calculable from the experimental osmotic coefficient.

In this equation, it is assumed that TBAB does not exist in the vapor phase, and it is a strong salt. It can be readily seen that the saturation pressure estimated from experimental osmotic coefficients match the prediction results of e-CPA very well.

In order to further investigate how organic salts perform in terms of saturation pressure, the experimental data of some organic salts aqueous solutions [84, 85, 86] are collected and analyzed, which are plotted in the Figure S3 in the Support Information. By comparing with saturation pressure data of TBAB aqueous solution, we can see that the saturation pressures of most salt aqueous solutions (including another Tetra-*n*-butyl ammonium salt TBANO₃ aqueous solution) are close to the values of NaCl aqueous solution in the given

molality range, while TBAB aqueous solutions show very different saturation pressure values. Therefore, more systematic measurements for the saturation vapor pressure are needed.

Figure 6. (a) Predicted saturation pressure of NaCl aqueous solution for 353.15 K and 363.15 K from the e-CPA EOS against experimental data [83]; (b) Saturation pressure of TBAB aqueous solution from e-CPA and experimental osmotic coefficients, and saturation pressure of NaCl aqueous solution from e-CPA, both at 298.15 K. Experimental data are taken from Kurzin et al. [79], and Zhang et al. [81].

4.4 Discussion

Thermodynamic modeling for TBAX aqueous solutions has been investigated with different approaches in the literature. Table 4 summarizes the properties studied with different models for the TBAX aqueous solutions in order to present a clear comparison of the different methodologies, and an extensive analysis of parameter estimation in e-CPA has been discussed in the Support Information.

In terms of general modeling approach, SAFT-VRE, MPT, e-CPA and e-NRTL considered TBAX as strong electrolytes in water, and the ion-pairs are not considered. Only AMSA-NRTL [20] can treat micelle formation because AMSA-NRTL electrolyte model includes a term of ion-pairs contribution. No model takes the possible hydrophobic effect into account.

In terms of density performance, in the $\varphi - \gamma$ approaches, the density of TBAX aqueous solutions was determined using correlation equations. In the $\varphi - \varphi$ approaches, both SAFT-VRE and e-CPA overestimate the experimental densities of TBAB solutions. Paricaud explained that it is because SAFT-VRE cannot represent formation of low-density ice-like structures around the large hydrophobic TBA^+ [11]. As reported in the section 4.1, the diameter of TBA^+ in all three models are smaller than the values published in literature (listed in Table 2). Moreover, as shown in Table S4 in the Support Information, the smaller the diameter of TBA^+ is used, the better density is obtained. These imply that the models might have not captured the essential aspects of physics of TBAX aqueous solution. It is demonstrated in this work that with a Peneloux parameter e-CPA can give a very good agreement with experimental data.

In terms of electrostatic contributions, SAFT-VRE uses a MSA term in Paricaud's work [11], MPT uses a Debye–Hückel term in Ma et al.' work [16], and in this work, e-CPA combines Debye–Hückel and Born terms. Naturally it is the developer's choice to use MSA or Debye–Hückel in an EOS model, as it has been proved that they perform similarly [87]. Different than both SAFT-VRE and MPT, e-CPA explicitly takes ion hydration into account via the Born equation, and the relative static permittivity of electrolyte solution is calculated

by a theoretical model, which extends the framework developed by Onsager, Kirkwood, and Fröhlich [88, 89, 90] to associating mixtures. This may increase the complexity of the model but make the model more reasonable.

In principle, SAFT-VRE, MPT, e-CPA and e-NRTL are ion specific by nature, while it is the users' choice when a salt-specific or an ion-specific should be followed, as well as the number of adjustable parameters to be used.

In Paricaud's work [11], the salt-specific approach was used in SAFT-VRE for TBAB, TBAC and TBAF aqueous solutions. For one single salt/single solvent system, there are three adjustable parameters at 298.15 K, one temperature dependent parameter. In the work of Ma et al. [16], the ion-specific approach was used in MPT for TBAB and TBAF aqueous solutions. For one single salt/single solvent system, there are four adjustable parameters at 298.15 K, no temperature dependent parameter.

The salt-specific approach was used in AMSA-NRTL for TBAB aqueous solution. For one single salt/single solvent system, AMSA-NRTL has five adjustable parameters. e-NRTL uses salt-specific approach, it has been applied for TBAB, TBAC and TBAF aqueous solutions. For one single salt/single solvent system, e-NRTL has two adjustable parameters. The temperature dependence of interaction energy parameters was neglected in AMSA-NRTL and e-NRTL for modelling of TBAX aqueous solution systems [21-24].

Unlike the approach using a different ion size for each salt in SAFT-VRE [11], in the presented e-CPA approach, the diameter of TBA^+ is first fitted to the TBAB data, and then the same value is used for other TBAX systems. In addition to the TBA^+ diameter, there are one adjustable interaction parameter at 298.15 K, and two temperature dependent interaction parameters.

5. Conclusions

This work presents a theoretical study on the thermodynamic modeling for TBAX aqueous solutions by using the e-CPA EOS, which includes Debye–Hückel and Born terms for electrostatic contributions. Several properties of these aqueous solutions as well as

various modeling approaches have been considered in order to investigate the effect of the number and type of adjustable parameters used.

The thermodynamic modeling of these systems is challenging, among other reasons because the TBA^+ ion has alkyl chains and low charges, thus exhibiting hydrophobic-like character. There is evidence that the unusual solution behavior of TBA^+ salts is related to the hydrophobicity of these salts in aqueous solutions.

The e-CPA parameters (ionic size of TBA^+ , interaction parameters) are estimated from mean ionic activity coefficients and osmotic coefficients. Using the obtained parameters, e-CPA was subsequently used to predict the densities of TBAB aqueous solutions and relative static permittivity of TBAX aqueous solutions. It can be concluded that e-CPA can correlate satisfactorily the mean ionic activity coefficients and osmotic coefficients of TBAX aqueous solutions over extensive temperature and concentration ranges. e-CPA with the parameters obtained in this work cannot describe the enhancement of the relative static permittivity due to the ion-pairs and hydrophobic effects. Adding dissociation equilibrium to the model is a potential solution for organic salt solutions where ion-pairs and hydrophobic effects exist.

Table 4. Properties studies for TBAX aqueous solutions at 298.15 K *

Appr.	Models	Max molality [mol/kg]			Adjustable parameters			Performance			ε_r used		
		TBAB	TBAC	TBAF	TBAB	TBAC	TBAF	$AAD (\gamma_{\pm}^m / \Phi)$				AAD	$AAD (P^{sat})$ (TBAB)
								(Liquid density) (TBAB)					
$\varphi - \varphi$	e-CPA	10.0	10.0	1.6	1 (TBA ⁺ size, from TBAB) + 1 (interaction param)			7.2% / 5.9%	6.6% / 4.5%	4.8% / 2.6%	9.2% (w/o C_i) 0.2% (with C_i)	7.7% (298.15 K) 5.9% (323.15 K)	a theoretical model [#]
	SAFT-VRE [11]	10.0	10.0	1.6	3			3.9% / 4.6%	-	-	Overestimate	-	Constant (equal to solvent)
	MPT [16]	-	-	-	4	-	4	-	-	-	-	-	
$\varphi - \gamma$	EOS + NRTL + correlation [25]	-	-	-	2	-	-	-	-	-		-	-
	EOS + e-NRTL [21-23]	27.0	15.0	1.6	2			3.29% / -	4.57% / -	1.40% / -	Correlation 0.06%	-	-
	EOS + AMSA- NRTL [24]	21.0	-	-	5	-	-	1.17% / 3.54%	-	-		-	-

* e-CPA with parameters in Table 3. For φ - γ approach, we treat the number of adjustable parameters in activity coefficient model as the total number of adjustable parameters. [#] It is composition and volume dependent.

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List of abbreviations/symbols

List of abbreviations

AMSA	Mean Spherical Approximation for Aqueous Electrolytes includes Ionic Hydration and Association
CPA	Cubic-Plus-Association
e-CPA	electrolyte Cubic-Plus-Association
e-NRTL	electrolyte Non-Random Two Liquid model
EOS	Equation of State
MPT	Modified Patel-Teja
NRTL	Non-Random Two Liquid model
PR	Peng–Robinson
SCH	Semi-Clathrate Hydrate
SAFT-VRE	Statistical Associating Fluid Theory with Variable Range for Electrolytes
SRK	Soave–Redlich–Kwong
TB	Trebble–Bishnoi
TBA ⁺	Tetra-n-butyl Ammonium Cation
TBP ⁺	Tetra-n-butyl Phosphonium Cation
TBAX	Tetra-n-butyl Ammonium Halides
TBAB	Tetra-n-butyl Ammonium Bromide
TBAC	Tetra-n-butyl Ammonium Chloride
TBAF	Tetra-n-butyl Ammonium Fluoride
TBPB	Tetra-n-butyl Phosphonium Bromide

List of symbols

a	SRK temperature dependent energy parameter $\left[\frac{\text{Pa}\cdot\text{m}^6}{\text{mol}^2}\right]$
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a_w	activity of water
A^{SRK}	residual Helmholtz energy contribution for the cubic Soave–Redlich–Kwong EOS [J/mol]
A^{ASSOC}	residual Helmholtz energy contribution for association [J/mol]
A^{DH}	residual Helmholtz energy contribution from the Debye–Hückel theory [J/mol]
A^{Born}	residual Helmholtz energy contribution Born hydration model [J/mol]
b	CPA co-volume [cm ³ /mol]
c_1	pure component temperature dependence parameter for Soave's $\alpha(T)$ -function
cL	molar concentration of salt [mol/L]
C_i	Peneloux volume correction parameter of component i [m ³ /mol]
d_i	hard-sphere diameter of ion i [Å]
e	the elementary charge. ($1.60217646 \times 10^{-19}$ [C])
$g^{E,\infty}$	excess Gibbs energy at infinite pressure [KJ/mol]
$g(\rho)$	radial distribution function
k_{ij}	binary interaction parameter between solvents
k_B	Boltzmann constant ($1.3806503 \times 10^{-23}$ [J/K])
n	total amount of component [mol]
N	number of data points
N_A	Avogadro constant (6.0221415×10^{23} [1/mol])
P	pressure
P_w^{sat}	saturation pressure of water
r_i	radius of the ion i [Å]
R	ideal gas constant (8.3144621 [J/mol/K])
$r_{Born,i}$	Born radius of the ion i [Å]
T	temperature [K]
T_C	critical temperature [K]
T_r	reduced temperature
T_{ref}	reference temperature (298.15 K)
$T_{\Delta U_{ij}}$	an adjustable parameter of the temperature dependency [K]; Eq. (7)
v	molar volume [m ³ /mol]
v^{EoS}	molar volume calculated from e-CPA [m ³ /mol]

V	volume [m^3]
x_i	mole fraction of component i
X_{Ai}	fraction of site A on molecule i that is not bonded to any other site
Z_i	charge of ion i

Greek Symbols

α_{ji}	NRTL non-randomness parameter; Eq. (5)
$\beta^{A_i B_j}$	association volume between site A on molecule i and site B on molecule j
$\gamma_{\pm}^m$	mean ionic activity coefficient
Γ	CPA reduced energy parameter (a_0/Rb) [K]
$\Delta_{A_i B_j}$	association strength (equilibrium constant) between site A on molecule i and site B on molecule j [m^3/mol]
ΔU_{ij}	Change in interaction energy between like and unlike interactions [J/mol]; Eq. (5)
ΔU_{ij}^{ref}	binary interaction parameter between ion and water at the reference temperature [J/mol]; Eq. (7)
$\varepsilon^{A_i B_j}$	association energy between site A on molecule i and site B on molecule j [bar.L/mol]
ε_0	vacuum permittivity (8.85419×10^{-12} [F/m])
ε_r	static permittivity relative to vacuum
η	packing factor; $\eta = b/4v$
κ	inverse Debye length [1/m]
ρ	molar density of fluid [mol/m^3]
Φ	osmotic coefficient
$\omega_{\Delta U_{ij}}$	linear dependency in interaction energy calculation [K]; Eq. (7)

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