Modeling thermodynamic properties of electrolytes: Inclusion of the mean spherical approximation (MSA) in the simplified SAFT equation of state

Y. Hajeb [1], A. A. Izadpanah [1,*], Sh. Osfouri [1]

1. Department of Chemical Engineering, Faculty of Petroleum, Gas and Petrochemical Engineering, Persian Gulf University, Bushehr, Iran

ARTICLE INFO

* Corresponding author;
E-mail: izadpanah@pgu.ac.ir
Tel.: +98 77 33222600
Fax: +98 77 33441495

ABSTRACT

In this work, an equation of state has been utilized for thermodynamic modeling of aqueous electrolyte solutions. The proposed equation of state is a combination of simplified statistical associating fluid theory (SAFT) equation of state (similar to simplified PC-SAFT) to describe the effect of short-range interactions and mean spherical approximation (MSA) term to describe the effect of long-range interactions. In this model, the salt-based approach or restricted primitive model has been used to adjust the four parameters of the model. The salt (ion) parameters have been estimated through simultaneous fitting to experimental mean ionic activity coefficient and liquid density data of strong electrolytes. Four strong electrolytes, three 1:1 and one 1:2 electrolytes have been used. Using adjusted ion parameters, osmotic coefficient of solvent has been predicted with 0.79% average relative deviation (ARD%). Results show that simplified SAFT, in combination with the MSA term has ARD% about 1% and less for correlating of density and mean ionic activity coefficient of electrolyte solutions.

1. Introduction

Electrolyte solutions are encountered in many processes and industries such as biological (pharmaceutical and protein purification), chemical (desalination of sea water, liquid extraction, distillation, waste water treatment, post combustion carbon dioxide absorption, sweetening of sour gases, crystallization and …) and geological (carbon capture sequestration, enhanced oil recovery, …). Therefore, knowledge and prediction thermodynamic properties of these systems are important. For modeling electrolyte solutions besides considering short range intermolecular forces it must require to consider long range electrostatic forces between charged particle and dipole and multi-pole forces between charged particles and solvent molecule. Then modeling electrolyte solutions are difficult than other systems.

During recent years, many different models have been proposed for describing thermodynamic properties of aqueous electrolyte solutions. There are two kinds of approaches to describe the non-ideality of electrolyte solutions; one is the application of activity coefficient models, and the other consists of equation of state (EoS) models. Despite the simplicity and vast application of activity coefficient models, there are some disadvantages as well; one disadvantage is that the density of solution cannot be derived from the model itself, and they are pressure-independent. The EoS does not have these disadvantages, but to extend the EoSs to electrolyte solutions, an additional Helmholtz free energy term is needed to consider the electrostatic interactions between charged particles. For this goal, long-range electrostatic terms such as the Debye-Huckel term [1] or the MSA term[2, 3] can be used.

Different activity coefficient models were used for strong electrolyte [4-6], weak electrolyte [7], multiple electrolyte solutions [8, 9] and multiple solvent electrolyte solutions [10-13].

The first development and application of EoS to electrolyte solution was done by Planche and Renon [14]. Afterward, the model of Furst and Renon [15], Myers et al. [16], Clarke and Bishnoi [17], Haghtalab and Mazloumi [18] are some examples. In these EoSs for electrolyte solutions, cubic equation of state such as SRK, PR, TB and square well were used to describe short range forces and MSA term was used to consider long range forces in the solution.

Wu and Prausnitz [19], Lin et al. [20] and Inchekel et al. [21] used CPA EOS and MSA term to describe properties of electrolyte solutions.

Collinet and Gmehling [22] combined volume translated PR EOS with group contribution model (LIFAC) and used this EoS to calculate properties of electrolyte solutions. This model was used to calculate vapor-liquid equilibrium of systems containing two or three constituents (two solvents and one electrolyte). For describing solubility of gas in electrolyte solutions one additional binary interaction parameter between contribution groups was needed.

Various versions of SAFT EoS and restricted primitive model (RPM) were used to model electrolyte solutions. Galindo et al. [23] used statistical association theory with variable potential range (SAFT VR) and restricted mean spherical approximation to model electrolyte solutions. The square well potential function was used in this SAFT VR. Only two adjustable parameters were used to describe interaction between ions and solvent molecules. Then Patel et al.

[24] used this model to study the effect of salinity of strong electrolyte on solubility of alkanes in water. Behzadi et al. [25] used SAFT VR with Yukawa potential function and non-restricted mean spherical approximation to model electrolyte solution. The solvents were water and alcohols. The model parameters were obtained by ion base and salt base approaches.

Tan et al. [26] used SAFT1 with restricted primitive model (RPM) to calculate properties of strong electrolyte solutions such as density, vapor pressure, mean ionic activity coefficient and osmotic coefficient of solvent. In SAFT1 EoS rather than other versions of SAFT one molecule can have two or more unequal segments. To extend the results to temperatures other than 25 $^{\circ}$C, they considered the volume of segment, energy and hydration radius of ions as functions of temperature. Ji et al. [27] extended the SAFT1-RPM to system H_2O+CO_2+NaCl. To calculate accurate phase equilibrium and density of this system, one adjustable parameter between CO_2 and Na^+ and Cl^- was required to modify short range interaction energy between gas and ions.

Tan et al. [28] extended the SAFT1-RPM to bivalent ions. It was done by using a new dispersion term in the SAFT1 EoS. The equation was named SAFT2. Ion base parameters for 5 cations and 6 anions (mono and bivalent) were obtained by regression of density and mean ionic activity coefficient of 24 electrolyte solutions. Ji et al. [29] used modified SAFT2-RPM and extended this model to bivalent ions. Also, this model was used to calculate thermodynamic properties of synthetic sea water, successfully. As well as, it was well-known that the properties of synthetic sea water depend on concentration of ions in it not concentration of salts.

Ji and Adidharma [30] used SAFT2 with ion based parameters. A new set of parameters for 5 cations (Li^+, Na^+, K^+, Ca^{2+}, Mg^+) and 6 anions (Cl^-, Br^-, I^-, NO_3^-, SO_4^{2-}) was obtained by fitting experimental density and mean ionic activity coefficient of single electrolyte at 298.15 K. Ji and Adidharma [31] extended SAFT2-RPM EoS to 473.15 K and 1000 bar. In order to correlate properties of electrolyte solutions at high pressure, they used binary interaction coefficient equal to 0.5 in mixing rule of short range dispersion energy term. Also, to correlate properties of electrolytes at temperature higher than 298.15 K, four ion parameters in the SAFT2-RPM EOS were depended on temperature as a polynomial of order two. Comparison between modeling results and experimental data at high temperature and pressure showed acceptable accuracy of this model.

Also, Cameretti et al. [32] and Held et al. [33] used PC-SAFT with DH term to model strong electrolyte solutions. Rozmus et al. [34] used PPC-SAFT with MSA term to model electrolyte solutions. Short range energy between water and ions was considered by association between water and ions.

In this work, the simplified SAFT (s-SAFT) equation of state in combination with MSA electrolyte term has been used to correlate the thermodynamic properties of four single-salt aqueous electrolyte solutions at 298 K and atmospheric pressure. For simplicity and reduction of computation time s-SAFT EoS similar to s-PC-SAFT EoS was used. The model is described first, and then the procedure of parameter estimation is presented. Finally, calculation of densities of solutions, mean ionic activity coefficients, and osmotic coefficients of solvent are given and compared to experimental data.

2. Equation of state

The equation of state used here is combination of simplified SAFT (s-SAFT), similar to s-PC-SAFT [35], and mean spherical approximation (MSA) to describe the long-range electrostatic (Coulombic) interactions between ions. The equation of state for electrolyte can be defined in terms of dimensionless residual Helmholtz free energy as follows

$$a^{res} = a^{hs} + a^{chain} + a^{disp} + a^{assoc} + a^{ion} \tag{1}$$

Where a=A/RT is dimensionless Helmholtz free energy and superscripts mean residual, hard-sphere, chain, dispersion, association, and ionic interactions, respectively. Except for the last term, which accounts for the long-range electrostatic interaction, the other terms on the right-hand side account for relatively short-range interactions. The association contribution is only considered for water molecules and dispersion interaction was considered between salt and water.

It should be emphasis the s-SAFT EoS for pure substances is reduced to SAFT EoS and parameters of the SAFT EoS can be used for pure substances.

2.1. Simplified SAFT equation of state for mixtures

The total residual Helmholtz free energy in the simplified SAFT equation of state is again given by

$$a^{res} = a^{hs} + a^{chain} + a^{disp} + a^{assoc} \tag{2}$$

In the hard sphere term the segments are not bonded to form chains, but are single hard spheres; therefore, the mixture is a hard sphere mixture. Based on the result of Mansoori et al. [36] for hard sphere mixtures, the Helmholtz energy is

$$\frac{a^{hs}}{RT} = \frac{6}{\pi N_{Av} \rho} \left[\frac{(\zeta_2)^3 + 3\zeta_1\zeta_2\zeta_3 - 3\zeta_1\zeta_2(\zeta_3)^2}{\zeta_3(1-\zeta_3)^2} - \left[\zeta_0 - \frac{(\zeta_2)^3}{(\zeta_3)^2} \right] \ln(1-\zeta_3) \right] \tag{3}$$

With

$$\zeta_k = \frac{\pi N_{Av} \rho}{6} \sum_{i=1}^{N} x_i m_i (d_{ii})^k \qquad k = 0-3 \tag{4}$$

Where ρ is the total molar density of molecules, x_i is the mole fraction of compound i, m_i is the number of segments per molecule i, and d_{ii} is the temperature dependent segment diameter.

Next we consider the attractive force between segments, again assuming that the attractive potential is the square-well potential. Helmholtz energy of dispersion term becomes

$$\frac{a^{disp}}{RT} = m \sum_{i=1}^{4} \sum_{j=1}^{9} D_{ij} \left[\frac{u}{kT} \right]^i \left[\frac{\eta}{\tau} \right]^j \tag{5}$$

Where D_{ij} is the universal constants fit to thermodynamic data of argon by Chen and Kreglewski [37] and listed in table 1, and m is the average segment number, u is the average segment energy, and η is the average reduced density (packing fraction).

$$m = \sum_{i=1}^{N} x_i m_i \tag{6}$$

$$\eta = \frac{\pi N_{Av} \rho}{6} \sum_{i=1}^{N} x_i m_i (d_{ii})^3 = \zeta_3 \tag{7}$$

$$\frac{u}{kT} = \frac{\sum_{i=1}^{N} \sum_{i=1}^{N} x_i x_j m_i m_j \upsilon_{ij}^0 (u_{ij}/kT)}{\sum_{i=1}^{N} \sum_{i=1}^{N} x_i x_j m_i m_j \upsilon_{ij}^0} \tag{8}$$

With

$$\upsilon_{ij}^0 = \left(\frac{1}{2} \left[(\upsilon_i^0)^{1/3} + (\upsilon_j^0)^{1/3} \right] \right)^3 \tag{9}$$

$$u_{ij} = \sqrt{u_{ii} u_{jj}} (1 - k_{ij}) \tag{10}$$

$$\upsilon_i^0 = \upsilon_i^{00} \left[1 - 0.12 \left(-\frac{3u_i^0}{kT} \right) \right]^3 \tag{11}$$

$$u_{ii} = u_i^0 \left(1 + \frac{e}{kT} \right) \tag{12}$$

The k_{ij} are binary interaction parameters that can be fit to experimental data.

Table 1. D_{ij} Universal constants [37]

	i=1	i=2	i=3	i=4
j=1	-8.8043	2.9396	-2.8225	0.34
j=2	4.1646270	-6.0865383	4.7600148	-3.1875014
j=3	-48.203555	40.137956	11.257177	12.231796
j=4	140.43620	-76.230797	-66.382743	-12.110681
j=5	-195.23339	-133.70055	69.248785	0.0
j=6	113.51500	860.25349	0.0	0.0
j=7	0.0	-1535.3224	0.0	0.0
j=8	0.0	1221.4261	0.0	0.0
j=9	0.0	-409.10539	0.0	0.0

Next chain molecules in the system are formed by the bonding of chain sites. The chain term for a mixture that derived by Chapman et al.[38] is:

$$\frac{a^{chain}}{RT} = \sum_{i=1}^{N} x_i (1 - m_i) \ln \left(g^{hs}(d_{ii}) \right) \tag{13}$$

$$g^{hs}(d_{ii}) = \frac{1 - (1/2)\eta}{(1-\eta)^3} \tag{14}$$

$$\eta = \frac{\pi N_{Av} \rho}{6} \sum_{i=1}^{n} x_i m_i d_{ii}^3 = \zeta_3 \tag{15}$$

Finally, the effect of association is considered. The association term for a mixture that given by Chapman et al. [38] is:

$$\frac{a^{assoc}}{RT} = \sum_{i=1}^{N} x_i \left[\sum_{A_i} \left[\ln X^{A_i} - \frac{X^{A_i}}{2} \right] + \frac{1}{2} M_i \right] \tag{16}$$

Where M_i is the total number of association sites on molecule i, and X^{A_i} is the mole fraction of molecule i not bonded at sites A and is given by

$$X^{A_i} = \left[1 + N_{Av}\rho \sum_{j=1}^{N} \sum_{B_j} x_j X^{B_j} \Delta^{A_i B_j} \right]^{-1} \tag{17}$$

Where $\Delta^{A_i B_j}$ is the association strength between site A_i, and B_j given by

$$\Delta^{A_i B_j} = g^{hs}\left(d_{ii}\right)\left[\exp\left(\frac{\varepsilon^{A_i B_j}}{kT}\right) - 1 \right]\sigma_{ij}^{3}\kappa^{A_i B_j} \tag{18}$$

Also in the association strength term in s-SAFT EoS the radial distribution function $g^{hs}(d_{ii})$ was replaced instead $g^{hs}(d_{ij})$.

The following combining rules were used to define the association parameters in equation (37)

$$\varepsilon^{A_i B_j} = \left(\varepsilon^{A_i A_i} + \varepsilon^{B_j B_j} \right)\big/2 \tag{19}$$

$$\sigma_{ij} = \left(\sigma_i + \sigma_j \right)\big/2 \tag{20}$$

$$\kappa^{A_i B_j} = \sqrt{\kappa^{A_i A_i}\kappa^{B_j B_j}} \tag{21}$$

Where $\varepsilon^{A_i B_i}$, and $\kappa^{A_i B_i}$ are the association energy and volume for an interaction between site A on molecule i and site B on molecule j.

In term of compressibility factor the s-SAFT EoS is written as follows:

$$Z = \frac{PV}{RT} = Z^{hs} + Z^{disp} + Z^{chain} + Z^{assoc} + 1 \tag{22}$$

With

$$Z^{hs} = \frac{6}{\pi N_{Av}\rho}\left[\frac{\zeta_0\zeta_3}{1-\zeta_3} + \frac{3\zeta_1\zeta_2}{\left(1-\zeta_3\right)^2} + \frac{3\zeta_2^3}{\left(1-\zeta_3\right)^3} - \frac{\zeta_3\zeta_2^3}{\left(1-\zeta_3\right)^3} \right] \tag{23}$$

$$Z^{disp} = m\sum_{i=1}^{4}\sum_{j=1}^{9} jD_{ij}\left[\frac{u}{kT} \right]^{i}\left[\frac{\eta}{\tau} \right]^{j} \tag{24}$$

$$Z^{chain} = \sum_{i=1}^{N} x_i\left(1-m_i\right)\left(\frac{\rho}{g^{hs}\left(d_{ii}\right)}\frac{\partial g^{hs}\left(d_{ii}\right)}{\partial\rho} \right) \tag{25}$$

$$Z^{assoc} = -\frac{1}{2}\left(1+\rho\left[\frac{\partial\ln\left(g^{hs}\left(d_{ii}\right)\right)}{\partial\rho} \right] \right)\sum_{i=1}^{N} x_i\sum_{A_i}\left(1-X^{A_i}\right) \tag{26}$$

2.2. Ionic term (MSA)

In this work, the contribution due to the electrostatic interactions between ions, cation and anion, is calculated using (restricted premitive model) mean spherical approximation (MSA) term[2, 3], also, it is assumed all ions in the system have the same diameter σ (salt base). With this assumption the ion contribution to the Helmholtz free energy of the system is:

$$a^{ion} = -\frac{2\Gamma^3}{3\pi N_{Av}\rho}\left(1+\frac{3}{2}\sigma\Gamma \right) \tag{27}$$

Where σ is the ion diameter, Γ is the MSA screening parameter and κ is the Debye screening length. These quantities are:

$$\Gamma = \frac{1}{2\sigma}\left[\sqrt{1+2\sigma\kappa}-1\right] \tag{28}$$

$$\kappa = \sqrt{\frac{e^2 N_{Av}^2 \rho}{\varepsilon_w \varepsilon_0 RT}\sum_{ions} x_i z_i^2} \tag{29}$$

Where e is the electronic unit charge (1.60219×10^{-19}C), ε_0 is the vacuum permittivity (8.8542×10^{-12}), and ε_w is the relative permittivity of pure water can be determined from the follow equation[39]

$$\varepsilon_w = 281.67 - 1.0912 T + 1.6644\times10^{-3} T^2 - 9.7592\times10^{-7} T^3 \tag{30}$$

The contribution of MSA term in the compressibility factor can be obtained as follows:

$$Z^{MSA} = \frac{\partial a^{MSA}}{\partial \rho} = \frac{\partial a^{ion}}{\partial \rho} = \left(\frac{\partial a^{MSA}}{\partial \Gamma}\right)\left(\frac{\partial \Gamma}{\partial \kappa}\right)\left(\frac{\partial \kappa}{\partial \rho}\right) \tag{31}$$

2.3. Thermodynamic properties

In electrolyte solutions, the mole fractions of solvent, cation, and anion, respectively, is:

$$x_{solvent} = \frac{1000/M_{solvent}}{1000/M_{solvent} + \nu m} \tag{32}$$

$$x_{cation} = \frac{\nu^+ m}{1000/M_{solvent} + \nu m} \tag{33}$$

$$x_{anion} = \frac{\nu^- m}{1000/M_{solvent} + \nu m} \tag{34}$$

Where $M_{solvent}$ is the molecular mass of the solvent, m is the molality, i.e., the mole number of salt in 1 kg of solvent, ν is the total number of molecules upon complete dissociation of one molecule of salt, and $\nu+$ and $\nu-$ are the number of cations and anions, respectively, in one molecule of the salt.

The activity coefficient of electrolyte is one of the important properties for phase equilibrium calculations. When applying an EoS approach, the activity coefficient should be derived from fugacity coefficients. The activity coefficient of a solvent species in an electrolyte solution is

$$\gamma_{solvent}(T,P,x) = \frac{\hat{\varphi}_{solvent}(T,P,x)}{\varphi_{solvent}^{pure}(T,P)} \tag{35}$$

Where $\varphi_{solvent}^{pure}(T,P)$ is the fugacity coefficient of pure solvent at the temperature and pressure of the system. The molality- based activity coefficient for a solute species is then calculated as

$$\gamma_i^m(T,P,x) = \left(\frac{1}{1+\nu m M_{solvent}}\right)\left[\frac{\hat{\varphi}_i(T,P,x)}{\hat{\varphi}_i(T,P,x_i=0)}\right] \tag{36}$$

Where $\hat{\varphi}_i(T,P,x_i=0)$ is the fugacity coefficient of species i at infinite dilution. Because activity coefficients of the individual ionic species in an electrolyte solution cannot be directly measured, an average activity coefficient for the dissolved salt is defined. For a solution consisting of a single salt, the mean ionic activity coefficient (MIAC) is defined as

$$\gamma_{\pm}^{m} = \left[\left(\gamma_{+}^{m} \right)^{\nu+} \left(\gamma_{-}^{m} \right)^{\nu-} \right]^{1/\nu} \tag{37}$$

In terms of eq 56, this becomes

$$\gamma_{\pm}^{m}(T,P,x) = \left(\frac{1}{1+\nu m M_{solvent}} \right) \left[\frac{\hat{\varphi}_{+}(T,P,x)}{\hat{\varphi}_{+}(T,P,x_{+,-}=0)} \right]^{\nu+/\nu} \left[\frac{\hat{\varphi}_{-}(T,P,x)}{\hat{\varphi}_{-}(T,P,x_{+,-}=0)} \right]^{\nu-/\nu} \tag{38}$$

Consequently, the osmotic coefficient in an electrolyte solution is determined from

$$\Phi(T,P,x) = -\frac{\ln\left[x_{solvent} \gamma_{solvent}(T,P,x) \right]}{\nu m M_{solvent}} \tag{39}$$

It should be noted that the MSA is in the McMillan-Mayer framework but equation of state is in the Lewis-Randall framework. In this work the conversion between these two frameworks was neglected and assumed to be compensated by parameters [16].

3. Results and Analysis

In this work, the salt-based approach or restricted primitive model has been utilized to obtain a set of salt or ionic parameters. Because of using salt-based approach, for each salt, the parameters for the cations and anions are the same. For the studied electrolyte solutions, short-range dispersion interaction between solvent-solvent as well as salt-solvent was considered in the model. For simplicity, the ions are considered as non-associating compounds. In the fitting of electrolytes parameters, interaction parameter between water, and salt was considered to zero and this effect was compensated by the salt parameters. We focused on aqueous electrolyte solutions at 25 °C and 1 bar and it was assumed that dissolved salt is fully ionized in the solution and no ion paring is occurred.

The equation of state proposed here has four adjustable parameters for each salt: the segment number m; the temperature independent segment molar volume in a closed-packed arrangement υ^{00}; the temperature independent interaction energy between segments u^{0}/k; and the ionic diameter σ. m, υ^{00} and u^{0}/k are relevant to the simplified SAFT EOS, and the last parameter σ is relevant to the MSA electrolyte term.

For this purpose, in the first step, four conventional salts including NaCl, KCl, NaBr, and CaCl₂ have been selected. Then, the simplified SAFT EOS (or SAFT) parameters for water were taken from Wolbach and Sandler [40]; as given in Table 2, and the salt-based parameters for electrolytes have been adjusted by simultaneous regression of experimental data on mean ionic activity coefficient (MIAC) and liquid density of solutions at 298K and 1bar. The following objective function has been used for parameter optimization:

$$OF = \frac{1}{N_{p}} \sum_{j=1}^{N_{P}} \left(\left| \frac{\gamma_{\pm,j}^{m,\exp} - \gamma_{\pm,j}^{m,cal}}{\gamma_{\pm,j}^{m,\exp}} \right| + \left| \frac{\rho_{j}^{\exp} - \rho_{j}^{cal}}{\rho_{j}^{\exp}} \right| \right) \tag{60-40}$$

where N_{p} is the number of data point. The results are reported in Table 3.

Table 2. Simplified SAFT equation of state parameters for pure water [40]

Association scheme	m	$v^{00}\left(\frac{mL}{mol}\right)$	$\frac{u^0}{k}(K)$	$\frac{\varepsilon^{AB}}{k}(K)$	$\kappa^{AB}\times 10^2$	$\frac{ARD\,(\%)^a}{P^{vap}}$	$\frac{ARD\,(\%)^a}{\rho^{liq}}$
4C	1.406	8.00	212.91	1809	9.109	1.74	2.89

$$^aARD\,(\%)=(100/N\,)\sum_{i=1}^{N}\left|1-\left(\Omega_i^{cal}/\Omega_i^{\exp}\right)\right|,\ \text{where}\ \Omega\ \text{is}\ \rho^{liq}\ \text{or}\ P^{vap}$$

Table 3. Simplified SAFT EOS with MSA electrolyte term parameters for electrolytes that fitted at 298K and 1bar

ion	Parameters					$ARD^a\,(\%)$		
	m	$v^{00}\left(\frac{mL}{mol}\right)$	$\frac{u^0}{k}(K)$	$\sigma(A)$	$m_{max}\left(\frac{mol}{kg}\right)$	ρ	$\gamma_m^{\pm}$	Φ
NaCl	6.1415	0.80483	230.26	4.8109	6.0	1.68	0.30	0.45
KCl	6.2753	1.5405	255.33	4.6576	4.5	1.58	0.12	0.34
NaBr	7.9412	1.1146	247.47	5.6808	8.0	0.63	0.59	0.77
CaCl₂	11.392	0.69712	231.96	7.0471	4.0	0.47	1.68	1.61
Average error (%)						1.09	0.67	0.79

$$^aARD\,(\%)=\left(\frac{100}{N}\right)\sum_{i=1}^{N}\left|\frac{\Omega^{cal}-\Omega^{\exp}}{\Omega^{\exp}}\right|,\ \text{where}\ \Omega\ \text{is}\ \rho,\ \gamma_{\pm}^{m},\ or\ \Phi$$

The results show that the proposed model can correlate the MIAC and densities of electrolyte solutions with acceptable accuracy. As shown in Table 3, the average deviations for density, MIAC, and osmotic coefficient are 1.09%, 0.67%, and 0.79%, respectively. Figure 1 and 2 show typical correlation of density of 1:1 and 1:2 electrolyte solutions. As can be seen form figure 1 for NaCl the correlation of density is over estimated by this model.
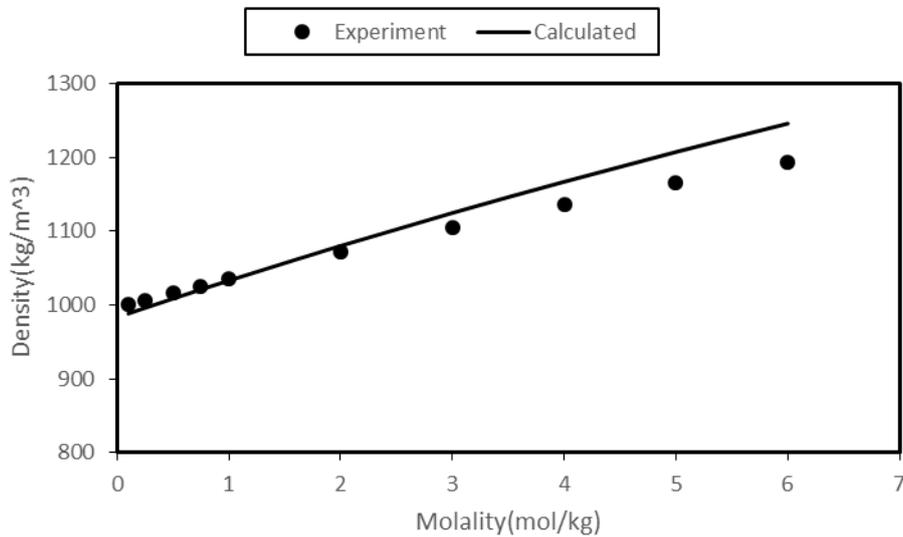

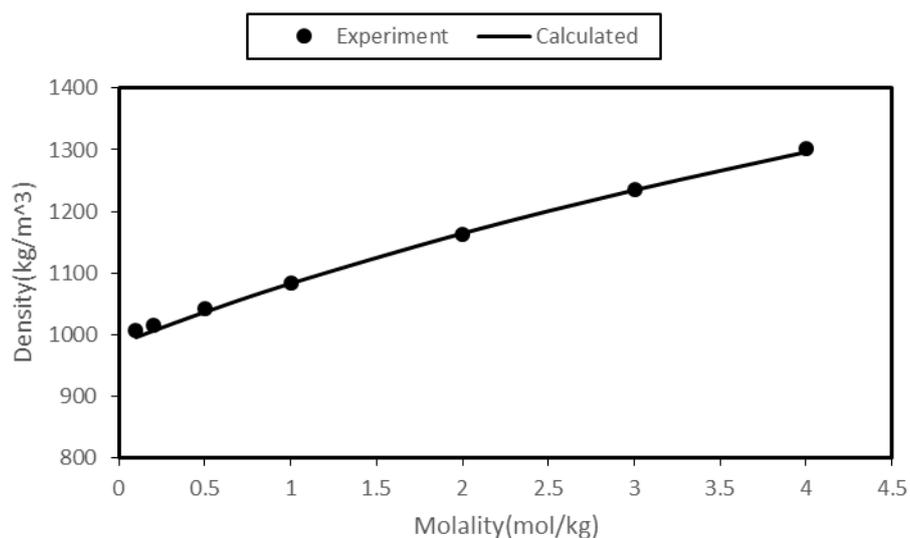Figure 1. Density of aqueous NaCl at 298K and 1bar. Experiment data from [41]

Figure 2. Density of aqueous $CaCl_2$ at 298K and 1bar. Experiment data from [42]

Figure 3 shows correlation of mean ionic activity coefficient for these 4 electrolyte solution. As can be shown by this figure the correlations are in good agreement with experimental data.
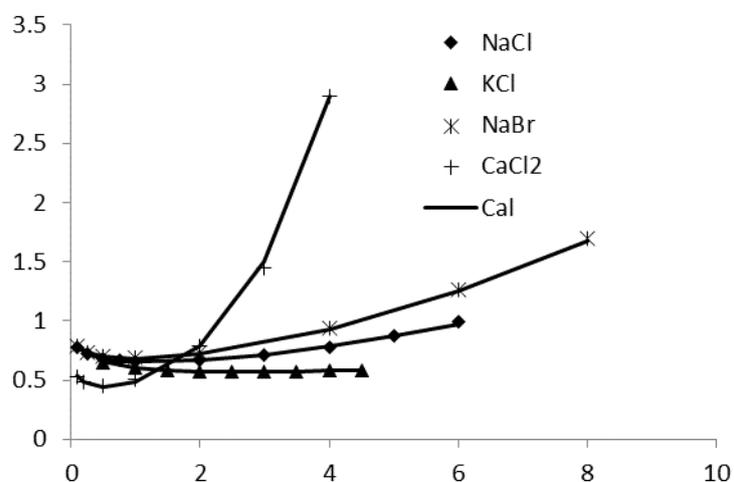

Figure 3. Experimental and calculated MIAC for electrolyte used in this work. Symbols show experimental data and line represents calculated results. Experimental data are from [41-44]

Then, by using these parameters, osmotic coefficient of solvent was predicted by this model. The average absolute deviation in predicted osmotic coefficient of solvent for these 4 electrolyte systems was 0.79% as depicted in table 3. Figure 4 shows experimental and predicted osmotic coefficient for these systems. The results show that the predicted osmotic coefficient with acceptable accuracy was achieved.
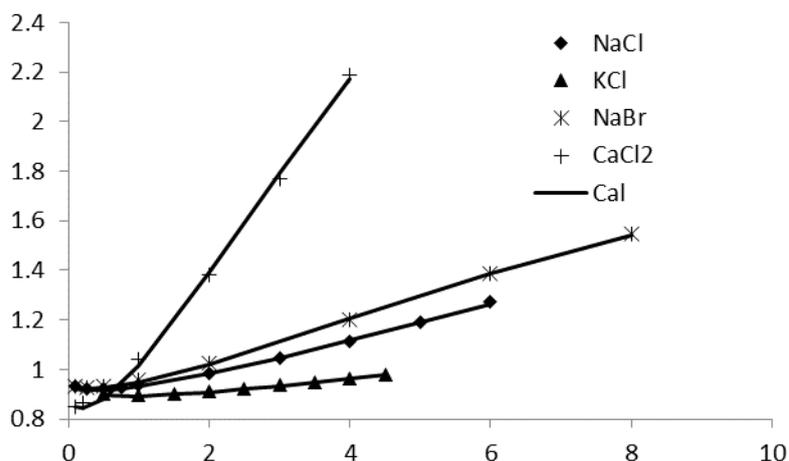
Figure 4. Experimental data and predicted osmotic coefficient of water for systems used in this work. Symbols show experimental data and line shows calculated results.

Although in this equation of state, parameters were obtained for each salt (relative to the parameters for each ion), and the equation of state used is also simpler than the equations in [26, 28, and 30], but comparing the results with other references, such as [26, 28, and 30], shows that this equation of state is also sufficiently precise to obtain the properties of the electrolyte solutions. Thus, by combining the MSA expression with simple equations of state, we can obtain the equation of state that has sufficient accuracy to calculate the properties of the electrolytes.

4. Conclusion

In this study, first, original SAFT equation of state was simplified to simplified SAFT equation of state, and then electrolyte simplified SAFT equation of state was applied to describe thermodynamic properties of aqueous electrolyte solutions. This equation of state was applied to strong aqueous electrolyte solutions of NaCl, KCl, NaBr and $CaCl_2$ to obtain the general salt-specific parameters at 298K and 1bar. The optimized parameters have been obtained through simultaneous regression of MIAC and solution densities, then by using this parameters osmotic coefficient of solvent was predicted with acceptable accuracy. The results showed that by inclusion of MSA expression in the equation of state, the properties of electrolyte solutions can be calculated and obtained using the equation of state with an acceptable accuracy. Also, the results showed that by fitting the parameters of the equation of state with density of solution and mean ionic activity coefficient and obtaining the electrolyte parameters in this way, the remaining solvent properties, including the osmotic coefficient of solvent and etc. can be predicted with an acceptable accuracy (about 1 percent).

Acknowledgment

References

[1] P. Debye, E. Hückel, "Zur Theorie der Elektrolyte. I. Gefrierpunktserniedrigung und verwandte Erscheinungen," *Phys. Z.*, vol. 24, pp. 185−206, 1923.

[2] L. Blum, "Mean Spherical Model for Asymmetric Electrolytes I. Method of Solution," *Mol. Phys.*, vol. 30, pp. 1529−1535, 1975.

[3] L. Blum, J.S. Hoye, "Mean Spherical Model for Asymmetric Electrolytes. 2. Thermodynamic Properties and the Pair Correlation Function," *J. Phys. Chem.*, vol. 81, pp. 1311−1316, 1977.

[4] C.-C. Chen, H.I. Britt, J.F. Boston, L.B. Evans, "Local composition model for excess Gibbs energy of electrolyte systems. Part I: Single solvent, single completely dissociated electrolyte systems," *AIChE Journal*, vol. 28, pp. 588-596, 1982.

[5] A. Haghtalab, S.H. Mazloumi, "A nonelectrolyte local composition model and its application in the correlation of the mean activity coefficient of aqueous electrolyte solutions," *Fluid Phase Equilibria*, vol. 275, pp. 70-77, 2009.

[6] A. Haghtalab, K. Peyvandi, "Electrolyte-UNIQUAC-NRF model for the correlation of the mean activity coefficient of electrolyte solutions," *Fluid Phase Equilibria*, vol. 281, pp. 163-171, 2009.

[7] C.-C. Chen, P.M. Mathias, H. Orbey, "Use of hydration and dissociation chemistries with the electrolyte–NRTL model," *AIChE Journal*, vol. 45, pp. 1576-1586, 1999.

[8] C.-C. Chen, L.B. Evans, "A local composition model for the excess Gibbs energy of aqueous electrolyte systems," *AIChE Journal*, vol. 32, pp. 444-454, 1986.

[9] J. Li, Y. Lin, J. Gmehling, "gE Model for Single- and Mixed-Solvent Electrolyte Systems. 3. Prediction of Salt Solubilities in Aqueous Electrolyte Systems," *Industrial & Engineering Chemistry Research*, vol. 44, pp. 1602-1609, 2005.

[10] B. Mock, L.B. Evans, C.-C. Chen, "Thermodynamic representation of phase equilibria of mixed-solvent electrolyte systems," *AIChE Journal*, vol. 32, pp. 1655-1664, 1986.

[11] C.S. Lee, S.B. Park, Y.S. Shim, "A Unified and Predictive Model for Mixed-Electrolyte, Aqueous Mixed-Solvent Systems Using Parameters for Ions and Solvents," *Industrial & Engineering Chemistry Research*, vol. 35, pp. 4772-4780, 1996.

[12] A. Rastogi, D. Tassios, "Thermodynamics of a single electrolyte in a mixture of two solvents," *Industrial & Engineering Chemistry Research*, vol. 26, pp. 1344-1351, 1987.

[13] A. Mohs, J. Gmehling, "A revised LIQUAC and LIFAC model (LIQUAC*/LIFAC*) for the prediction of properties of electrolyte containing solutions," *Fluid Phase Equilibria*, vol. 337, pp. 311-322, 2013.

[14] H. Planche, H. Renon, "Mean Spherical Approximation Applied to a Simple but Non-primitive Model of Interaction for Electrolyte Solutions and Polar Substances," *J. Phys. Chem.*, vol. 5, pp. 3924−3929, 1981.

[15] W. Fürst, H. Renon, "Representation of excess properties of electrolyte solutions using a new equation of state," *AIChE Journal*, vol. 39, pp. 335-343, 1993.

[16] J.A. Myers, S.I. Sandler, R.H. Wood, "An Equation of State for Electrolyte Solutions Covering Wide Ranges of Temperature, Pressure, and Composition," *Industrial & Engineering Chemistry Research*, vol. 41, pp. 3282-3297, 2002.

[17] M.A. Clarke, P.R. Bishnoi, "Development of a new equation of state for mixed salt and mixed solvent systems, and application to vapour–liquid and solid (hydrate)–vapour–liquid equilibrium calculations," *Fluid Phase Equilibria*, vol. 220, pp. 21-35, 2004.

[18] A. Haghtalab, S.H. Mazloumi, "A square-well equation of state for aqueous strong electrolyte solutions," *Fluid Phase Equilibria*, vol. 285, pp. 96-104, 2009.

[19] J. Wu, J.M. Prausnitz, "Phase Equilibria for Systems Containing Hydrocarbons, Water, and Salt: An Extended Peng−Robinson Equation of State," *Industrial & Engineering Chemistry Research*, vol. 37, pp. 1634-1643, 1998.

[20] Y. Lin, K. Thomsen, J.-c. de Hemptinne, "Multicomponent equations of state for electrolytes," *AIChE Journal*, vol. 53, pp. 989-1005, 2007.

[21] R. Inchekel, J.-C. de Hemptinne, W. Fürst, "The simultaneous representation of dielectric constant, volume and activity coefficients using an electrolyte equation of state," *Fluid Phase Equilibria*, vol. 271, pp. 19-27, 2008.

[22] E. Collinet, J. Gmehling, "Prediction of phase equilibria with strong electrolytes with the help of the volume translated Peng-Robinson group contribution equation of state (VTPR)," *Fluid Phase Equilibria*, vol. 246, pp. 111-118, 2006.

[23] A. Galindo, A. Gil-Villegas, G. Jackson, A.N. Burgess, "SAFT-VRE: Phase Behavior of Electrolyte Solutions with the Statistical Associating Fluid Theory for Potentials of Variable Range," *The Journal of Physical Chemistry B*, vol. 103, pp. 10272-10281, 1999.

[24] B.H. Patel, P. Paricaud, A. Galindo, G.C. Maitland, "Prediction of the Salting-Out Effect of Strong Electrolytes on Water + Alkane Solutions," *Industrial & Engineering Chemistry Research*, vol. 42, pp. 3809-3823, 2003.

[25] B. Behzadi, B.H. Patel, A. Galindo, C. Ghotbi, "Modeling electrolyte solutions with the SAFT-VR equation using Yukawa potentials and the mean-spherical approximation," *Fluid Phase Equilibria*, vol. 236, pp. 241-255, 2005.

[26] S.P. Tan, H. Adidharma, M. Radosz, "Statistical Associating Fluid Theory Coupled with Restricted Primitive Model To Represent Aqueous Strong Electrolytes," *Industrial & Engineering Chemistry Research*, vol. 44, pp. 4442-4452, 2005.

[27] X. Ji, S.P. Tan, H. Adidharma, M. Radosz, "SAFT1-RPM Approximation Extended to Phase Equilibria and Densities of CO2−H2O and CO2−H2O−NaCl Systems," *Industrial & Engineering Chemistry Research*, vol. 44, pp. 8419-8427, 2005.

[28] S.P. Tan, X. Ji, H. Adidharma, M. Radosz, "Statistical Associating Fluid Theory Coupled with Restrictive Primitive Model Extended to Bivalent Ions. SAFT2: 1. Single Salt + Water Solutions," *The Journal of Physical Chemistry B*, vol. 110, pp. 16694-16699, 2006.

[29] X. Ji, S.P. Tan, H. Adidharma, M. Radosz, "Statistical Associating Fluid Theory Coupled with Restrictive Primitive Model Extended to Bivalent Ions. SAFT2: 2. Brine/Seawater Properties Predicted," *The Journal of Physical Chemistry B*, vol. 110, pp. 16700-16706, 2006.

[30] X. Ji, H. Adidharma, "Ion-Based SAFT2 to Represent Aqueous Single- and Multiple-Salt Solutions at 298.15 K," *Industrial & Engineering Chemistry Research*, vol. 45, pp. 7719-7728, 2006.

[31] X. Ji, H. Adidharma, "Ion-Based Statistical Associating Fluid Theory (SAFT2) to Represent Aqueous Single-Salt Solutions at Temperatures and Pressures up to 473.15 K and 1000 bar," *Industrial & Engineering Chemistry Research*, vol. 46, pp. 4667-4677, 2007.

[32] L.F. Cameretti, G. Sadowski, J.M. Mollerup, "Modeling of Aqueous Electrolyte Solutions with Perturbed-Chain Statistical Associated Fluid Theory," *Industrial & Engineering Chemistry Research*, vol. 44, pp. 3355-3362, 2005.

[33] C. Held, L.F. Cameretti, G. Sadowski, "Modeling aqueous electrolyte solutions: Part 1. Fully dissociated electrolytes," *Fluid Phase Equilibria*, vol. 270, pp. 87-96, 2008.

[34] J. Rozmus, J.-C. de Hemptinne, A. Galindo, S. Dufal, P. Mougin, "Modeling of Strong Electrolytes with ePPC-SAFT up to High Temperatures," *Industrial & Engineering Chemistry Research*, vol. 52, pp. 9979-9994, 2013.

[35] N. Von Solms, M.L. Michelsen, G.M. Kontogeorgis, "Computational and Physical Performance of a Modified PC-SAFT Equation of State for Highly Asymmetric and Associating Mixtures," *Ind. Eng. Chem. Res.*, vol. 42, pp. 1098-1105, 2003.

[36] G.A. Mansoori, N.F. Carnahan, K.E. Starling, T.W. Leland, "Equilibrium Thermodynamic Properties of the Mixture of Hard Spheres," *J. Chem. Phys.*, vol. 54, pp. 1523-1525, 1971.

[37] S.S. Chen, A. Kreglewski, "Applications of the Augmented van der Waals Theory of Fluids. I. Pure Fluids.," *Ber. Bunsen-Ges. Phys. Chem.*, vol. 81, pp. 1048-1052, 1977.

[38] W.G. Chapman, K.E. Gubbins, G. Jackson, M. Radosz, "New reference equation of state for associating liquid," *Ind. Eng. Chem. Res.*, vol. 29, pp. 1709-1721, 1990.

[39] S.P. Tan, H. Adidharma, M. Radosz, "Statistical Associating Fluid Theory Coupled with Restricted Primitive Model To Represent Aqueous Strong Electrolytes," *Ind. Eng. Chem. Res.*, vol. 44, pp. 4442−4452, 2005.

[40] J.P. Wolbach, S.I. Sandler, "Using Molecular Orbital Calculations To Describe the Phase Behavior of Hydrogen-Bonding Fluids," *Ind. Eng. Chem. Res.*, vol. 36, pp. 4041-4051, 1997.

[41] D. Archer, "Thermodynamic Properties of the NaCl+H2O System. II. Thermodynamic Properties of the NaCl(aq), NaCl-H2O(cr), and Phase Equilibria.," *J. Phys. Chem. Ref. Data*, vol. 21, 1992.

[42] J. Ananthaswamy, G. Atkinson, "Thermodynamics of Concentrated Electrolyte Mixtures. 5. A Review of the Thermodynamic Properties of Aqueous Calcium Chloride in the Temperature Range 273.15-373.15 K," *J. Chem. Eng. Data*, vol. 30, 1985.

[43] W.J. Hamer, Y.C. Wu, "Osmotic coefficients and mean activity coefficients of uni-univalent electrolytes in water at 25°C," *J. Phys. Chem. ref. Data*, vol. 1, pp. 1047-1110, 1972.

[44] D. Archer, "Thermodynamic Properties of the NaBr+H2O System," *J. Phys. Chem. Ref. Data*, vol. 20, 1992.

مدل‌سازی ترمودینامیکی الکترولیت‌ها: ترکیب تقریب متوسط کروی (MSA) و معادله حالت SAFT ساده شده

یاسین حاجب ۱، امیر عباس ایزدپناه ۱،*، شهریار عصفوری ۱

۱. بوشهر، دانشگاه خلیج فارس، دانشکده مهندسی نفت، گاز و پتروشیمی، گروه مهندسی شیمی

چکیده	مشخصات مقاله

در این کار از یک معادله حالت برای مدل سازی ترمودینامیکی محلول های الکترولیتی آبی استفاده شده است. معادله حالت استفاده شده ترکیبی از معادله حالت SAFT ساده شده (شبیه معادله حالت -PC SAFT ساده شده) برای در نظر گرفتن نیروهای برد کوتاه و تقریب کروی متوسط برای در نظر گرفتن نیروهای برد بلند می باشد. در این مدل، روش بر مبنای نمک یا مدل محدود شده برای به دست اوردن چهار پارامتر موجود در مدل به کار برده شده است. پارامترهای مربوط به هر نمک با استفاده از برازش داده‌های آزمایشگاهی ضریب فعالیت متوسط یونی و دانسیته محلول الکترولیت قوی به دست آمده است. چهار الکترولیت قوی، سه تا الکترولیت قوی ۱:۱ و یکی ۱:۲ بکار برده شده است. با استفاده از پارامترهای نمک بهینه شده، ضریب اسمزی حلال، با در خطای متوسط نسبی ۰/۷۹ درصد پیش بینی شده است. نتایج نشان داد که معادله حالت SAFT ساده شده و ترکیب شده با تقریب متوسط کروی متوسط خطای نسبی ۱٪ و کمتر برای به دست آوردن ضریب فعالیت متوسط یونی و دانسیته محلول‌های الکترولیت قوی دارد.

* عهده‌دار مکاتبات؛

رایانامه:

izadpanah@pgu.ac.ir

تلفن: ۶۰۰+۹۸ ۷۷ ۳۳۲۲۲

دورنگار: ۹۸ ۷۷ ۳۳۴۴۱۴۹۵+