Statistical Associating Fluid Theory Coupled with Restricted Primitive Model to Represent Aqueous Strong Electrolytes: Multiple-Salt Solutions

4 AUTHORS, INCLUDING:

Sugata P. Tan
Planetary Science Institute
29 PUBLICATIONS **595** CITATIONS

SEE PROFILE

Statistical Associating Fluid Theory Coupled with Restricted Primitive Model To Represent Aqueous Strong Electrolytes

Sugata P. Tan, Hertanto Adidharma, and Maciej Radosz*

Department of Chemical and Petroleum Engineering, University of Wyoming, Laramie, Wyoming 82071-3295

Statistical Associating Fluid Theory coupled with Restricted Primitive Model (SAFT1-RPM) represents the mean ionic activity coefficient, density, osmotic coefficient, and vapor pressure of several aqueous alkali halide solutions, in a framework that is analogous to the nonelectrolyte framework. SAFT1 alone represents pure water, including the density anomaly. Each SAFT1 salt molecule consists of two segments: cation and anion.

Introduction

In the pharmaceutical industry, understanding the electrolytes present in our body is relevant to drug delivery systems and understanding electrolytes containing a polymer, such as poly(ethylene glycol), is relevant to protein extraction.[1] In the chemical industry, electrolyte solutions play an important role, for example, in desalination, extraction, wastewater treatment, etc. In enhanced oil recovery, one needs to understand and account for the formation brine that naturally exists in the reservoir, is injected during the water flood, or is introduced along with CO_2 injection to inhibit the fingering in the oil.[2] Salts reduce the solubility of CO_2 in water, which was shown to increase the oil recovery.[3]

In general, salts form electrolyte solutions in solvents that have large dielectric constants, such as water. Salts dissociate into a positively charged cation and a negatively charged anion in such solvents: the higher the degree of dissociation, the stronger the electrolyte solution. In strong electrolyte solutions, where salt molecules are completely dissociated, ions are assumed to be free particles interacting with each other and with solvent molecules. Therefore, electrolyte solutions are nominally two-component systems that, however, contain three species: solvent molecules, cations, and anions. They are different from normal ternary solutions that contain three molecular species in that the concentrations of the cation and anion must always satisfy the electroneutrality condition.[4] This is the principal difference between the thermodynamic frameworks for electrolytes and nonelectrolytes,[4,5] which were critically reviewed by Wilczek-Vera and Vera.[6]

The two-component versus three-species dichotomy is reflected in the definition of the mole fraction of the salt:

$$x_{salt} = \frac{C_m}{1000/M_{solvent} + \nu C_m} \quad (1)$$

where C_m is the molality, i.e., the mole number of salt in 1 kg of solvent, $M_{solvent}$ is the molecular weight of the solvent (in g/mol), and ν is the sum of the stoichiometric coefficients of the salt:

$$\nu = \nu_+ + \nu_- \quad (2)$$

The issue with eq 1 is that the mole fractions do not add up to unity;[4] the denominator on the right-hand side is the mole number of all freely interacting species (solvent molecules and ions) present in the solution, while the numerator is the mole number of the salt (ion pairs).

The three-species character of electrolyte solutions is supported, for example, by the vapor pressure data of aqueous mixed salts with swapping pairs of ions, such as NaCl + KBr and NaBr + KCl, which have the same vapor pressures at the same temperature and the same salt concentration.[7] This can be explained by the free-particle behavior of individual ions. By contrast, in phase-separated systems, each bulk phase is electrically neutral, so that ions must move in pairs between phases.[8] This behavior is consistent with the mean ionic activity coefficient, which is measurable while the individual-ion activity coefficients are generally not. In other words, the activity coefficient is the property of the salt, not of the ions.

Furthermore, the association between ions and solvent molecules referred to as solvation, or, specifically, hydration if the solvent is water, introduces an additional complexity to the modeling of electrolyte solutions. There are two hypotheses of how ions are hydrated by water: hydrated as ion pairs or hydrated as individual ions. Direct experimental probes do not provide a definitive answer yet; e.g., X-ray diffraction[9] and neutron scattering[10] suggest individual-ion hydration, while IR spectroscopy suggests that ions are hydrated in pairs.[11]

This dual nature of the electrolyte solution, individual ions versus salt, is accounted for by excess free energy models, such as the electrolyte nonrandom two-liquid[12] model and Pitzer's[13] model. However, these models by themselves cannot be used to calculate the density, which is also an important property of electrolyte solutions. To predict the density, we need an equation of state (EOS), such as a statistical associating fluid theory (SAFT) like or cubic EOS.

The EOS parameters can be defined with respect to individual ions, which means that ions can have different parameters, or with respect to salt, which essentially means that both ions have identical parameters. We refer to the former as the individual-ion approach and to the latter as the salt approach. In the individual-ion approach, the ion parameters are universal and, hence, transferable to different salts containing the same ion. Such an approach can greatly reduce the number of parameters needed to represent electrolytes. This is

* To whom correspondence should be addressed. Tel.: (307) 766-2500. Fax: (307) 766-6777. E-mail: Radosz@uwyo.edu.

reminiscent of group-contribution approaches. In the salt approach, on the other hand, each salt component has a unique set of parameters derived from experimental data for that salt.

SAFT-VR is an example of an EOS that has been used with individual-ion parameters to represent the vapor pressure and density of aqueous strong 1/1 electrolyte solutions.[14,15] SAFT-VR has been used to predict the salting-out effect of strong electrolytes on water + alkanes solutions.[16] However, the mean ionic activity coefficient (for NaCl at 25 °C) is only qualitatively reproduced.[15] Peng–Robinson is an example of a cubic EOS that has been used with salt parameters to correlate the mean activity coefficient, osmotic coefficient, free energy of hydration, and density of aqueous electrolytes.[17] This approach allows for the existence of free ions but forces them to have the same parameters if they belong to the same salt. After this work was documented and submitted, Liu et al.[18] proposed SAFT with a Lennard-Jones potential for single-salt solutions using two salt parameters per salt and, implicitly, one ion parameter (the number of association sites on each ion).

The goal of this preliminary work is to explore a hybrid approach that has both the individual-ion and salt parameters and, hence, can represent all of the electrolyte properties, not only the mean ionic activity coefficient, osmotic coefficient, and vapor pressure but also the density. The key to such a hybrid approach is an EOS that can treat the salt as a molecule composed of two *different* segments corresponding to the cation and anion. Most EOSs treat molecules as collections of identical segments. However, SAFT1[19] and copolymer SAFT[20] allow for different segments of the same molecule; we select SAFT1 for this work. In such an approach, the electroneutrality condition is automatically satisfied; the aqueous electrolyte can be treated as a binary solution containing water and salt, and hence the mean ionic activity coefficient is calculated as the salt activity coefficient. We want to test such a SAFT1 electrolyte model on aqueous solutions of alkali halides, which are examples of aqueous strong 1/1 electrolyte solutions.

Definitions and Approximations

We define the fraction of an ion in a salt molecule with respect to the total stoichiometric number of ions in the salt:

$$\chi_j = \nu_j/\nu \qquad (j = +, -) \qquad (3)$$

Such fractions are used to average the number of segments per salt molecule, m_1, which is needed later, and the molecular weight of the salt, M_1, as follows:

$$m_1 = \sum_j \chi_j m_j \qquad (4)$$

$$M_1 = \sum_j \chi_j M_j \qquad (5)$$

The mole fraction of the salt in the aqueous solution can now be defined as

$$x_1 = \frac{\nu C_m}{1000/M_2 + \nu C_m} \qquad (6)$$

which makes the mole fractions add up to 1. Subscripts 1 and 2 refer to the salt and water, respectively. These definitions make the SAFT1 framework the same for both nonelectrolytes and electrolytes (see the Appendix).

SAFT1 can be defined in terms of the dimensionless residual Helmholtz free energy as follows:

$$\tilde{a}^{res} = \tilde{a}^{hs} + \tilde{a}^{disp} + \tilde{a}^{chain} + \tilde{a}^{assoc} + \tilde{a}^{ion} \qquad (7)$$

where the superscripts mean residual, hard-sphere, dispersion, chain, association, and ionic interactions, respectively. Except for the last term, which accounts for the long-range electrostatic interactions, the other terms on the right-hand side account for relatively short-range interactions.

If the ions and water molecules are treated as spherical particles (each consists of a single segment), the chain term can be eliminated from eq 7. For such spherical ions, according to eq 4, the average segment number of the salt molecule is equal to 1. For hard-sphere and dispersion terms, the species (water and the ions) have their own SAFT1 parameters, i.e., the segment volume, the segment energy, and the parameter associated with the square-well interaction range.

The ionic term in eq 7 can be approximated from integral-equation theory for simple charged hard spheres,[21] e.g., from the mean spherical approximation (MSA) such as the Restricted Primitive Model (RPM) or the Primitive Model (PM), in which the charged hard spheres are placed in a medium having a uniform dielectric constant. The main difference between these two models lies in the estimation of the ion diameters. In RPM, ions are assumed to have a common diameter, while in PM, ions are allowed to have different diameters.

Because both RPM and PM produce similar results,[22] we prefer RPM for this work. Instead of using two bare-ion diameters in the ionic term (PM), we use a single hydrated-ion diameter in RPM for each salt, the hydrated diameter for short, and fit it to the salt properties. In this way, the ionic term also absorbs the hydration effect.

In RPM, the contribution of the long-range Coulombic interactions to the Helmholtz free energy is given by[21]

$$\tilde{a}^{ion} = -\frac{3x^2 + 6x + 2 - 2(1 + 2x)^{3/2}}{12\pi\rho N_A d^3} \qquad (8)$$

where ρ is the molar density, N_A is Avogadro's number, d is the hydrated diameter, and x is a dimensionless quantity defined by

$$x = \kappa d \qquad (9)$$

where κ is the Debye inverse screening length given by

$$\kappa^2 = \frac{4\pi}{\epsilon_w kT}\sum_j \rho_{n,j} q_j^{\ 2} = \alpha_0^{\ 2}\sum_j \rho_{n,j} z_j^{\ 2} \qquad (10)$$

and where

$$\alpha_0^{\ 2} = \frac{4\pi e^2}{\epsilon_w kT} \qquad (11)$$

In eq 10, ϵ_w is the permittivity of water, $\rho_{n,j}$ is the number density of ion j, q_j is the charge of ion j ($=z_j e$), z_j is the valence of the charged ion j, e is the charge of

an electron ($=-4.803 \times 10^{-10}$ esu), and the summation is over all ions in the mixture.

In the MSA, one assumes ions to be hard spheres. Therefore, the dispersion term in eq 7 is calculated assuming that the dispersion interactions among electrical charges are zero. The dispersion term accounts only for the water−water and water−ion dispersion interactions.

The association interaction in eq 7 originates from the self-association of water molecules, the cross-association of water molecules and the ions, and the association of the ions. The water−ion cross-association contribution is accounted for by the hydrated diameter in the ionic term. The ionic association is significant only at high temperatures because of the decrease of the water dielectric constant,[23] and hence it can be neglected up to moderately high temperatures. Therefore, the association term in eq 7 only accounts for the self-association of water molecules. We assign the associating sites to water molecules according to model 4C.[24]

The ionic segment volumes (v_j), ionic segment energies (u_j/k), hydrated ionic diameters (d_j), and dielectric constant of water (ϵ_w) are allowed to vary with temperature as follows:

$$v_j = v_{25,j}\left[\frac{1 + c_{1,j}\exp(c_{2,j}/T)}{1 + c_{1,j}\exp(c_{2,j}/298.15)}\right]^3 \quad (12)$$

$$\frac{u_j}{k} = \frac{u_{25,j}}{k}\left[1 + c_{3,j}\left(\frac{1}{T} - \frac{1}{298.15}\right)\right] \quad (13)$$

$$d = d_{25}\left[1 + c_4\left(\frac{1}{T} - \frac{1}{298.15}\right)\right] \quad (14)$$

$$\epsilon_w = 281.67 - 1.0912T + 1.6644 \times 10^3 T^2 - 9.7592 \times 10^7 T^3 \quad (15)$$

These equations have seven parameters: $c_{1,j}$, $c_{2,j}$, $c_{3,j}$, and c_4 (subscript j refers to cation or anion). Subscript 25 in eqs 12−14 refers to 25 °C. We use the values at 25 °C as a reference because most experimental data are available at 25 °C. We obtain $u_{25,j}$ by setting e/k, i.e., a constant accounting for noncentral forces in SAFT,[19,24] equal to zero. The temperature-dependent dielectric constant for water in eq 15 is correlated on the basis of experimental data from the literature.[25] In this preliminary study, the water dielectric constant is made density-independent.

For the record, MSA is within the McMillan−Mayer framework, while EOS is within the Lewis−Randall framework. However, the discrepancy between the two frameworks is small enough to be absorbed by the fitted parameters.[17]

Fitting of the Ionic Parameters

The following SAFT1 parameters of the ions are to be derived from experimental data at 25 °C: segment volume ($v_{25,j}$), segment energy ($u_{25,j}/k$), and λ. In addition, the hydrated diameter (d_{25}) and the seven parameters needed for eqs 12−14 ($c_{1,j}$, $c_{2,j}$, $c_{3,j}$, and c_4) are also derived from the experimental data. There are no binary interaction parameters applied between the ions and water molecules.

Saturated vapor pressure is one choice of the experimental input. However, as found for SAFT-VR,[13] fitting
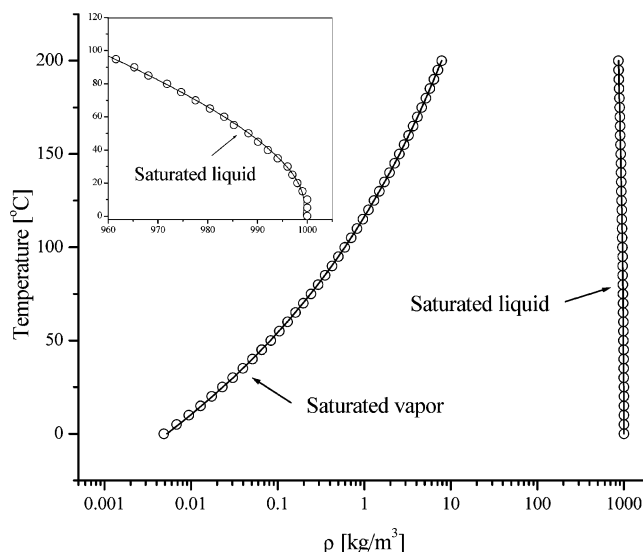

Figure 1. Coexisting density ($T-\rho$ diagram) of pure water, experimental (points), and calculated (curves).

Table 1. SAFT1 Parameters for Pure Water

parameter	value
segment volume, v^{00}	9.4837 [cm³/mol]
segment energy, u^0/k	313.8758 [K]
λ	1.5423
association energy, ϵ^{HO}/k	1527.72 [K]
association volume, κ^{HO}	0.058 48

of the vapor pressures alone does not suffice. Another choice is the osmotic coefficient, which usually is directly calculated from the vapor pressure at low pressures by

$$\Phi^m = -\frac{\ln(P_2/P_2^0)}{\nu C_m M_2} \times 1000 \quad (16)$$

where superscript m refers to the molality scale. In the logarithm is the ratio of the partial pressure of water to the vapor pressure of pure water.

However, we use neither the vapor pressure nor the osmotic coefficient for fitting in this work. Instead, we use the mean ionic activity coefficient, which we feel is a better choice (more on this later). Even though it is related to the osmotic coefficient through

$$\ln \gamma_{\pm} = \Phi - 1 + 2\int_0^m \frac{\Phi - 1}{\sqrt{C_m}}\, d(\sqrt{C_m}) \quad (17)$$

it can also be derived independently from electromotive force data. Furthermore, the mean ionic activity coefficient is more effective than the osmotic coefficient for fitting of the ionic parameters because the integration in eq 17 makes it more sensitive to calculation errors.

Fitting of the parameters can produce multiple parameter sets. To obtain an effective set of parameters, we also include density data in addition to the mean ionic activity coefficient data in the fitting process. This is analogous to the fitting of parameters for nonelectrolytes to vapor pressure and liquid density data.

The activity coefficient of the salt in a binary aqueous solution is equivalent to the mean ionic activity coefficient ($\gamma_{\pm}$), as demonstrated in the Appendix. These terms are, therefore, interchangeable in this work.
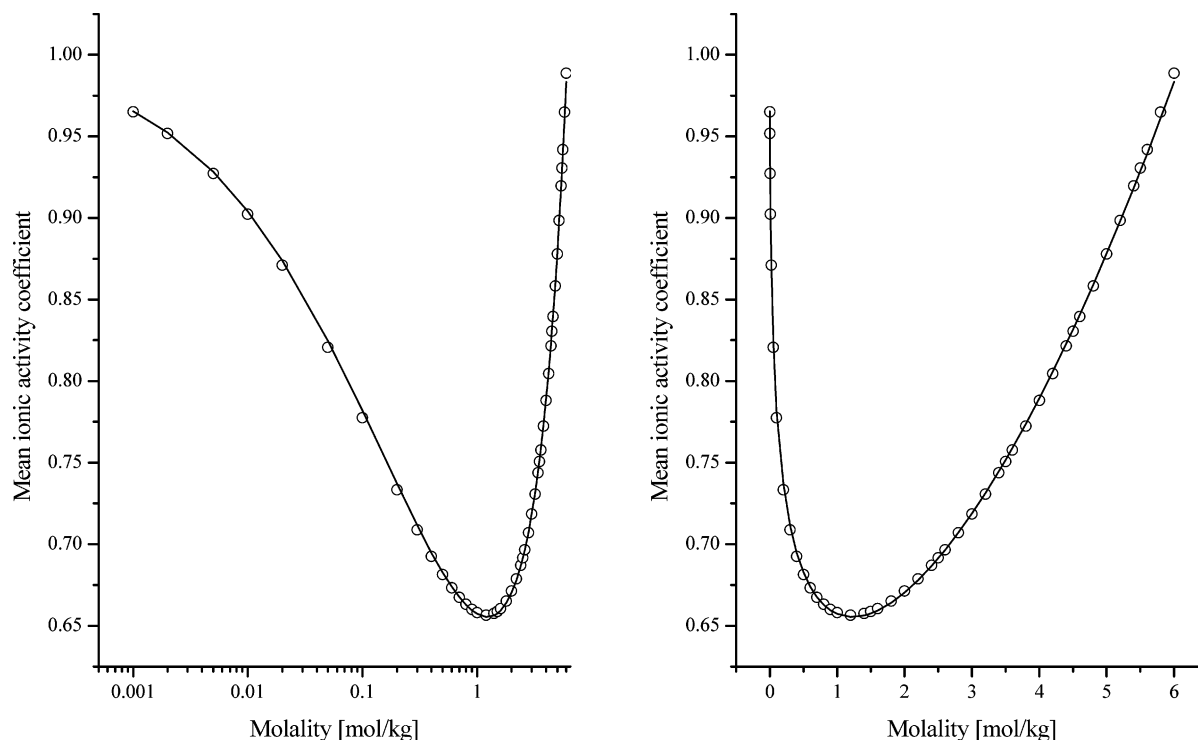
Figure 2. Correlated mean ionic activity coefficient of NaCl + water at 25 °C.

The molality-based activity coefficient is defined as

$$\gamma_1{}^{m} = \gamma_{\pm}{}^{m} = \frac{\gamma_1{}^{x}}{1 + 0.001\nu C_m M_2} \qquad (18)$$

where the mole-fraction-based activity coefficient is defined as the ratio of the fugacity coefficient in the solution to its value at infinite dilution.

$$\gamma_1{}^{x} = \frac{\hat{\phi}_1}{\hat{\phi}_1{}^{\infty}} = \frac{\hat{\phi}_1}{\phi_2{}^{0}} \exp\left[\left[\left(\frac{\partial \tilde{a}^{res}}{\partial x_2}\right)_{x_1,\rho,T} - \left(\frac{\partial \tilde{a}^{res}}{\partial x_1}\right)_{x_2,\rho,T}\right]_{x_2 \to 1}\right] \qquad (19)$$

Superscripts ∞ and 0 mean infinite dilution and pure component, respectively. The fugacity coefficient of the salt at infinite dilution can be calculated from the fugacity coefficient of pure water, as shown in the second expression of eq 19 (see eq A10 in the Appendix for the derivation).

The density of the electrolyte solution, $\hat{\rho}$ in kg/m³, is calculated from the solution molar density, in mol/cm³, as follows:

$$\hat{\rho} = \rho[x_1 M_1 + x_2 M_2] \times 1000 \qquad (20)$$

where the salt molecular weight, M_1, is calculated from eq 5.

Results for Water

Prior to estimating the properties of aqueous electrolyte solutions, one needs to determine the SAFT1 parameters for pure water, in our case, by fitting of the saturated vapor pressure and liquid volume data in the temperature range of 10−200 °C.[26] The parameters are given in Table 1, and the result is shown in Figure 1. The average relative deviation (ARD, defined in the Nomenclature section) is 0.9% for the saturated pressures and 0.06% for the liquid volumes.
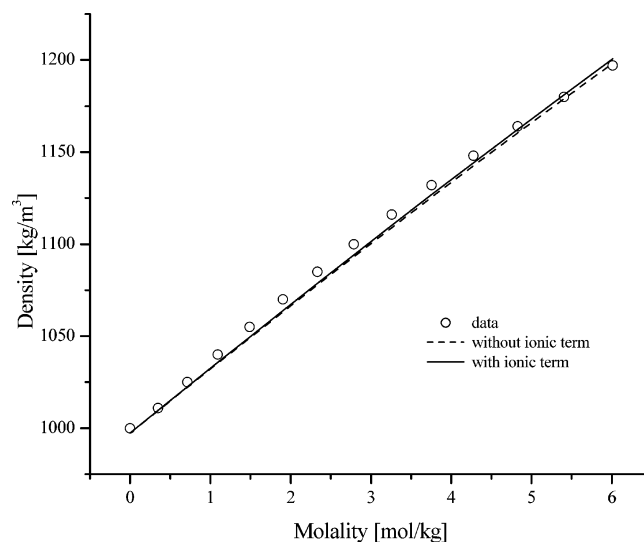

Figure 3. Correlated density of NaCl + water at 25 °C.

The extrapolation to lower temperatures (<10 °C) correctly reflects the anomalous maximum density of water. This is shown in the inset in Figure 1. All in all, the SAFT1 representation of pure water is reliable enough to use as a basis for aqueous electrolytes.

Results for NaCl + Water at 25 °C

The most common electrolyte, sodium chloride (NaCl), dissociates in water into two ions, Na^+ and Cl^-. The ionic parameters are determined by fitting of the mean ionic activity coefficient data[27] and the density data[28] at 25 °C.

Figures 2 and 3 show the goodness of fit at 25 °C for the salt activity coefficient and density, respectively. As in all other figures, the curves are calculated from SAFT1 and the symbols are experimental data from the literature. Figure 2 (left) has a logarithmic abscissa to
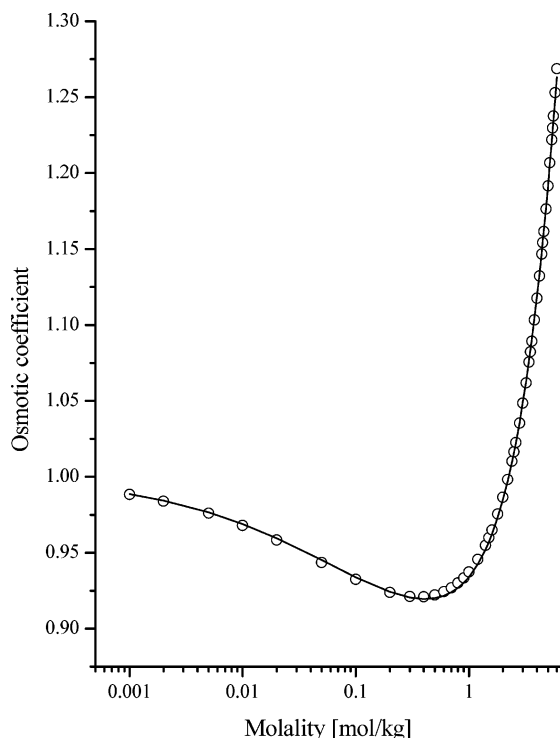
Figure 4. Predicted osmotic coefficient of NaCl + water at 25 °C.

Table 2. SAFT1 Parameters from Fitting NaCl + Water at 25 °C

ion	v_{25} [cm³/mol]	u_{25}/k [K]	λ	d_{25} [Å]
Na⁺	0.7891	3064.1083	1.70	4.9373
Cl⁻	2.0424	527.3565	1.80	

show the fit in the dilute region. The fitting of ARDs of the mean ionic activity coefficient and density are 0.17% and 0.38%, respectively. The parameters obtained from these fits are listed in Table 2, where the first three ionic parameters are associated with short-range interactions, in which the ions behave as free individual particles with their own parameters, while the hydrated diameter in the last column is the salt property.

The SAFT1 parameters obtained from the fitting of the mean ionic activity coefficient and density data, reported in Table 2, are then used without readjustment to predict the molality-based osmotic coefficient of the solvent (water):
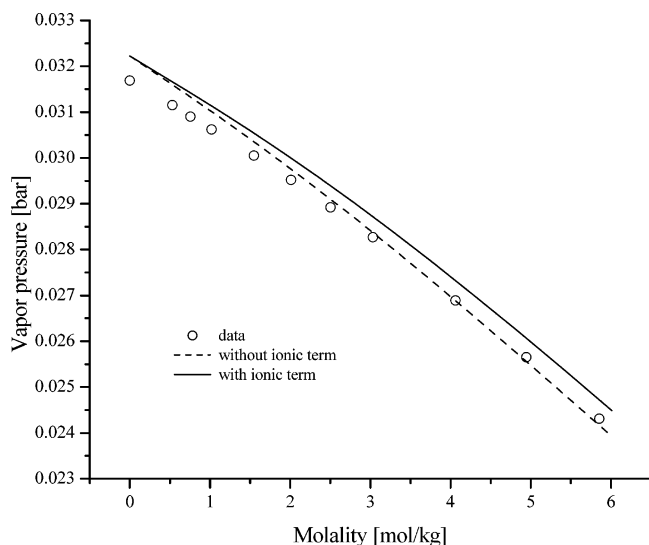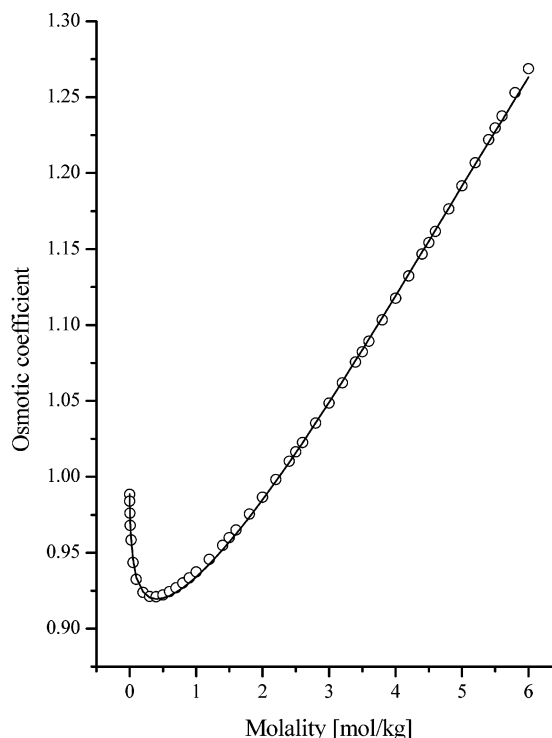
$$\Phi^{m} = -\frac{\ln(x_2\gamma_2^{x})}{\nu C_m M_2} \times 1000 \qquad (21)$$

where the mole-fraction-based activity coefficient of water is

$$\gamma_2^{x} = \hat{\phi}_2/\phi_2^{0} \qquad (22)$$

Figure 4 shows that the predicted osmotic coefficient of NaCl + water at 25 °C agrees with the experimental data;[27] the ARD is 0.16%.

These parameters can also be used to predict the vapor pressure. One can estimate the vapor pressure from the EOS, assuming that the salt concentration in
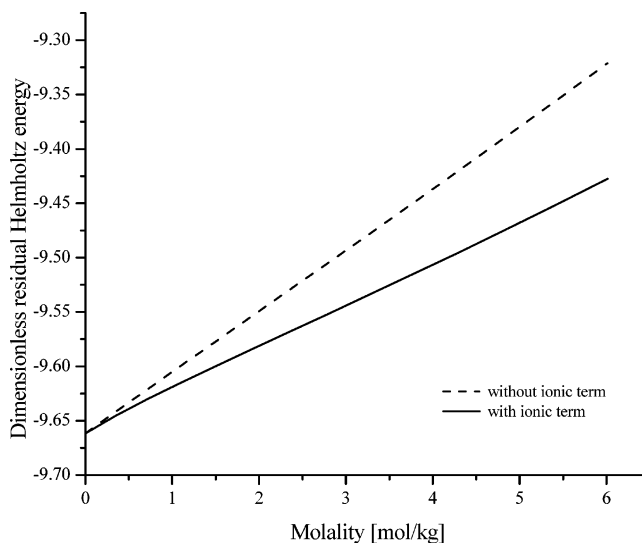

Figure 5. Predicted vapor pressure of NaCl + water at 25 °C.

Figure 6. Residual Helmholtz energy in SAFT1 for NaCl + water at 25 °C using parameters from Table 2.

Table 3. Residual Helmholtz Energy Terms in SAFT1 for NaCl + Water at 25 °C and 3.26 m

$\tilde{a}^{hs}$	$\tilde{a}^{disp}$	$\tilde{a}^{assoc}$	$\tilde{a}^{ion}$	$\tilde{a}^{res}$
2.6045	−5.7089	−6.3755	−0.0638	−9.4960

Table 4. SAFT1-RPM Parameters for Na⁺, K⁺, Cl⁻, Br⁻, and I⁻

ion	v_{25} [cm³/mol]	u_{25}/k [K]	λ
Na⁺	1.2797	3349.7979	1.70
K⁺	7.6715	580.4178	1.20
Cl⁻	0.7797	413.9908	1.80
Br⁻	3.4268	400.3327	1.20
I⁻	8.3130	104.2698	1.80

the vapor phase is zero; in fact, only a trace amount of salt was found in the vapor phase.[29] Figure 5 shows that the predicted vapor pressure also agrees with the experimental data;[30] the ARD is 1.70%.

We confirm that when we use the osmotic coefficient for fitting of the parameters, we get a good fit for the osmotic coefficient but a less accurate prediction for the mean ionic activity coefficient. As mentioned before, this is because the mean ionic activity coefficient is more sensitive to calculation errors and hence more effective for fitting of the parameters.

Using the parameters reported in Table 2, the residual Helmholtz energy is calculated for two cases, i.e., with and without the ionic term, and presented in Figure 6. As inferred from the figure, the contribution of the ionic term is very small (1.3% of the residual Helmholtz energy at a molality of 6), and hence it does not affect the density and vapor pressure much, as shown in Figures 3 and 5. For vapor pressure, shown in Figure 5, the ionic term gives the correct slope of the curve; the overestimate is not caused by the ionic term but by the small error in predicting the vapor pressure of pure water. This analysis suggests that the density and vapor pressure are mainly determined by the short-range interactions among water molecules and ions as individual particles.

Table 3 shows typical values of the energy terms. The last column is the total residual Helmholtz energy according to eq 7. Table 3 further illustrates how small the ionic term is compared to the other terms.

However, even though the ionic term is small, it is crucial to the mean ionic activity coefficient because the mean ionic activity coefficient reflects the long-range electrostatic interactions accounted for by the ionic term in the EOS.

Results for Other Salts + Water

In the individual-ion approach, the ionic parameters determined for one salt solution, for example, those determined for the NaCl + water solution (v_{25}, u_{25}/k, and in Table 2), should be applicable to other electrolytes that contain Na⁺ or Cl⁻. This requires a simultaneous correlation over several electrolyte solutions, similar to that in group-contribution approaches, to obtain universal ionic parameters.

We select four salts to illustrate this approach: NaCl, KCl, NaBr, and KBr. We want the common ions to have the same parameters. The parameters obtained for the four ions, i.e., Na⁺, K⁺, Cl, and Br, are listed in Table 4. The mean ionic activity coefficients of all salts other than NaCl are taken from Hamer and Wu.[31] The densities are taken from Zaytsev and Aseyev.[28] The hydrated diameter for each salt is obtained as follows: 5.7765 Å (0.55% and 0.38%) for NaCl, 3.6611 Å (0.73% and 0.26%) for KCl, 4.5054 Å (0.45% and 0.65%) for NaBr, and 4.2321 Å (0.48% and 0.45%) for KBr. The percentage numbers in parentheses are the ARD values of the mean ionic activity coefficient and density, respectively. Fitting the data of aqueous NaI and aqueous KI using the Na⁺ and K⁺ parameters, we obtain the iodide (I⁻) parameters. The hydrated diameters of the iodide salts are 3.8469 Å (1.1% and 1.2%) for NaI and 4.4477 Å (0.15% and 0.61%) for KI. Figure 7 illustrates the calculations for the salt activity coef-
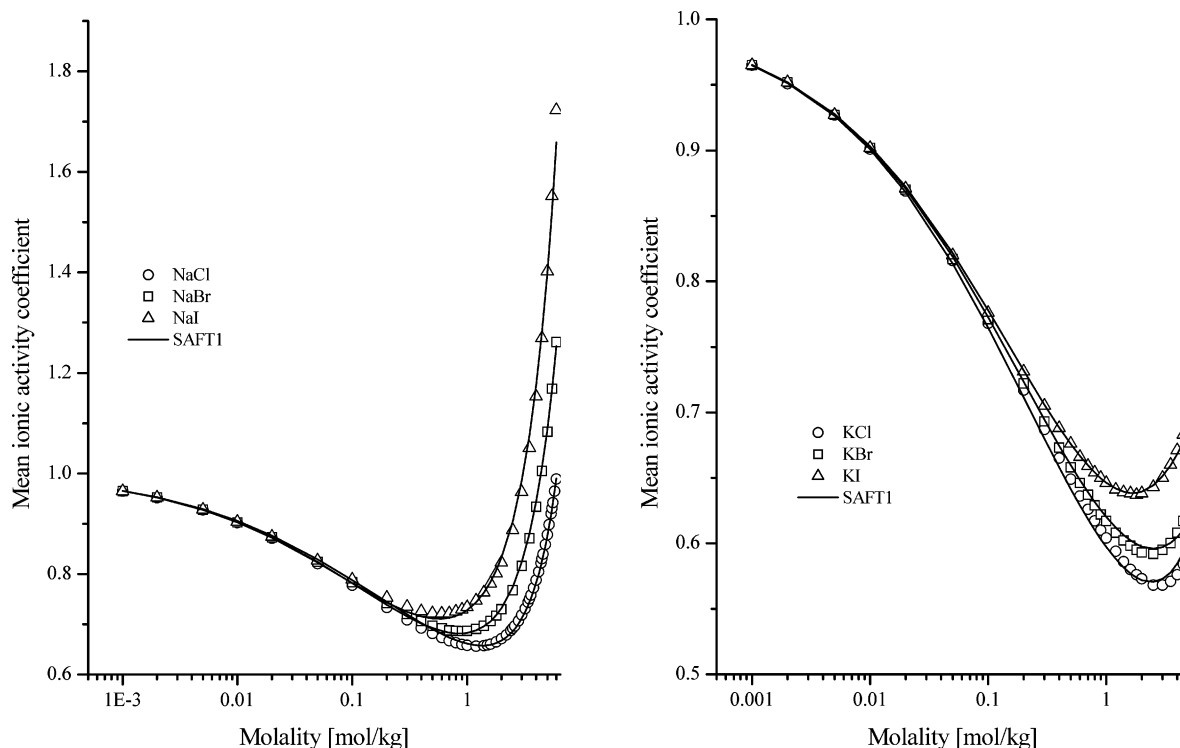
Figure 7. Correlated mean ionic activity coefficient of several salt + water systems at 25 °C.
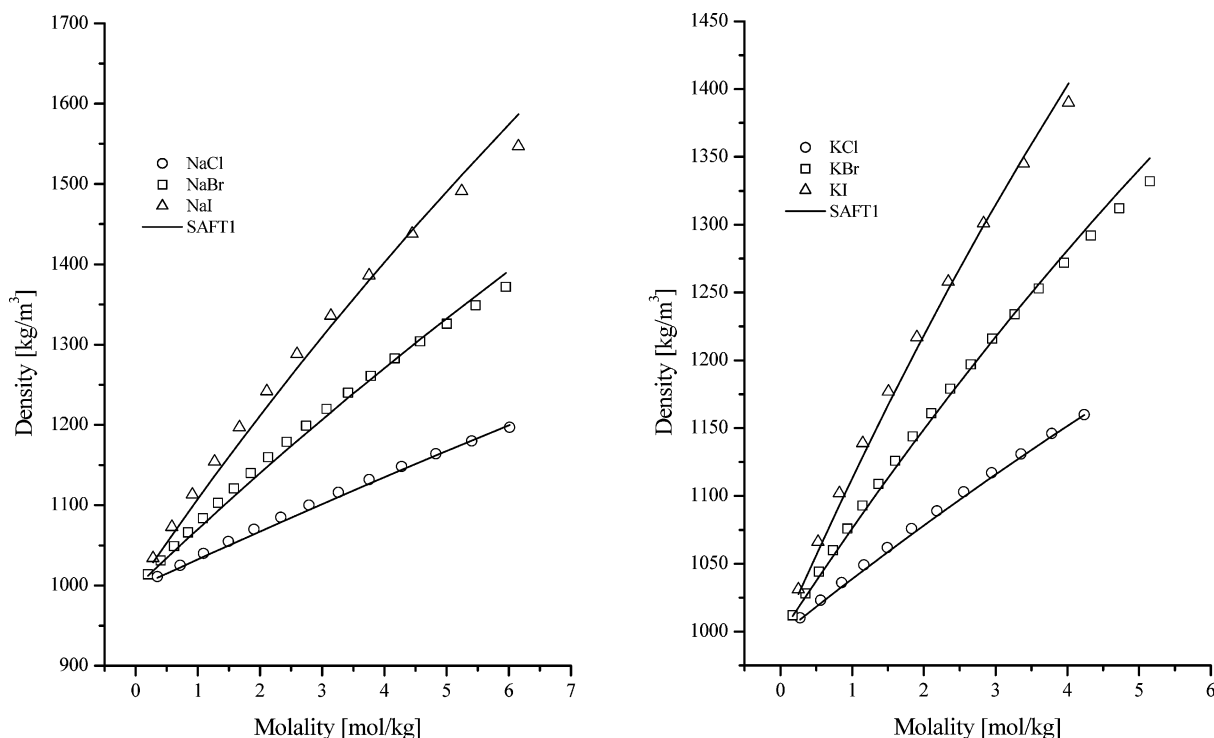
Figure 8. Correlated density of several salt + water systems at 25 °C.
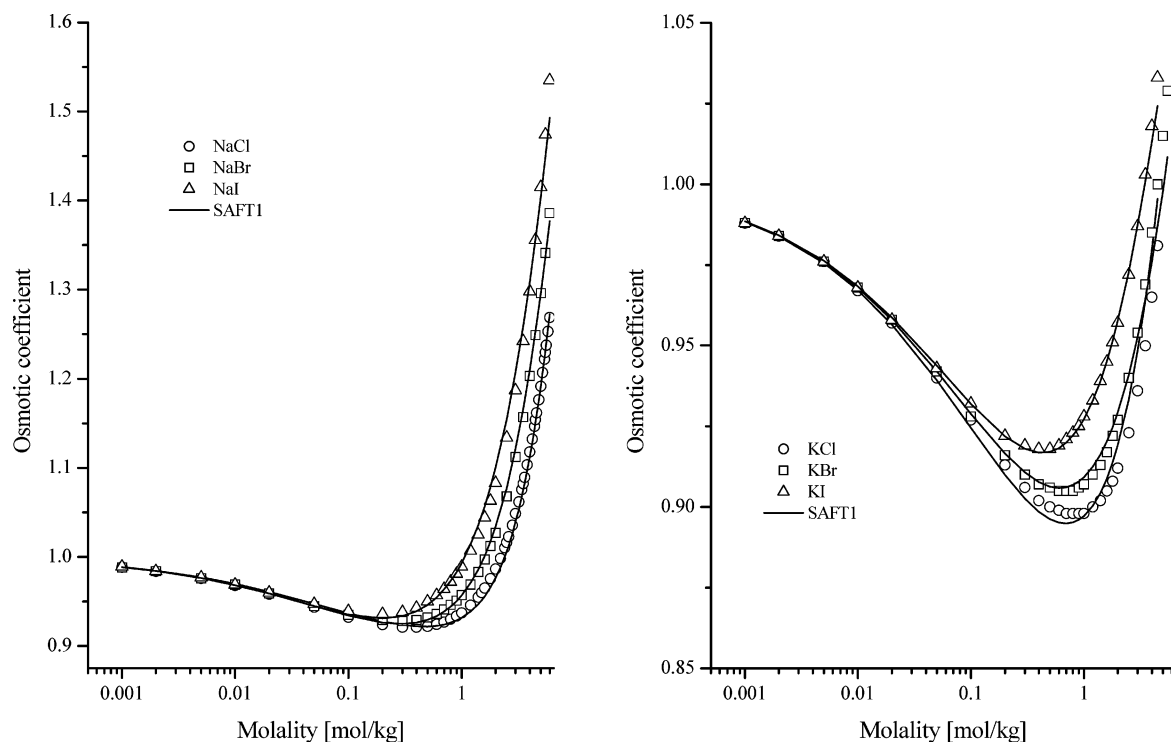

Figure 9. Predicted osmotic coefficient of several salt + water systems at 25 °C.

ficients, and Figure 8 illustrates the calculations for the density. The parameters reported for Na^+ and Cl^- in Table 4 are somewhat different from those reported in Table 2. The representation of the NaCl properties using the parameter set reported in Table 4 is not as accurate as that using the parameter set reported in Table 2, but the set reported in Table 2 does not work well for the other salts.

The hydrated diameters obtained above are consistent with those obtained from other models. For example, Myers et al.[17] obtained values in the range of 3.925–

4.551 Å for the six salts considered, Ghotbi et al.[32] obtained values in the range of 2.983–3.711 Å using the Kelvin–MSA model for the same salts, and Parkhurst[33] obtained the ion-size parameters of 4.32 Å for Na^+ and 3.71 Å for both K^+ and Cl^- using a Debye–Huckel-type formula.

The parameters reported in Table 4 are used to predict the osmotic coefficient, as shown in Figure 9: left for the sodium salts and right for the potassium salts. ARD is 0.47% (NaCl), 0.48% (KCl), 0.30% (NaBr), 0.34% (KBr), 0.72% (NaI), and 0.11% (KI).
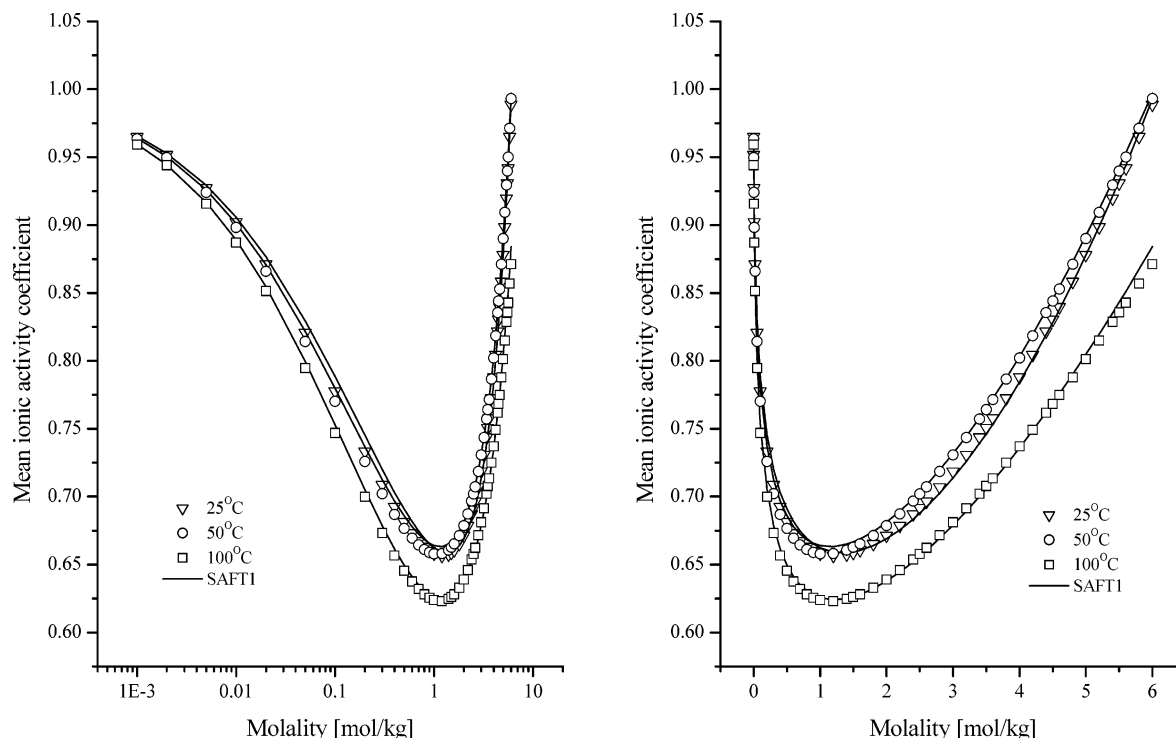
Figure 10. Correlated mean ionic activity coefficient of NaCl + water at 25, 50, and 100 °C.
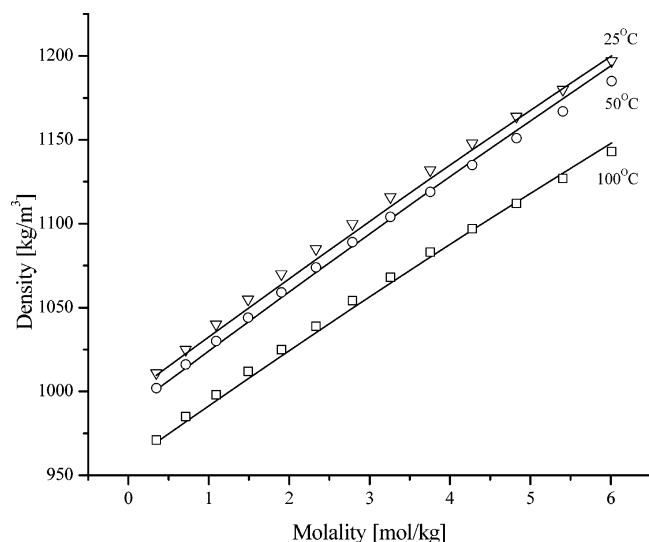

Figure 11. Correlated density of NaCl + water at 25, 50, and 100 °C.

Results for NaCl + Water at 50 and 100 °C

To probe for the temperature dependence of the solution properties, as an example, we fit the mean ionic activity coefficient and density data for NaCl at 50 and 100 °C. The parameters at 25 °C used in eqs 12−14 are those in Table 4. The other parameters obtained from this fit are as follows: $c_1 = (-8.371\,56 \times 10^{-3}$ and $-6.753\,35 \times 10^{-4})$, $c_2 = (1125.1474$ and $1915.5243)$ [K], $c_3 = (236.8101$ and $236.8101)$ [K], and $c_4 = 664.4214$ [K]. The values of c_1, c_2, and c_3 are in pairs, for Na^+ and Cl^-, respectively. ARDs for the mean ionic activity coefficient are 0.50% (50 °C) and 0.39% (100 °C). ARDs for the density are 0.29% (50 °C) and 0.30% (100 °C). The results of this fit are shown in Figure 10 for the mean ionic activity coefficient and in Figure 11 for the density.

For the record, SAFT1 captures the NaCl mean ionic activity coefficient crossover in going from 25 to 50 °C at a molality of about 1; in a high-salt-concentration region, the activity coefficient at 50 °C is higher than that at 25 °C, as shown in Figure 10b.

Using the same parameters, with no further readjustment, one can demonstrate that the predicted osmotic coefficients at 50 and 100 °C and the predicted vapor pressures at 50 and 100 °C agree with the experimental data, as shown in Figures 12 and 13. The osmotic coefficient at 25 °C, shown in Figure 9a, is not shown in Figure 12 for clarity. ARDs for the osmotic coefficient are 0.30% (50 °C) and 0.32% (100 °C). ARDs for the vapor pressure are 0.20% (50 °C) and 0.35% (100 °C).

As for the fitting at 25 °C, the temperature dependence also needs to be fitted simultaneously over other aqueous electrolytes to obtain universal parameters, which is the subject of future work aimed at a universal model applicable to strong electrolytes, including those relevant to bioseparations and enhanced oil recovery.

Comparison with Other Models

Table 5 shows examples for six salts estimated from the model developed in this work and from two other models, Myers' model[17] and Liu's model.[18] Each of these models has a different number of parameters and fits different properties of the aqueous electrolyte solutions in different ranges of molality. Also, these models use different types of parameters, either salt parameters or ion parameters. The ion parameters are transferable among common ions in different salts, while salt parameters are unique to individual salts. Our model has a total of three parameters per ion and one parameter per salt, which means that it will require fewer parameters than the other models because the ion parameters are transferable from salt to salt. For example, if we need parameters for 25 salts made up of 5 anions and 5 cations, the Myers model[17] will require a total of 75 parameters, the Liu model[18] will require a total of 60
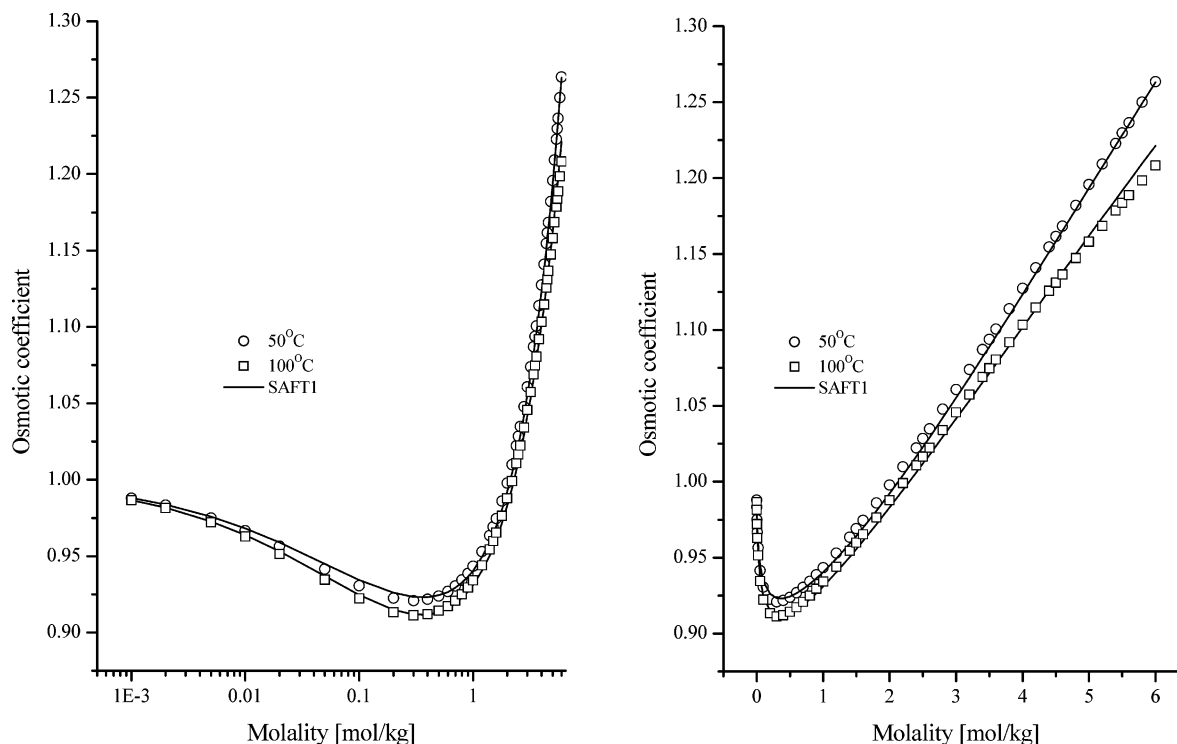
Figure 12. Predicted osmotic coefficient of NaCl + water.

Table 5. Model Comparison for Six Salts at 25 °C

		Myers' model[17]	Liu's model[18]	this model
no. of salt parameters		3	2	1
no. of ion parameters		0	1	3
properties fitted		$\gamma_\pm$	$\gamma_\pm$	$\gamma_\pm$ and density
ARD[a]	NaCl	0.08%; − (0.1−6.0)	0.07%; 0.16% (0.1−6.0)	0.55%; 0.38% (0.001−6.0)
	NaBr	0.09%; − (0.1−4.0)	0.08%; 0.21% (0.1−4.0)	0.45%; 0.65% (0.001−6.0)
	NaI	0.19%; − (0.1−3.5)	0.18%; 0.19% (0.1−3.5)	1.1%; 1.2% (0.001−6.0)
	KCl	0.08%; − (0.1−4.5)	0.54%; 1.68% (0.1−4.5)	0.73%; 0.65% (0.001−4.5)
	KBr	0.09%; − (0.1−5.5)	0.35%; 1.88% (0.1−5.5)	0.48%; 0.45% (0.001−5.5)
	KI	0.20%; − (0.1−4.5)	0.18%; 1.41% (0.1−4.5)	0.15%; 0.61% (0.001−4.5)

[a] For each salt, the first entry is the ARD of $\gamma_\pm$ and the second entry is the ARD of the density; the molality range used is given in the parentheses.

parameters (per salt) and no ion parameters; its salt parameters are obtained from the fitting of individual salts, which means a better goodness of fit for each individual salt. However, such models with multiple-salt-specific parameters are hard or impossible to extend to multiple-salt solutions, which is one of the ultimate goals of electrolyte models. With only one salt parameter, our model can be readily extended to mixed electrolyte solutions using a simple mixing rule.[34]

Conclusion

The SAFT1-RPM model represents the mean ionic activity coefficient, density, osmotic coefficient, and vapor pressure of the aqueous solutions of NaCl, NaBr, NaI, KCl, KBr, and KI in a framework that is analogous to the nonelectrolyte framework. SAFT1 alone represents pure water, including the density anomaly. SAFT1 salt consists of two segments, cation and anion.
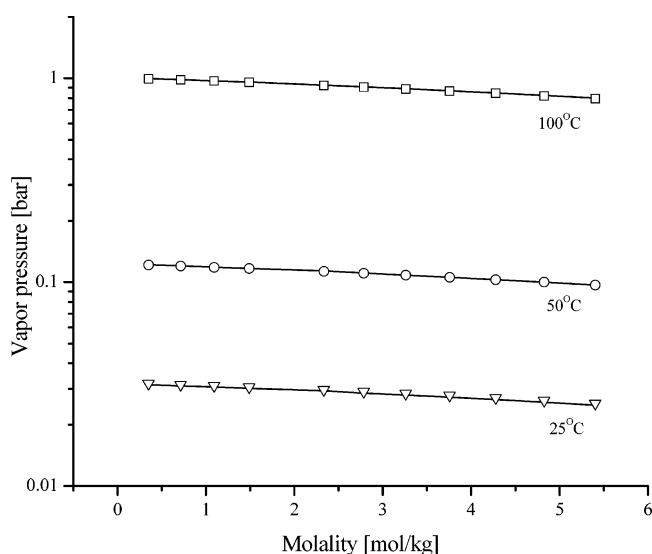

Figure 13. Predicted vapor pressure of NaCl + water.

parameters, and our model will require a total of 55 parameters. In general, the higher the number of salt parameters, the better the goodness of fit because the interdependency among salts having common ions is reduced. For example, the Myers model has three salt

Appendix

To account for the electroneutrality constraint, the mean ionic activity coefficient is obtained from the chemical equilibrium in the ionic dissociation:

$$\gamma_{\pm} = [(\gamma_+^{\nu_+})(\gamma_-^{\nu_-})]^{1/\nu} \tag{A1}$$

where the total number of ions in the salt is given by eq 2. The ionic activity coefficients on the right-hand side are not independently measurable.

The activity coefficient is unsymmetrically normalized, in the spirit of Henry's law; that is, the mean ionic activity coefficient approaches 1 if the ion (salt) concentration approaches 0. It is expressed in terms of the fugacity coefficients as[16]

$$\gamma_{\pm} = \frac{\hat{\phi}_{\pm}}{\hat{\phi}_{\pm}^{\infty}} = \left[\left(\frac{\hat{\phi}_+}{\hat{\phi}_+^{\infty}}\right)^{\nu_+}\left(\frac{\hat{\phi}_-}{\hat{\phi}_-^{\infty}}\right)^{\nu_-}\right]^{1/\nu} \tag{A2}$$

where the superscript ∞ means the infinite-dilution state.

The fugacity coefficient of component i in a mixture is derived from the residual Helmholtz energy as usual:

$$\ln \hat{\phi}_i = \tilde{a}^{\text{res}} + \left(\frac{\partial \tilde{a}^{\text{res}}}{\partial x_i}\right)_{T,\rho,x_{k \neq i}} - \sum_j x_j \left(\frac{\partial \tilde{a}^{\text{res}}}{\partial x_j}\right)_{T,\rho,x_{k \neq j}} + \rho\left(\frac{\partial \tilde{a}^{\text{res}}}{\partial \rho}\right)_{T,x} - \ln\left[1 + \rho\left(\frac{\partial \tilde{a}^{\text{res}}}{\partial \rho}\right)_{T,x}\right] \tag{A3}$$

If the ions of the salt are treated as two different "components" in water, we use eq A3 twice, once for each ion. After multiplying with the corresponding number of ions, we add those two resulting equations to get

$$\ln(\hat{\phi}_+^{\nu_+}\hat{\phi}_-^{\nu_-})^{1/\nu} = \tilde{a}^{\text{res}} + \frac{\nu_+}{\nu}\left(\frac{\partial \tilde{a}^{\text{res}}}{\partial x_+}\right)_{T,\rho,x_-,x_{\text{water}}} + \frac{\nu_-}{\nu}\left(\frac{\partial \tilde{a}^{\text{res}}}{\partial x_-}\right)_{T,\rho,x_+,x_{\text{water}}} - \sum_{j=+,-,\text{water}} x_j \left(\frac{\partial \tilde{a}^{\text{res}}}{\partial x_j}\right)_{T,\rho,x_{k \neq j}} + \rho\left(\frac{\partial \tilde{a}^{\text{res}}}{\partial \rho}\right)_{T,x} - \ln\left[1 + \rho\left(\frac{\partial \tilde{a}^{\text{res}}}{\partial \rho}\right)_{T,x}\right] \tag{A4}$$

The expression inside the logarithm on the left-hand side of eq A4 is the mean ionic fugacity coefficient, $\hat{\phi}_{\pm}$, needed in eq A2.

If the salt is now treated as the component in equilibrium with water, the salt fugacity coefficient equivalent to the mean ionic fugacity coefficient is

$$\ln \hat{\phi}_{\text{salt}} = \tilde{a}^{\text{res}} + \left(\frac{\partial \tilde{a}^{\text{res}}}{\partial x_{\text{salt}}}\right)_{T,\rho x_{\text{water}}} - \sum_{j=\text{salt},\text{water}} x_j \left(\frac{\partial \tilde{a}^{\text{res}}}{\partial x_j}\right)_{T,\rho,x_{k \neq j}} + \rho\left(\frac{\partial \tilde{a}^{\text{res}}}{\partial \rho}\right)_{T,x} - \ln\left[1 + \rho\left(\frac{\partial \tilde{a}^{\text{res}}}{\partial \rho}\right)_{T,x}\right] \tag{A5}$$

Equations A4 and A5 become equivalent for the following equalities:

$$\left(\frac{\partial \tilde{a}^{\text{res}}}{\partial x_{\text{salt}}}\right)_{T,\rho,x_{\text{water}}} = \frac{\nu_+}{\nu}\left(\frac{\partial \tilde{a}^{\text{res}}}{\partial x_+}\right)_{T,\rho,x_-,x_{\text{water}}} + \frac{\nu_-}{\nu}\left(\frac{\partial \tilde{a}^{\text{res}}}{\partial x_-}\right)_{T,\rho,x_+,x_{\text{water}}} \tag{A6}$$

$$\sum_{j=\text{salt},\text{water}} x_j \left(\frac{\partial \tilde{a}^{\text{res}}}{\partial x_j}\right)_{T,\rho,x_{k \neq j}} = \sum_{j=+,-,\text{water}} x_j \left(\frac{\partial \tilde{a}^{\text{res}}}{\partial x_j}\right)_{T,\rho,x_{k \neq j}} \tag{A7}$$

These equalities can be justified by defining the mole fraction of the salt as in eq 6 so that

$$x_{\text{salt}} = \frac{\nu}{\nu_+}x_+ = \frac{\nu}{\nu_-}x_- \tag{A8}$$

which verifies eq A6:

$$\left(\frac{\partial \tilde{a}^{\text{res}}}{\partial x_{\text{salt}}}\right)_{T,\rho,x_{\text{water}}} = \left(\frac{\partial \tilde{a}^{\text{res}}}{\partial x_+}\right)_{T,\rho,x_-,x_{\text{water}}} \frac{\partial x_+}{\partial x_{\text{salt}}} + \left(\frac{\partial \tilde{a}^{\text{res}}}{\partial x_-}\right)_{T,\rho,x_+,x_{\text{water}}} \frac{\partial x_-}{\partial x_{\text{salt}}}$$

$$= \frac{\nu_+}{\nu}\left(\frac{\partial \tilde{a}^{\text{res}}}{\partial x_+}\right)_{T,\rho,x_-,x_{\text{water}}} + \frac{\nu_-}{\nu}\left(\frac{\partial \tilde{a}^{\text{res}}}{\partial x_-}\right)_{T,\rho,x_+,x_{\text{water}}} \tag{A9}$$

Consecutively, eq A7 is verified using eq A9, together with the definition of the salt mole fraction in eq 6.

Therefore, the mean ionic activity coefficient, $\gamma_{\pm}$, can be equivalently expressed as the salt activity coefficient, γ_{salt}; the latter has the form that is consistent with the common thermodynamic framework for nonelectrolytes, where the salt is treated as a molecule that consists of two different segments corresponding to the cation and anion.

We can calculate the infinite-dilution salt fugacity coefficient by taking the limit $x_{\text{salt}} \to 0$ or equivalently $x_{\text{water}} \to 1$ in eq A3:

$$\ln \hat{\phi}_{\text{salt}}^{\infty} = \lim_{x_{\text{salt}} \to 0}\left\{\tilde{a}^{\text{res}} + \rho\left(\frac{\partial \tilde{a}^{\text{res}}}{\partial \rho}\right)_{T,x} - \ln\left[1 + \rho\left(\frac{\partial \tilde{a}^{\text{res}}}{\partial \rho}\right)_{T,x}\right]\right\} + \lim_{x_{\text{salt}} \to 0}\left\{\left(\frac{\partial \tilde{a}^{\text{res}}}{\partial x_{\text{salt}}}\right)_{T,\rho,x_{\text{water}}} - \sum_{j=\text{salt},\text{water}} x_j \left(\frac{\partial \tilde{a}^{\text{res}}}{\partial x_j}\right)_{T,\rho,x_{k \neq j}}\right\} \tag{A10}$$

The first limit is the logarithm of the fugacity coefficient of pure water. The second limit is the expression in the exponent in eq 19, so that eq 19 is verified.

Nomenclature

$\tilde{a}$ = dimensionless residual Helmholtz free energy
ARD = average relative deviation = $(1/N)\sum_{n=1}^{N}(|\Delta_n^{\text{calc}} - \Delta_n^{\text{exp}}|/\Delta_n^{\text{exp}})$, where N = number of data points, Δ_n = nth data point (superscripts calc = calculated and exp = experimental)
C_{m} = molality
m_i = segment number of component i
d = hydrated diameter
d_j = hydrated ionic diameter of ion j

e = electric charge of an electron
k = Boltzmann constant
m_i = segment number of component i
M_i = molecular weight (g/mol) of component i
N_A = Avogadro's number
P = pressure
q_j = electric charge of ion j
T = absolute temperature
u_j = segment energy of ion j
v_j = segment volume of ion j
x = dimensionless quantity defined in RPM
x_i = mole fraction of component i
z_j = valence of ion j
α_0 = quantity defined in RPM
χ_i = activity coefficient of component i
$\gamma_{\pm}$ = mean activity coefficient
ϵ_w = dielectric constant of water
$\hat{\phi}_i$ = fugacity coefficient of component i in the solution
Φ = osmotic coefficient
κ = Debye inverse screening length
λ = SAFT1 parameter
ν = sum of the stoichiometric coefficients
ν_j = stoichiometric coefficient of ion j
ρ = density
ρ_n = number density
χ_j = fraction of ion j in salt

Subscripts

i = ith component (1 = salt; 2 = water)
j = jth ion (+, −)

Superscripts

m = molality-based
x = mole-fraction-based
0 = pure component
∞ = infinite dilution

Literature Cited

(1) Hatti-Kaul, R., Ed. *Aqueous Two-Phase Systems, Methods and Protocols*; Humana Press Inc.: Totowa, NJ, 2000.

(2) Enick, R. M.; Klara, S. M. CO_2 Solubility in Water and Brine Under Reservoir Conditions. *Chem. Eng. Commun.* **1990**, *90*, 23.

(3) Enick, R. M.; Klara, S. M. Effects of CO_2 Solubility in Brine on the Compositional Simulation of CO_2 Floods. *SPE Res. Eng.* **1992**, *7*, 253.

(4) Prausnitz, J. M.; Lichtenthaler, R. N.; de Azevedo, E. G. *Molecular thermodynamics of fluid-phase equilibria*, 3rd ed.; Prentice Hall PTR: Upper Saddle River, NJ, 1999; Chapter 9.

(5) Tester, J. W.; Modell, M. *Thermodynamics and Its Applications*, 3rd ed.; Prentice Hall PTR: Upper Saddle River, NJ, 1997; Chapter 12.

(6) Wilczek-Vera, G.; Vera, J. H. Peculiarities of the Thermodynamics of Electrolyte Solutions: A Critical Discussion. *Can. J. Chem. Eng.* **2003**, *81*, 70.

(7) Hsu, H.-L.; Wu, Y.-C.; Lee, L.-S. Vapor Pressures of Aqueous Solutions with Mixed Salts of NaCl + KBr and NaBr + KCl. *J. Chem. Eng. Data* **2003**, *48*, 514.

(8) Haynes, C. A.; Benitez, F. J.; Blanch, H. W.; Prausnitz, J. M. Application of Integral-Equation Theory to Aqueous Two-Phase Partitioning Systems. *AIChE J.* **1993**, *39*, 1539.

(9) Magini, M. *X-ray diffraction of ions in aqueous solutions: hydration and complex formation*; CRC Press: Boca Raton, FL, 1988.

(10) Cummings, S.; Enderby, J. E.; Neilson, G. W.; Newsome, J. R.; Howe, R. A.; Howells, W. S.; Soper, A. K. Chloride ions in aqueous solutions. *Nature* **1980**, *287*, 714.

(11) Max, J.-J.; Chapados, C. IR Spectroscopy of Aqueous Alkali Halide Solutions: Pure Salt-solvated Water Spectra and Hydration Numbers. *J. Chem. Phys.* **2001**, *115*, 2664.

(12) Chen, C. C.; Britt, H. I.; Boston, J. F.; Evans, L. B. Local composition model for excess Gibbs energy of electrolyte systems. Part I: Single solvent, single completely dissociated electrolyte systems. *AIChE J.* **1982**, *28*, 588.

(13) Pitzer, K. S. Thermodynamics of Electrolytes. I. *J. Phys. Chem.* **1973**, 77, 268.

(14) Galindo, A.; Gil-Villegas, A.; Jackson, G.; Burgess, A. N. SAFT-VRE: Phase Behavior of Electrolyte Solutions with the Statistical Associating Fluid Theory for Potentials of Variable Range. *J. Phys. Chem. B* **1999**, *103*, 10272.

(15) Gil-Villegas, A.; Galindo, A.; Jackson, G. A Statistical Associating Fluid Theory for Electrolyte Solutions (SAFT-VRE). *Mol. Phys.* **2001**, *99*, 531.

(16) Patel, B. H.; Paricaud, P.; Galindo, A.; Maitland, G. C. Prediction of the Salting-Out Effect of Strong Electrolytes on Water + Alkane Solutions. *Ind. Eng. Chem. Res.* **2003**, *42*, 3809.

(17) Myers, J. A.; Sandler, S. I.; Wood, R. H. An Equation of State for Electrolyte Solutions Covering Wide Ranges of Temperature, Pressure, and Composition. *Ind. Eng. Chem. Res.* **2002**, *41*, 3282.

(18) Liu, Z.; Wang, W.; Li, Y. An equation of state for electrolyte solutions by a combination of low-density expansion of nonprimitive mean spherical approximation and statistical associating fluid theory. *Fluid Phase Equilib.* **2005**, *227*, 147.

(19) Adidharma, H.; Radosz, M. Prototype of an Engineering Equation of State for Heterosegmented Polymers. *Ind. Eng. Chem. Res.* **1998**, *37*, 4453.

(20) Banaszak, M.; Chen, C. K.; Radosz, M. Copolymer SAFT Equation of State. Thermodynamic Pertubation Theory Extended to Heterobonded Chains. *Macromolecules* **1996**, *29*, 6481.

(21) Lee, L. L. *Molecular Thermodynamics of Nonideal Fluids*; Butterworth Publishers: Stoneham, MA, 1988.

(22) Tan, S. P.; Adidharma, A.; Radosz, M. Statistical Associating Fluid Theory for Aqueous Electrolyte Solutions. Presented the AIChE Annual Meeting, San Francisco, CA, Nov 16−21, 2003; Paper 230a.

(23) Pitzer, K. S. *Thermodynamics*, 3rd ed.; McGraw-Hill: New York, 1995; p 271.

(24) Huang, S. H.; Radosz, M. Equation of State for Small, Large, Polydisperse, and Associating Molecules. *Ind. Eng. Chem. Res.* **1990**, *29*, 2284.

(25) Fernández, D. P.; Goodwin, A. R. H.; Lemmon, E. W.; Levelt Sengers, J. M. H.; Williams, R. C. A Formulation for the Static Permittivity of Water and Steam at Temperatures from 238 K to 873 K at Pressures up to 1200 MPa, Including Derivatives and Debye−Hückel Coefficients. *J. Phys. Chem. Ref. Data* **1997**, *26*, 1125.

(26) Sandler, S. I. *Chemical and Engineering Thermodynamics*, 2nd ed.; John Wiley & Sons: Singapore, 1989.

(27) Clarke, E. C. W.; Glew, D. N. Evaluation of the Thermodynamic Functions for Aqueous Sodium Chloride from Equilibrium and Calorimetric Measurements below 154 °C. *J. Phys. Chem. Ref. Data* **1985**, *14*, 489.

(28) Zaytsev, I. D., Aseyev, G. G., Eds. *Properties of Aqueous Solutions of Electrolytes*; CRC Press: Boca Raton, FL, 1992.

(29) Parisod, C. J.; Plattner, E. Vapor−liquid equilibriums of the sodium chloride−water system in the temperature range 300−440 °C. *J. Chem. Eng. Data* **1981**, *26*, 16.

(30) Pepela, C. N.; Dunlop, P. J. A Re-examination of the Vapor Pressures of Aqueous Sodium Chloride Solutions at 25 °C. *J. Chem. Thermodyn.* **1972**, *4*, 255.

(31) Hamer, W. J.; Wu, Y.-C. Osmotic coefficients and mean activity coefficients of uniunivalent electrolytes in water at 25 deg. *J. Phys. Chem. Ref. Data* **1972**, *1*, 1047.

(32) Ghotbi, C.; Azimi, G.; Taghikhani, V.; Vera, J. H. On the Correlation of the Activity Coefficients in Aqueous Electrolyte Solutions Using the K-MSA Model. *Ind. Eng. Chem. Res.* **2003**, *42*, 1270.

(33) Parkhurst, D. L. Ion-Association Models and Mean Activity Coefficient of Various Salts. In *Chemical modeling of aqueous systems II*; Melchior, D. C., Bassett, R. L., Eds.; ACS Symposium Series 416; American Chemical Society: Washington, DC, 1990; pp 31−43.

(34) Ji, X.; Tan, S. P.; Adidharma, H.; Radosz, M. Statistical Associating Fluid Theory Coupled with Restricted Primitive Model To Represent Aqueous Strong Electrolytes: Multiple-Salt Solutions. *Ind. Eng. Chem. Res.* **2005**, submitted for publication.