Phase Equilibria for Systems Containing Hydrocarbons, Water, and Salt: An Extended Peng–Robinson Equation of State

Jianzhong Wu and John M. Prausnitz*

Department of Chemical Engineering, University of California, Berkeley, and Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720

The empirical success of the Peng–Robinson equation of state (PREOS) is unmatched; there is no other simple equation of state of the van der Waals form that has shown such wide and reliable applicability to the calculation of vapor–liquid equilibria (VLE) for systems containing light hydrocarbons, permanent gases, carbon dioxide, and hydrogen sulfide. PREOS is one of the great success stories of applied chemical engineering thermodynamics. However, PREOS also has limitations; two of these are addressed here. Theoretically based extensions are presented, first, for including water and aqueous hydrocarbon mixtures and, second, for including salt in water and in aqueous hydrocarbon mixtures. Illustrative examples show that these extensions are successful for VLE (where L refers to a hydrocarbon liquid dilute in water) and for VLE (where L refers to saline water). Because the extension to include water, based on SAFT (statistical association fluid theory), cannot properly take into account the well-documented hydrophobic effect, it is not yet possible to give a good representation of phase equilibria when one of the phases is a dilute aqueous liquid solution of hydrocarbon where the hydrophobic effect is significant.

Introduction

Within a few years following its publication in 1976, the Peng–Robinson equation of state (PREOS) has become a standard tool for calculation of vapor–liquid equilibria for fluid mixtures, especially for those mixtures encountered in the natural-gas and petroleum industries. Although the literature is rich with hundreds of variations of the original van der Waals equation of state of 1873, no variation has been as useful or as widely accepted as the PREOS. It is no exaggeration to claim that the PREOS is one of the greatest success stories in the history of applied chemical thermodynamics. Somehow, by design, determination, experience, and a bit of luck, Peng and Robinson constructed the optimum balance of repulsive and attractive terms such that the sum of those terms gives a remarkably close representation of the configurational thermodynamic properties of a large number of pure fluids and their mixtures.

While the notable positive qualities of the PREOS are properly acclaimed and utilized in a variety of engineering applications, the limitations of this justly famous equation of state are also well-known: inaccurate liquid densities; poor representation in the critical region; unreliable for fluids with very large molecules; and inapplicable to highly polar fluids, hydrogen-bonded fluids (especially water), and electrolytes.

In this work, we do not consider the critical region nor very large molecules. Our concern here is with extension of the PREOS to systems containing water and electrolytes (in particular, sodium chloride) in addition to the usual hydrocarbons and, perhaps, gases such as nitrogen, carbon dioxide, and hydrogen sulfide.

Numerous attempts have been made to extend the PREOS to systems containing water. Nearly all of these are strictly empirical in the sense that no fundamental changes were made; only PREOS constants were adjusted to fit water properties. There is no need here to summarize these attempts because, fortunately, Economou and Tsonopoulos (1997) have recently published a splendid critical and comprehensive review that gives essentially all pertinent references. To our best knowledge, however, there has been no previous discussion of how the PREOS may be applied, in at least a semi-theoretical way, toward constructing an equation of state for aqueous hydrocarbon systems that also contain sodium chloride.

In this work we present a theoretically based procedure for establishing an equation of state that is applicable to mixtures containing water, salt, and the "usual" components that have classically been described by the PREOS. Our procedure is similar to that used by a few others (see Economou and Tsonopoulos (1997)) in the sense that we use the PREOS for giving the Helmholtz energy of a reference system that contains all molecules of interest but without hydrogen bonding and without electric charges. We then propose additional contributions to the Helmholtz energy due to hydrogen bonding (based on a well-known theory called SAFT, statistical association fluid theory) and due to electric charging of ions and subsequent ion–ion and ion–solvent interactions.

Consistent with similar studies by others (see the review by Economou and Tsonopoulos (1997)), we find that PREOS with SAFT is useful for describing pure water as well as aqueous vapor mixtures and liquid mixtures rich in hydrocarbon. Again, consistent with the work of others, we find that PREOS with SAFT is not useful for liquid hydrocarbon–water mixtures rich in water.

The inability of SAFT to describe the solubility of a hydrocarbon in water is especially pronounced at low temperature where the hydrophobic effect is dominant because that effect is not included in SAFT nor in any
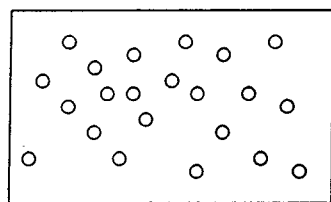

We start with a normal-fluid mixture where repulsive interactions are like those of hard spheres, and attractive interactions are dominated by dispersion (van der Waals) interactions. The PR-EOS is applied to describe the thermodynamic properties of this mixture where characteristic parameters a, and b are obtained from the critical properties for hydrocarbons, and from dispersion and volumetric properties for water and ions.
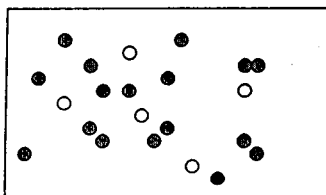
In Step I, we introduce hydrogen bonding between water molecules. The additional Helmholtz energy is taken into account using the SAFT theory. Here the three-site model is used to represent a water molecule.
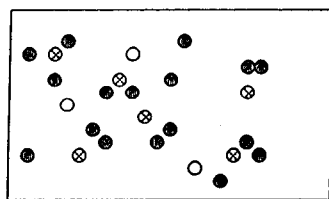
In Step II, ions are formed from neutral species, requiring three additional contributions to the Helmholtz energy, i.e, Born energy, ion hydration and Coulomb interaction. The Born energy refers to the electrostatic work done in charging an neutral molecule in a solvent medium; ion hydration refers to additional electrostatic interactions between charged ions and solvent molecules; Coulomb interaction refers to electrostatic ion-ion interactions in the solvent medium.

○   molecule of normal fluid
◉   water molecule
⊗   ion

Figure 1. Hypothetical path of formation of a system containing hydrocarbons, water, and salt.

other commonly available theory. However, the PREOS augmented by SAFT and appropriate electrostatic terms is able to describe the properties of an aqueous solution of salt over a wide range of temperature and salt concentration. Further, at temperatures above 100 °C, the PREOS plus SAFT plus electrostatic contributions give a good representation of high-pressure phase equilibria for water−methane−sodium chloride.

A Model for the Helmholtz Energy

For systems containing hydrocarbons, water, and ions, a rational molecular-thermodynamic model should take into account hydrogen bonding, ion hydration, and electrostatic (Coulomb) interactions, in addition to the usual hard-core repulsion and dispersion−attraction interactions. This model should be applicable to pure hydrocarbons and pure water as well as to hydrocarbon mixtures, water−hydrocarbon mixtures, aqueous electrolyte solutions, and aqueous solutions containing electrolytes and hydrocarbons.

To develop the desired model, we assume that the Helmholtz energy A of a system containing hydrocarbon, water, and salt can be constructed by summing separate contributions:

$$A = A^{\mathrm{r}} + A^{\mathrm{assoc}} + A^{\mathrm{Born}} + A^{\mathrm{Coul}} \qquad (1)$$

where superscripts r, assoc, Born, and Coul indicate, respectively, the reference system, association, Born energy, and Coulomb interaction. The reference system refers to a mixture of normal fluids that takes into account short-range repulsive interactions and van der

Waals attractive interactions among all molecules (or ions). The contribution from association considers hydrogen bonding among water molecules and electrostatic interactions between ions and water molecules. A^{Born} concerns the Helmholtz energy of ion formation in a continuous medium, and A^{Coul} is the contribution due to Coulombic ion−ion interactions.

Thermodynamic properties are readily derived from eq 1 by standard differentiation. For example, the equation of state is given by

$$P = -\left(\frac{\partial A}{\partial V}\right)_{T,n} \qquad (2)$$

and the chemical potential of component i by

$$\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_{j\neq i}} \qquad (3)$$

where T stands for absolute temperature and V for total volume, n is the total number of moles, and n_i is the number of moles of component i. (For electrolyte solutions, cations and anions are considered as different species).

Figure 1 illustrates the hypothetical path of the formation of a closed mixture containing hydrocarbons, water, and salt at constant temperature and volume. We start with a reference system that contains all molecules (hydrocarbons, water, ions) as normal (non-hydrogen-bonded and bearing no electric charge) molecules; the Helmholtz energy of that system is A^{r}. We then consider two steps: in the first step, we add

hydrogen bonding among water molecules in the mixture; in the second step, we introduce electric charge to the ions and consider the consequences.

(a) Reference System. In this work, we use the Peng−Robinson equation of state (PREOS) to provide the thermodynamic properties of the reference fluid.

The Helmholtz energy of the reference fluid is given by (Peng and Robinson, 1976)

$$\frac{A^r}{nRT} = \frac{A^{IG}}{nRT} + \ln\left(\frac{v}{v-b}\right) +$$
$$\frac{a}{2\sqrt{2}bRT} \ln\left(\frac{v+(1-\sqrt{2})b}{v+(1+\sqrt{2})b}\right) \quad (4)$$

Here R stands for the gas constant and v for molar volume; the superscript IG refers to the ideal gas at system temperature, composition, volume, and total number of moles. For a hydrocarbon component i, a_i, and b_i are given by

$$a_i = a_i^0[1 + (0.37464 + 1.54226\omega_i -$$
$$0.26992\omega_i^2)(1 - \sqrt{T/T_{c_i}})]^2 \quad (5)$$

with

$$a_i^0 = 0.45724\frac{R^2 T_{c_i}^2}{P_{c_i}} \quad (6)$$

and

$$b_i = 0.07780\frac{RT_{c_i}}{P_{c_i}} \quad (7)$$

where T_c and P_c stand for critical temperature and pressure, respectively, and ω denotes acentric factor. For mixtures, characteristic parameters a and b vary with mole fraction x according to the conventional mixing rules

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad (8)$$

$$b = \sum_i x_i b_i \quad (9)$$

with $a_{ij} = (a_i a_j)^{1/2}(1 - k_{ij})$. Binary interaction parameter k_{ij} is adjustable; for the purpose of this work, $k_{ij} = 0$. When eq 2 is applied to eq 4, we obtain the well-known PREOS. We use eqs 5, 6, and 7 only for hydrocarbons, not for water or ions.

(b) Pure Water. For pure water, we need to consider hydrogen bonding among water molecules in addition to the interactions included in the reference system. However, we must first establish a theoretically based procedure for calculating a and b for water. Parameter a reflects attractive (dispersion) forces, while parameter b reflects molecular size.

To establish generalized relations for a^0 and b in terms of significant properties, we calculate a^0 and b for 10 simple normal fluids using eqs 6 and 7. We find that parameter b is well correlated with v_c, the critical volume, and parameter a^0 is well correlated with B/v_c,

Table 1. Dispersion Properties, Critical Volumes, and a^0 and b for the PREOS[a]

	$\alpha_0/(4\pi\epsilon_0)$ (Å³)	I (ev)	ϵ/k (K)	v_c (cm³/mol)	b (cm³/mol)	a^0 (J·m³)
He	0.205	24.587	10.2	57.8	14.86	0.0038
Ne	0.3956	21.564	35.7	41.7	10.56	0.0229
H₂	0.8023	15.427	38	65	16.61	0.0270
F₂	1.38	15.7	112	66.2	17.66	0.1246
O₂	1.5812	12.063	113	74.4	19.83	0.1496
Ar	1.6411	15.759	124	75.2	20.08	0.1482
N₂	1.7403	15.576	91.5	90.1	24.05	0.1483
CH₄	2.6	12.6	137	99.3	26.58	0.2477
Kr	2.4844	13.999	178.9	92.2	24.62	0.2519
CO₂	2.911	13.769	190	94	26.64	0.3960
H₂O	1.45	12.6		56	(14.48)	(0.1873)
Na⁺	0.21		(147.4)	(26.1)	(5.825)	(0.0299)
Cl⁻	3.02		(225.4)	(126.1)	(34.73)	(0.5563)

[a] α_0, I, and ϵ are obtained from *CRC Handbook of Chemistry and Physics* (66th ed.) and v_c, T_c, and P_c for neutral molecules from *The Properties of Gases & Liquids* (4th ed.); a^0 and b are calculated from eqs 6 and 7. Quantities in parentheses are from Figure 2.

where B is the London coefficient related to polarizability α_0 and first ionization potential I by

$$B = \frac{3I}{4}\left(\frac{\alpha_0}{4\pi\epsilon_0}\right)^2 \quad (10)$$

where ϵ_0 is the permittivity of free space; $\epsilon_0 = 8.854\,19 \times 10^{-12}$ C·V⁻¹·m⁻¹. (According to London's theory, the dispersion potential energy between two molecules is approximated by $-B/r^6$, where B is a characteristic constant and r is the center-to-center distance.)

Parts a and b respectively, of Figure 2 present the correlations and equations for obtaining b and a^0. Table 1 gives the molecular properties, α_0 and I, as well as the experimental critical volume v_c and parameters a^0, b of the PREOS for 10 simple fluids; Table 1 also gives a^0 and b for water obtained from the calculations. The experimental critical volume of water is used for obtaining b. Values obtained from the linear plots are indicated by parentheses.

The temperature dependence of parameter a is intimately linked with the method used to calculate A^{assoc} for pure water. That method is described in the next paragraphs.

The Helmholtz energy contribution from hydrogen bonding is obtained from the SAFT theory with the assumption of a three-site model for water, i.e., two donor sites for the two hydrogen atoms and one acceptor site for the oxygen atom of each water molecule. As discussed by Chapman et al. (1990)

$$\frac{A^{assoc}}{nRT} = \sum_S \left(\ln X^S + \frac{1 - X^S}{2}\right) \quad (11)$$

where superscript S indicates an association site. Association exists only between (donor) hydrogen and (acceptor) oxygen sites. X^S stands for the mole fraction of water molecules not bonded at site S, given by

$$X^S = (1 + \sum_{S'}\rho X^{S'}\Delta^{SS'})^{-1} \quad (12)$$

with

$$\Delta^{SS'} = d^3 g^{hs}(d) \kappa^{SS'}\left[\exp\left(\frac{\varepsilon^{SS'}}{kT}\right) - 1\right] \quad (13)$$

Table 2. Final Adjustable Parameters for Water[a]

b_w (cm³/mol)	a^0_w (J·m³)	k_a	ζ_{ww}/k (K)	κ_{ww}
15.29	0.2601	1.223	1477	0.4567

[a] For comparison, b_w calculated from the correlation between b and v_c is 14.48 cm³/mol. From eq 7, using experimental critical temperature and pressure, it is 18.93 cm³/mol. a^0_w calculated from the correlation between B/v_c and a^0_w is 0.1873 J·m³. From eq 6, using experimental critical temperature and pressure, it is 0.5987 J·m³.

Here k stands for Boltzmann constant and ρ for the number density of water molecules; $\kappa^{SS'}$ is a dimensionless parameter related to the bonding volume; $\zeta^{SS'}$ denotes bonding energy between sites S and S'; d represents the effective diameter of a water molecule, obtained from

$$d^3 = \frac{3}{2\pi} \frac{b}{N_A} \tag{14}$$

where b is the characteristic size parameter of the PREOS and N_A is Avogadro's number; $g^{hs}(d)$ is the contact value of the pair correlation function of a hard-sphere fluid given by

$$g^{hs}(d) = \frac{2 - \eta}{2(1 - \eta)^3} \tag{15}$$

where packing fraction $\eta = (\pi/6)\rho d^3$.

The model parameters for pure water include a, b for the PREOS and ζ, κ for the association interaction between hydrogen sites and oxygen sites. While the independently correlated values of a^0 and b can be used without further adjustment, ζ and κ are adjustable parameters obtained from pure-water volumetric and vapor-pressure data.

Although the SAFT model provides a big improvement for representing the properties of water, it is not satisfactory for fitting both the experimental saturated-liquid density and vapor pressure of water over a wide range of temperatures. As is well-known, the uniqueness of water is related to its tetrahedral liquid structure that is much different from that of a hard-sphere fluid. Therefore, to obtain good agreement with experiment, we assign a simple temperature dependence for parameter a for water

$$a_w = a^0_w(1 + k_a(1 - \sqrt{T/T_{cw}}))^2 \tag{16}$$

where $T_{cw} = 647.3$ K is the critical temperature of water and k_a is an adjustable parameter. [Equation 6 was also used by Kontogeorgis et al. (1996) in their model coupling the SAFT theory with the Soave−Redlich−Kwong equation of state.] With three adjustable parameters, k_a, ζ, and κ, our model can successfully fit the vapor pressure of water within 1% absolute relative deviation from the triple point to the critical point. The error for the liquid density is about 8% in the same temperature range.

To improve agreement further, we adjust parameters a^0_w and b_w to obtain the best fit of water properties. Table 2 gives final parameters for water. Figure 3a compares our calculated phase diagram of pure water with experiment; Figure 3b gives experimental and calculated vapor pressures. While, in general, the

model captures well the saturated properties from the triple point to the critical point, it misses the abnormal liquid density at temperatures near the triple point. Overall, calculated vapor pressures agree with experiment to within ±1%. Saturated liquid densities show a deviation of about ±3%. (Maximum errors appear near the triple point and the critical point.)

(c) Water−Hydrocarbon Mixtures. For water−hydrocarbon mixtures, the total Helmholtz energy also includes two parts, one from the reference system, and the other from association among water molecules. The Helmholtz energy from the reference part is given by eq 4, with mixing rules given by eqs 8 and 9. Parameters for water are given in Table 2.

Both in pure water and in a water−hydrocarbon mixture, we take association into account through donor hydrogen sites and acceptor oxygen sites of water molecules. However, the probability of bonding in an aqueous solution of hydrocarbons is different from that in pure water. According to the SAFT theory, the Helmholtz energy from association is given by

$$\frac{A^{assoc}}{nRT} = x_w \sum_S \left(\ln X^S + \frac{1 - X^S}{2} \right) \tag{17}$$

Here x_w stands for the mole fraction of water and superscript S for an association site. The summation is over all three association sites of water. Similar to eq 12, X^S is given by

$$X^S = (1 + \sum_{S'} \rho_w X^{S'} \Delta^{SS'})^{-1} \tag{18}$$

with

$$\Delta^{SS'} = d^3_w g^{hs}_{ww}(d_w) \kappa^{SS'} \left[\exp\left(\frac{\zeta^{SS'}}{kT}\right) - 1 \right] \tag{19}$$

Here, subscript w denotes water. $g^{hs}_{ww}(d_w)$ is the contact value of the pair-correlation function of a hard-sphere mixture given by

$$g^{hs}_{ww}(d_w) = \frac{1}{1 - \xi_3} + \frac{3d_w}{2} \frac{\xi_2}{(1 - \xi_3)^2} + \frac{d^2_w}{2} \frac{\xi^2_2}{(1 - \xi_3)^3} \tag{20}$$

where $\xi_2 = (\pi/6)\sum_i \rho_i d^2_i$ and $\xi_3 = (\pi/6)\sum_i \rho_i d^3_i$. The effective diameter for a hydrocarbon molecule is given by eq 14.

Vapor−liquid equilibria for water−hydrocarbon systems are calculated using conventional computational methods (Sandler, 1989). Figures 4−6 show the predicted vapor−liquid-equilibrium compositions of binary mixtures of water−methane, water−ethane, and water−propane for a variety of temperatures and pressures. These predictions do not use any adjustable binary constants. Predicted values agree well with experimental results for both liquid and vapor phases. However, the agreement becomes less satisfactory at high pressures, probably because the simple *(v−b)* repulsive term of the PREOS is unsatisfactory. Further, predicted solubilities of hydrocarbons in water at temperatures below 100 °C are too small because of inappropriate representation of water structure in the SAFT model. When hydrocarbon molecules are mixed with water at low temperatures, they are surrounded by structured
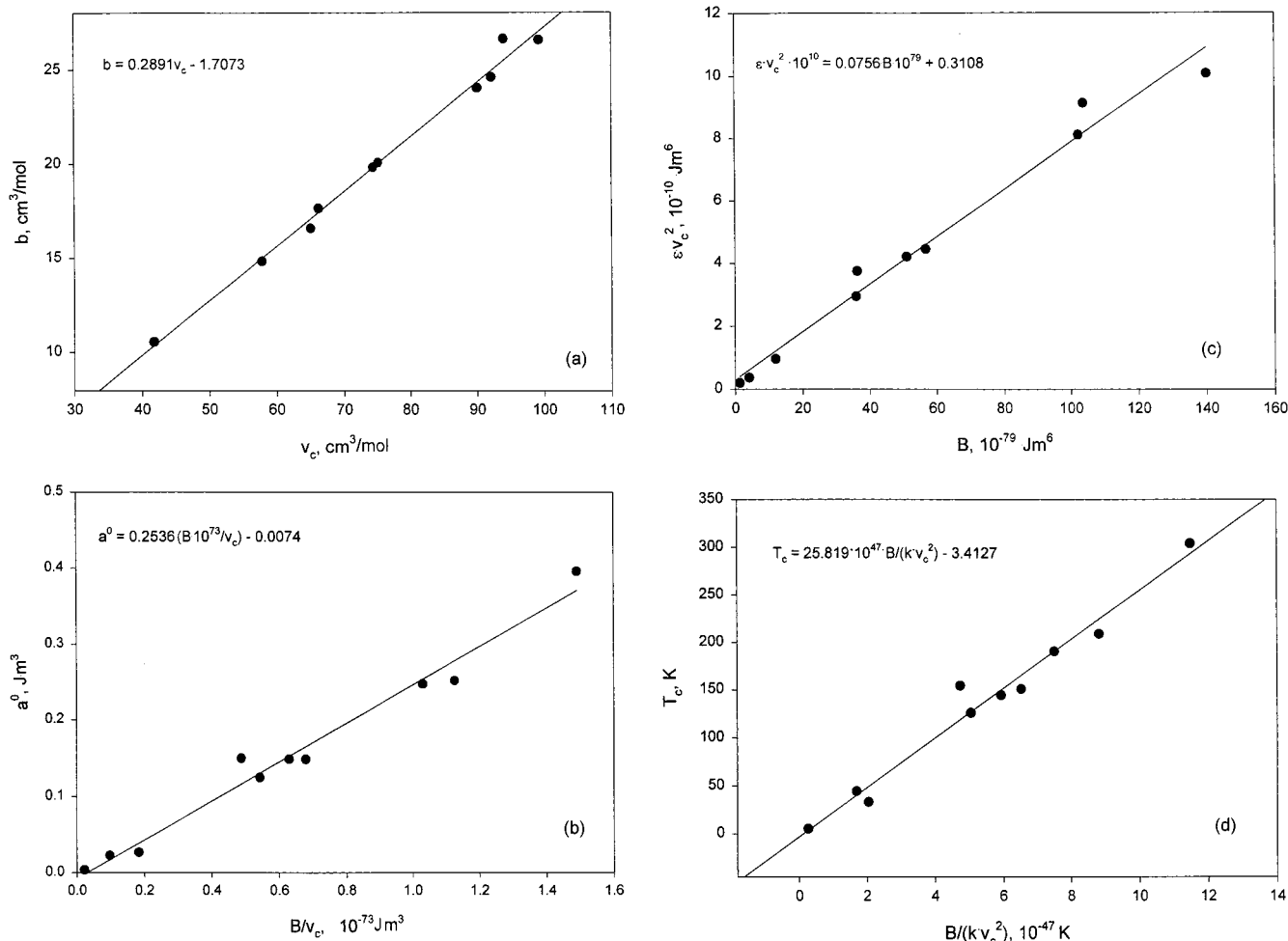
Figure 2. Correlations between a^0, b of the PREOS and molecular properties from 10 small normal fluids: (a) b vs critical volume v_c; (b) a^0 vs the ratio of the London parameter to critical volume v_c; (c) ϵv_c^2 vs the London coefficient B; (d) T_c vs $B/(kv_c^2)$.

water molecules (icebergs) that induce a large negative entropy of mixing; this entropic effect is known as the hydrophobic interaction. Because of this entropic effect, the extent of hydrogen bonding in a water-rich water−hydrocarbon mixture is larger than that in pure water. Regrettably, in the SAFT model, the solubility of hydrocarbon in water is underestimated because in that model, mixing of water and hydrocarbons is always entropically favorable; the SAFT model erroneously says that association between water molecules decreases due to the dilution effect of hydrocarbon molecules. The SAFT model ignores the hydrophobic effect. Fortunately, the hydrophobic effect becomes less important for small hydrocarbons at high temperatures, in excess of (about) 100 °C. But for larger hydrocarbons, the hydrophobic effect remains significant at temperatures in excess of 100 °C.

The performance of our model for VLE could be improved if a binary parameter between water and a hydrocarbon is used. An example is shown in Figure 6, where the dotted lines show calculated results with $k_{ij} = -0.057$. While there is little change in the vapor phase, the solubility of propane in water is much improved. However, such correction cannot improve VLLE predictions.

Figure 7 shows VLLE compositions, molar volumes, and saturated vapor pressures for binary mixtures of water and n-hexane at temperatures from 370 to 470

K. The predicted results for the vapor pressures and molar volumes are excellent. While the predicted compositions of the vapor phase and the n-hexane-rich liquid phase agree with experiment, the model seriously underpredicts the solubility of n-hexane in water because of the hydrophobic effect.

(d) Electrolyte Solutions. For an aqueous electrolyte solution, the Helmholtz energy contains all four contributions given in eq 1.

For an electrolyte solution, to use the PREOS for the reference system, we need to know characteristic parameters a and b for each ion. We would like to use the correlations given in Figure 2a,b to estimate a and b for ions, but we have no critical volumes for ions. Therefore, for ions, we develop correlations for hypothetical critical volume, London coefficient B, and the Lennard-Jones energy parameter ϵ. Figure 2c gives the correlation between ϵv_c and B for the 10 simple fluids. The Lennard-Jones energy parameters are from the *Handbook of Chemistry and Physics*. They were obtained from reduction of second-virial-coefficient and gas-phase-viscosity data.

The Lennard-Jones energy parameter for an ion can be estimated by (Jin and Donohue, 1988)

$$\frac{\epsilon_{ion}}{k} = 356\left(\frac{\alpha_{0,ion}}{4\pi\epsilon_0}\right)^{1.5}\frac{n_e^{0.5}}{(\sigma_{ion}/2)^6} \qquad (21)$$

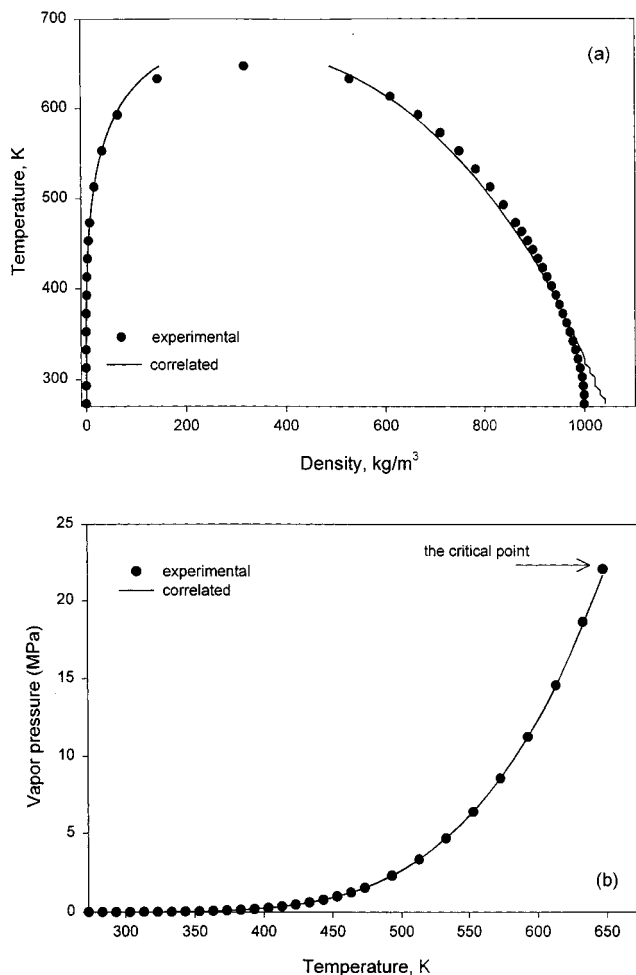**Figure 3.** (a) Phase diagram for pure water. (b) Saturated vapor pressure of water from the triple point to the critical point.

Figure 4. Vapor−liquid equilibria for water−methane. Here y_w denotes the mole fraction of water in the vapor phase, x_{CH_4} the mole fraction of CH_4 in the liquid phase. Solid lines are predicted; points are experimental. In these calculations, there are no adjustable binary parameters. (Experimental data are from Olds et al. (1942).)

where σ_{ion} denotes the diameter of an ion; n_e is the number of electrons of the ion. (In eq 21, the units are nm for σ and A^3 for $\alpha_0/(4\pi\epsilon_0)$. With these units, ϵ/k is in kelvin.) The London coefficient for an ion can be obtained by comparing the Lennard-Jones potential with the London equation for the dispersion potential. This comparison gives

$$B_{ion} = 4\epsilon_{ion}\sigma_{ion}^6 \tag{22}$$

When eq 21 is substituted into eq 22, σ_{ion} cancels. However, we must use an independent measure of σ_{ion} to find ϵ_{ion} from eq 21 as required in Figure 2c to find v_c. For NaCl aqueous solution, σ_{ion} is 0.19 nm for Na^+ and 0.382 nm for Cl^- (Lee, 1988). Parameters a^0 and b of the PREOS for (uncharged) ions then can be calculated using correlations given in Figure 2a,b. Table 1 gives a^0 and b for (uncharged) Na^+ and Cl^- and related properties used in the correlations. To calculate the characteristic parameter a for an ion, we use eq 5 with zero acentric factor for each ion. Here, the hypothetical critical temperature for an (uncharged) ion is obtained from the correlation between T_c and $B/(kv_c^2)$ shown in Figure 2d. It is 102.1 K for Na^+ and 326.34 K for Cl.

Once a and b are fixed for (uncharged) ions and for water, the Helmholtz energy for the reference system can be calculated using eq 4 with mixing rules given in eqs 8 and 9.
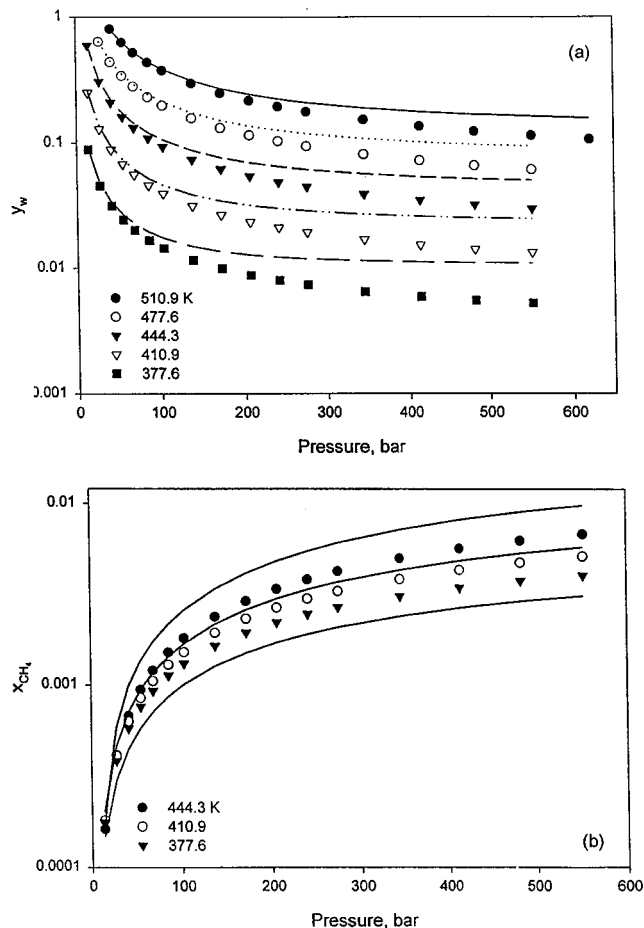
An old equation proposed by Born (Israelachvili, 1991) gives the change in Helmholtz energy in charging neutral particles in a medium of dielectric constant D

$$A^{Born} = \sum_{ions}\frac{(z_{ion}e)^2 N_A}{4\pi\epsilon_0 D\sigma_{ion}}n_{ion} \tag{23}$$

where z_{ion} denotes valence, e elementary charge, and n_{ion} moles of ions. Equation 23 accounts for the total electrostatic work done to charge each ion from the neutral state against its own electrostatic field. Equation 23 gives only part of the change in Helmholtz energy due to charging neutral particles because the interaction between water and the charged particles also depends on the electrostatic states; that interaction is not included in the Born equation. Therefore, we introduce additional association interactions between ions and solvent (water) molecules to represent interactions between charged ions and water, as discussed in the next paragraphs.

For a single-solvent electrolyte solution, D is a constant at a given temperature and pressure. Equation 23 makes no contribution to the chemical potential of the solvent because the derivative of A^{Born} (eq 23) with
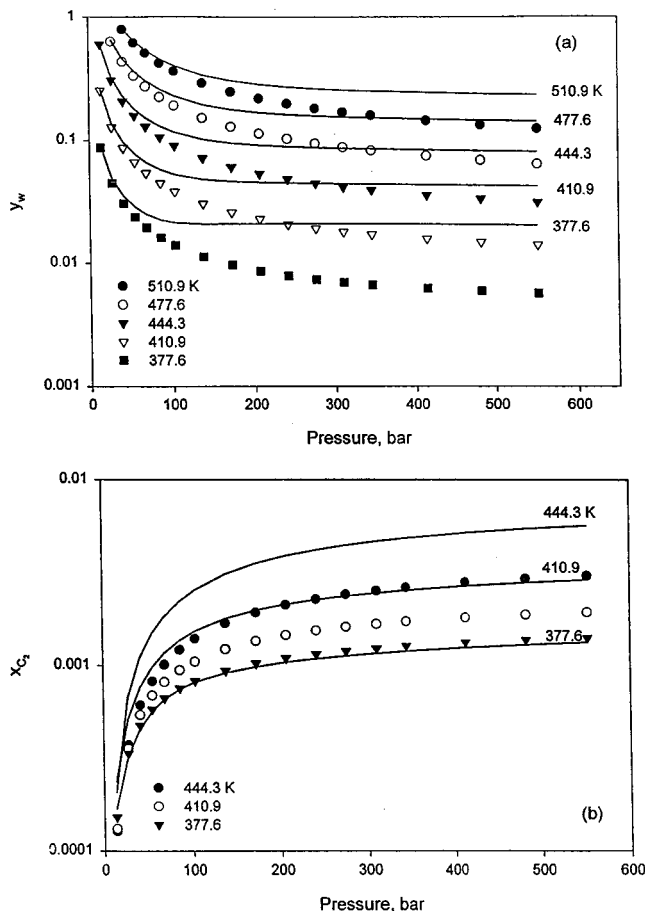
Figure 5. Vapor−liquid equilibria for water−ethane binary mixture. Notation is similar to that in Figure 3. (Experimental data are from Reamer et al. (1943).)

Figure 6. Vapor−liquid equilibria for water−propane. Notation is similar to that in Figure 3. The dotted line gives calculated results with $k_{ij} = -0.057$ at 327 K. (Experimental data are from Kobayashi et al. (1953).)

respect to the moles of solvent is zero. Further, for each ion, at constant temperature and volume, the partial derivative of A^{Born} with respective to n_{ion} is a constant. Therefore, eq 23 has no effect on the ionic activity coefficients. (However, for a mixed-solvent electrolyte solution, D depends on solvent composition; the Born energy then contributes to the chemical potential of each solvent.)

For solutions containing ions, the association part must take into account not only the Helmholtz energy contributed from hydrogen bonding between water molecules but, in addition, electrostatic interaction between water and ions. Here, we assume that the electrostatic interactions between ions and water molecules can be approximated by specific association interactions. We specify a fixed number of association sites for cations and for anions, i.e., 10 sites for each cation for interaction with oxygen sites of water and 14 sites for each anion for interaction with hydrogen sites of water. (While these numbers are somewhat arbitrary, they are not sensitive to our model's performance.)

The hydration number for Na$^+$ is about 6, Cl$^-$ about 7 (Marcus, 1985). Because the extent of water−ion bonding depends on the bonding energy and on steric interactions, and because each water molecule has two hydrogen atoms, the numbers of sites for each cation and each anion are larger than the hydration numbers. The Helmholtz energy contributed from associations
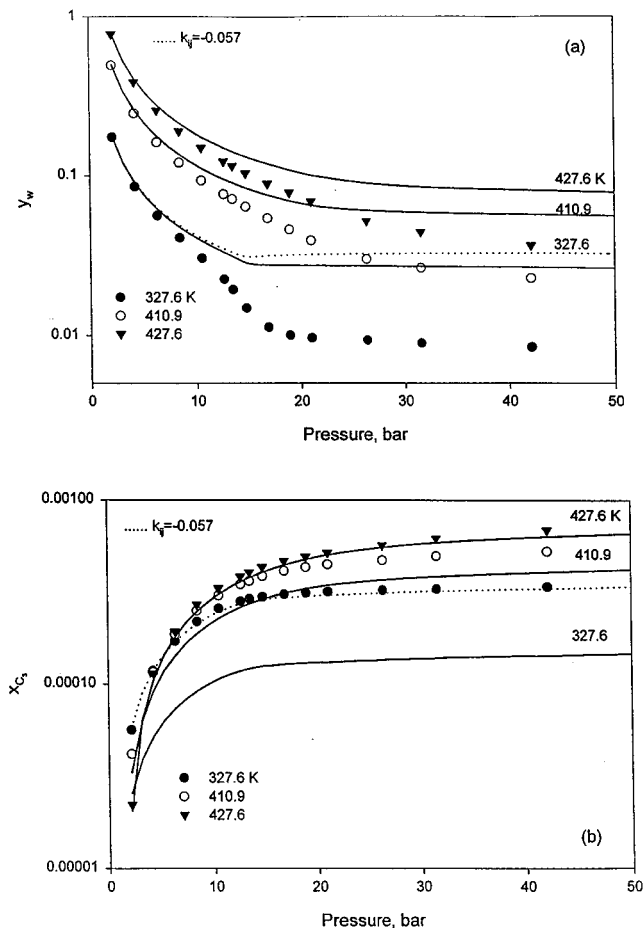
between water and water, and between water and ion in an electrolyte solution, is given by

$$\frac{A^{\text{assoc}}}{nRT} = \sum_i x_i \sum_{S_i} \left(\ln X^{S_i} + \frac{1 - X^{S_i}}{2} \right) \qquad (24)$$

where the superscript S_i indicates an association site at molecule i, and n is the total number of moles. Equation 24 is similar to eq 17 for water−hydrocarbon mixtures. Here x_i is the mole fraction of species i ($i =$ cation, anion, or water). The difference is that here association takes place between the same species (water−water) as well as between different species (water−ion). (Equation 17 considers only association between water molecules.) X^{S_i} now is given by

$$X^{S_i} = (1 + \sum_j \sum_{S'_j} \rho_j X^{S'_j} \Delta^{S_i S'_j})^{-1} \qquad (25)$$

with

$$\Delta^{S_i S'_j} = d_{ij}^3 g_{ij}^{\text{hs}}(d_{ij}) \, \kappa^{S_i S'_j} \left[\exp\left(\frac{\varsigma^{S_i S'_j}}{kT} \right) - 1 \right] \qquad (26)$$

In eqs 25 and 26, subscripts i and j are indices of species; superscripts S_i and S'_j stand for an association site at molecule i and j, respectively. Diameter $d_{ij} = (d_i + d_j)/2$
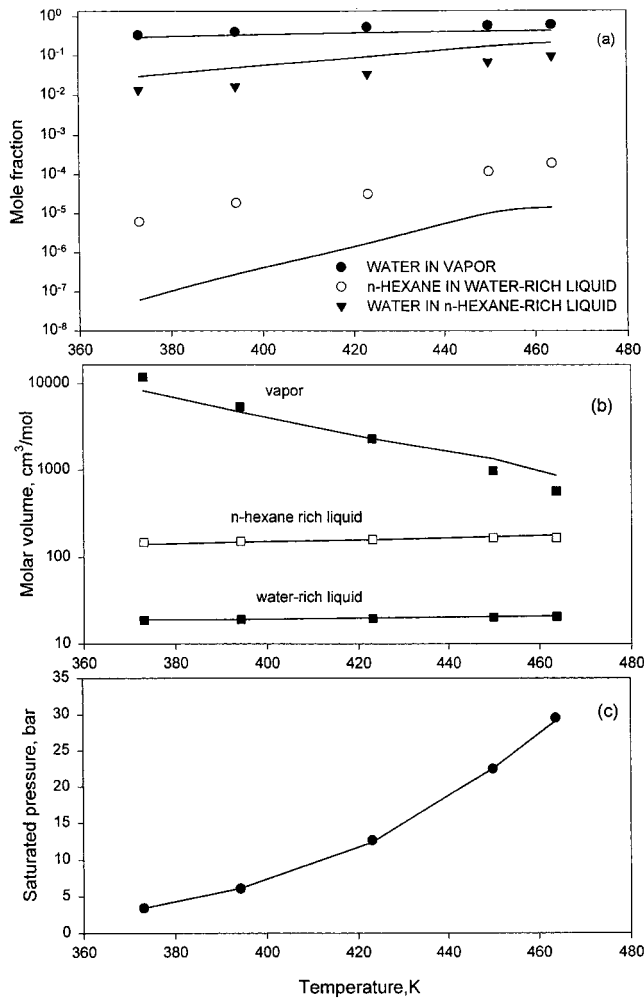
Figure 7. Vapor−liquid−liquid equilibria, molar volumes, and saturated pressures for water−*n*-hexane. Hydrophobic effect is still significant for *n*-hexane in water at this temperature; calculated solubilities of *n*-hexane in water are much too low. (Experimental data are from Barrufet et al. (1996).)

and $g_{ij}^{hs}(d_{ij})$ is the contact value of the pair-correlation function in a hard-sphere mixture given by

$$g_{ij}^{hs}(d_{ij}) = \frac{1}{1 - \xi_3} + \frac{3 d_i d_j}{d_i + d_j} \frac{\xi_2}{(1 - \xi_3)^2} + \\ 2 \left(\frac{d_i d_j}{d_i + d_j} \right)^2 \frac{\xi_2^2}{(1 - \xi_3)^3} \quad (27)$$

The effective diameter for an ion, d_i, is also obtained from eq 14; it is different from diameter σ_i. Functions ξ_2 and ξ_3 are given after eq 20.

The Coulomb interaction between ions is taken into account using the mean spherical approximation (MSA) for electrolyte solutions (Blum and Høye, 1977). The additional Helmholtz energy due to electrostatic interaction between ions in a medium is given by

$$A^{Coul} = -\frac{V e^2}{4 \pi \epsilon_0 D} \left\{ \Gamma \sum_{ions} \rho_{ion} z_{ion}^2 / (1 + \Gamma \sigma_{ion}) + \frac{\pi}{2 \Theta} \Omega P_n^2 \right\} + \\ \frac{V \Gamma^3}{3 \pi} kT \quad (28)$$

The symbols in eq 28 are defined as follows:

$$\Theta = 1 - \frac{\pi}{6} \sum_{ions} \rho_{ion} \sigma_{ion}^3, \quad \Omega = 1 + \frac{\pi}{2 \Theta} \sum_{ions} \frac{\rho_{ion} \sigma_{ion}^3}{1 + \Gamma \sigma_{ion}},$$

$$P_n = \frac{1}{\Omega} \sum_{ions} \frac{\rho_{ion} \sigma_{ion} z_{ion}}{1 + \Gamma \sigma_{ion}},$$

$$\Gamma = \frac{1}{2} \frac{e}{\sqrt{\epsilon_0 kTD}} \left\{ \sum_{ions} \rho_{ion} \left[\left(z_{ion} - \frac{\pi}{2 \Theta} \sigma_{ion}^2 P_n \right) \middle/ \right. \right. \\ \left. \left. (1 + \Gamma \sigma_{ion}) \right]^2 \right\}^{1/2} \quad (29)$$

Γ, Ω, P_n are three MSA parameters that can be solved by an iteration method.

For each ion, there are two association parameters ζ and κ. We assume that κ is a universal constant, equal to 0.001 for all ions. ζ is obtained from fitting experimental mean ionic activity coefficients and water activities at different temperatures. For NaCl aqueous solution, ζ_{wNa^+} and ζ_{wCl^-} are given, respectively, by

$$\zeta_{wNa^+}/k = 1072.9 + 9.5769 T - 0.0035 T^2 \text{ (K)} \quad (30)$$

$$\zeta_{wCl^-}/k = 1590 \text{ (K)} \quad (31)$$

where T is in kelvin.

We set ζ_{wCl^-} independent of temperature because calculated results are not sensitive to that parameter. Parts a and b of Figure 8 give calculated and experimental ionic mean activity coefficients $\gamma_\pm$ and water activities a_w at ambient conditions and at high temperatures, respectively. Figure 8c compares the predicted results with experiment at 3000 bar, room temperature, and 300 °C. With only a few adjustable parameters, it appears that our model can represent the properties of NaCl aqueous solutions over a wide range of temperature, pressure, and composition.

(e) Water−Hydrocarbon−Salt Systems. The Helmholtz energy for a water−hydrocarbon−salt mixture is similar to that for an aqueous electrolyte solution because the solubility of hydrocarbon in water is low at ordinary temperatures. However, the effect of hydrocarbon follows from the dielectric constant of the medium (mixed solvent), D, that depends on solvent composition. Therefore, the Born energy affects the chemical potentials of the solvents. For the systems of interest here, the mixed solvent is dominated by water. We assume that the dielectric constant for a dilute solution of hydrocarbon in water is given by

$$\frac{1}{D} = \frac{1}{D_w}(1 + k_D x_{HC}) \quad (32)$$

where the subscripts w, HC indicate water and hydrocarbon, respectively; k_D is a dimensionless constant that depends on the hydrocarbon; and x_{HC} stands for mole fraction of hydrocarbon in the ion-free, binary water−hydrocarbon mixture.

As in the single-solvent electrolyte solution, the contribution to the Helmholtz energy from Coulomb interactions is represented by the MSA (eq 28); that contribution is in the McMillan−Mayer framework. To evaluate the Coulomb contribution to the chemical potential of a solvent, we need to transform the McMillan−Mayer framework to the Lewis−Randall frame-
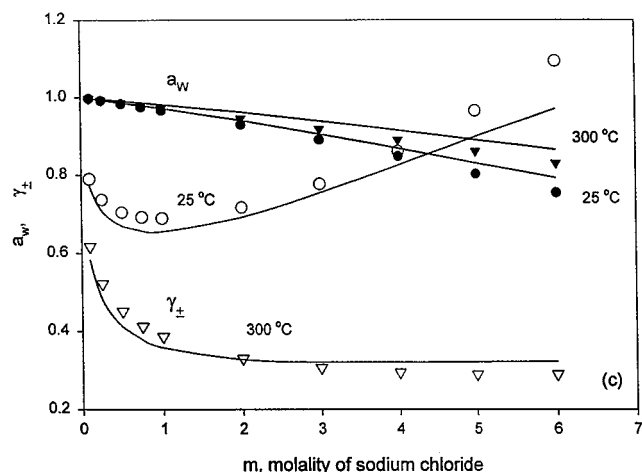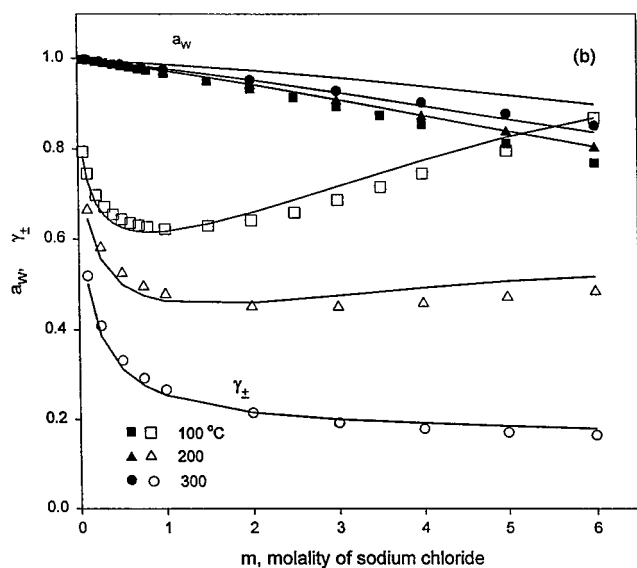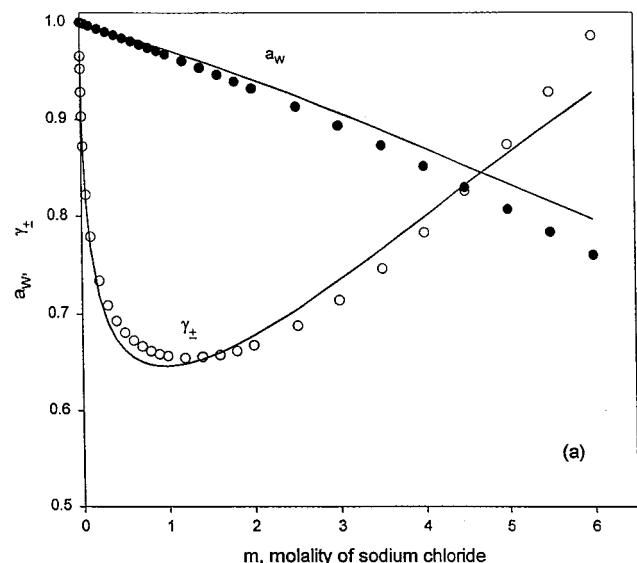
Figure 9. Solubility of methane in pure water, and in 1 and 4 m aqueous NaCl solutions at 125 °C. (Experimental data are from O'Sullivan et al. (1970).)

tial of solvent i due to the long-range Coulomb interaction is given by

$$\mu_i^{\text{Coul}} = -\bar{v}_i\Pi^{\text{MSA}} \tag{33}$$

where $\bar{v}_i$ is the partial molar volume of solvent i in the mixed-solvent electrolyte solution. Here we assume that $\bar{v}_i$ is equal to the molar volume of pure i. Π^{MSA} stands for the osmotic pressure due to Coulomb interaction as given by MSA:

$$\Pi^{\text{MSA}} = -\left[\frac{\Gamma^3}{3\pi} + \frac{\alpha^2}{8\rho}\left(\frac{P_n}{\Delta}\right)^2\right]kT \tag{34}$$

When the Coulomb interaction is given in a McMillan–Mayer framework, its contribution to the chemical potential of a solvent is *not* obtained by differentiation of the dielectric constant with respect to the composition of solvent, as discussed by Marcio et al. (1987).

Tables 1 and 2 give the parameters for water and ions, but we also require an estimate of the parameter k_D in eq 32. We can then predict the solubility of hydrocarbons in aqueous electrolyte solutions using conventional Newton–Raphson procedures for calculating vapor–liquid equilibria (Sandler, 1989). For a binary mixture of water and methane, we use $k_D = 6.372$. Figure 9 shows predicted solubilities of methane in salt-free water and in aqueous solution of 1 and 4 M sodium chloride from 100 to 600 bar at 125 °C. Agreement with experiment is excellent. Due to inconsistency of experimental data on the effect of temperature, we did not calculate the methane solubilities in NaCl solution at other temperatures. In general, k_D depends on temperature.

Conclusion

In this work we have used the Peng–Robinson equation of state to provide the Helmholtz energy of a reference system. Additional contributions to the Helmholtz energy follow from hydrogen bonding and from electrostatics due to electrically charged ions; we propose relations for these contributions based on theoretical arguments. Our results show that the extended Peng–Robinson equation of state is useful for describing systems containing the "usual" components described by the original Peng–Robinson equation of state in

Figure 8. (a) Water activity (a_w) and ionic mean activity coefficient ($\gamma_\pm$) for aqueous NaCl solution at 25 °C and 1 atm. (b) Water activity and ionic mean activity coefficient for aqueous NaCl solution at high temperatures and saturated pressures. (c) Water activity and ionic mean activity coefficient for aqueous NaCl solution at 1000 bar, 25 and 300 °C. (Experimental data are from Pitzer et al. (1984).)

work. As discussed by Pailthorpe et al. (1984), for a mixed-solvent electrolyte solution, the chemical poten-
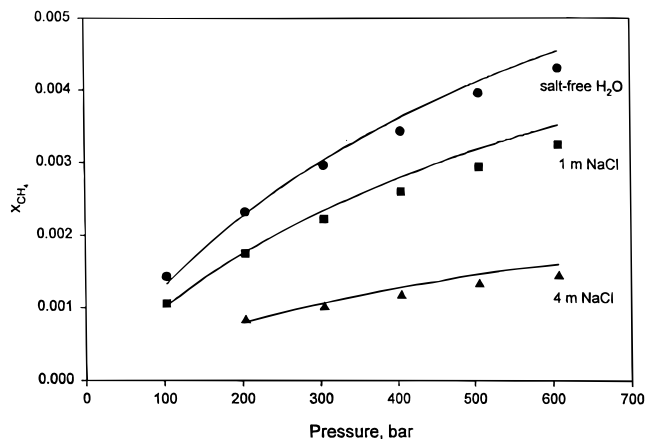
addition to water and sodium chloride. However, consistent with the critical review by Economou and Tsonopoulos (1997), our theoretical framework is not adequate for those systems where the hydrophobic effect is significant, i.e., for solutions of hydrocarbons in water at temperatures below (about) 100 °C. For such solutions we require a new theory not currently available. Efforts to construct such a theory, based on ideas proposed by Hummer et al. (1996), are now in progress.

Acknowledgment

Nomenclature

A = Helmholtz energy
a = PREOS parameter
a^0 = nonpolar part of the PREOS parameter a
a_w = PREOS parameter for water or water activity
B = London coefficient
b = PREOS parameter
d = effective molecular diameter
D = dielectric constant
e = elementary charge
$g(r)$ = pair-correlation function
I = first ionization potential
k = Boltzmann constant
k_a = adjustable parameter
k_D = dimensionless constant
k_{ij} = binary interaction parameter for PREOS
n = total number of moles
N_A = Avogadro's number
n_e = number of electrons of an ion
n_i = number of moles of component i
P = pressure
P_n = MSA parameter
r = molecular center-to-center distance
R = gas constant
T = absolute temperature
V = total volume
v = molar volume
$\bar{v}_i$ = partial molar volume of component i
X^S = mole fraction of site S that is not bonded
x_i = mole fraction of component i in liquid phase
y_i = mole fraction of component i in vapor phase
z = valence
α_0 = polarizability
ϵ_0 = permittivity of free space
ϵ = Lennard-Jones energy parameter
Γ = MSA parameter
$\gamma_\pm$ = ionic mean activity coefficient
η = packing fraction
$\kappa^{SS'}$ = dimensionless SAFT parameter
μ_i = chemical potential of component i
π = osmotic pressure
Ω = MSA parameter
ω = acentric factor
ρ = molecular number density
σ_{ion} = diameter of an ion
ξ = packing parameter for hard spheres
$\zeta^{SS'}$ = bonding energy between sites S and S'

Superscripts

assoc = association
Born = Born energy
Coul = Coulomb interaction

IG = ideal gas
MSA = mean spherical approximation
r = reference system
S = an association site

Subscripts

c = critical condition
HC = hydrocarbon
i, j = component index
w = water

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