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Water/Hydrocarbon Phase Equilibria Using the Thermodynamic Perturbation Theory

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Two equations of state, the cubic plus association (CPA) and the statistical associating fluid theory (SAFT), which account explicitly for the effect of hydrogen bonding on the thermodynamic properties of associating fluids using the perturbation theory of Wertheim (*J. Stat. Phys.* **1986**, *42*, 459, 477), are applied to predict the phase equilibrium of pure water, *n*-alkanes, and 1-alkenes as well as the low- and high-pressure phase equilibrium of water/hydrocarbon mixtures. The pure compound parameters for the two equations are estimated by fitting experimental vapor pressure and saturated liquid density data that cover a very wide temperature range from approximately the triple point to very close to the critical point. One temperature-independent binary interaction parameter is calculated for each of the mixtures examined. The analysis of the results shows that the increased complexity of SAFT over CPA does not offer any improvement in modeling highly nonideal fluid behavior, at least for the systems examined here.

Introduction

The accurate description of the phase equilibria of aqueous mixtures,[3,4] at both low and high pressure, is particularly important for a variety of chemical engineering applications such as those related to the refining and petrochemical industry and to the treatment of industrial liquid wastes.

Modeling of phase equilibria of water/hydrocarbon mixtures, which is the objective of this work, is a difficult and challenging problem because such systems show extremely nonideal behavior because of the hydrogen bonding of the water molecules. The strong hydrogen bonding results in a limited miscibility of water and hydrocarbons over a broad range of conditions. The solubilities in the coexisting phases are strongly asymmetric: the solubility of the hydrocarbon in water is several orders of magnitude lower than the solubility of water in the hydrocarbon. Moreover, the hydrocarbon solubility has a minimum value at relatively low temperatures, whereas the water solubility is a monotonic function of temperature.

Cubic equations of state (EoS), such as the Soave−Redlich−Kwong (SRK) and the Peng−Robinson (PR) EoS, were applied in the past to water/hydrocarbon mixtures using local composition (Tsonopoulos and Heidman[3] and Economou et al.[4]) and density-dependent mixing rules (Mathias and Copeman[5]) with a single temperature-independent cross-interaction parameter but with limited success. Alternatively, Michel et al.[6] proposed an unconventional mixing rule for the attractive term parameter of a cubic EoS, with additional temperature-dependent parameters, to correlate mutual

solubilities of water/hydrocarbon mixtures. However, for vapor−liquid equilibrium (VLE) calculations a density dependence in the parameter had to be introduced.

In the last 20 years numerous investigations have been carried out toward the development of EoS suitable for associating fluids. We are referring to EoS derived (a) from the chemical theory (Heidemann and Prausnitz,[7] Ikonomou and Donohue,[8] and Anderko[9]), (b) from the perturbation theory, where the most popular equation of state here is the statistical associating fluid theory (SAFT) EoS (Chapman et al.[10] and Huang and Radosz[11,12]) [in the same category also belong the Elliott−Suresh−Donohue (ESD) (Suresh and Elliott[13]), the group-contribution-associating (GCA) EoS (Gros et al.[14]) and the cubic plus association (CPA) EoS (Kontogeorgis et al.[15])], and (c) from the lattice/quasi-chemical theory (Panayiotou and Sanchez[16]).

In this work, we apply the SAFT and the CPA EoS to model the phase equilibria of water/hydrocarbon systems. After the original development of the SAFT model by Chapman et al.[10] and by Huang and Radosz,[11,12] several versions of SAFT were proposed. For example, Fu and Sandler[17] proposed a "simplified" SAFT model using the relatively simple attractive term of Lee et al.[18] instead of the Taylor series expansion in density and in inverse temperature used in the original SAFT. Galindo et al.[19] proposed a SAFT model that treats molecules as chains of spheres that interact through a simple van der Waals attractive potential. The model was used by Galindo et al.[19] for the calculation of the high-pressure critical behavior of water/*n*-alkane mixtures, and good agreement with experimental data was obtained. Kraska and Gubbins[20] proposed the Lennard-Jones SAFT where a Lennard-Jones EoS is used for the segmental contributions instead of the BACK equation (Chen and Kreglewski[21]) used in the original SAFT. The Lennard-Jones SAFT was used to correlate the solubility of water in methane and in ethane at high pressure (Kraska and Gubbins[22]). Adidharma and Radosz[23] pro-

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Table 1. CPA Parameters for the Components Examined in This Work and Correlation of Experimental Data (for Water, $\epsilon^{AB} = 1793.6$ K and $\beta^{AB} = 0.1151$)

component	T (K)	b (L/mol)	α_0 (bar L^2/mol)	c_1	ΔP^a (%)	$\Delta \rho^b$ (%)
water	278–641	0.0146	0.801	1.751	0.92	1.54
methane	95–189	0.0284	2.278	0.444	0.64	3.27
ethane	131–302	0.0424	5.485	0.573	1.13	2.07
propane	159–366	0.0578	9.091	0.655	0.91	2.05
n-hexane	218–502	0.1071	23.221	0.878	2.62	1.21
n-octane	244–563	0.1423	35.965	0.983	0.68	0.91
1-hexene	217–499	0.1020	21.983	0.843	0.68	1.22
1-octene	244–561	0.1378	33.630	0.970	1.22	0.99

[a] ΔP% is the average absolute percent deviation in vapor pressure defined as (eq A13). [b] $\Delta \rho$ % is the average absolute percent deviation in saturated liquid densities defined as (eq A14).

Table 2. SAFT Parameters for the Components Examined in This Work and Correlation of Experimental Data (for Water, $\epsilon/k = 1634.7$ K and $\kappa = 0.3374$)

component	T (K)	m	v^{00} (cm^3/mol)	u^0/k (K)	ΔP (%)	$\Delta \rho$ (%)
water	278–641	2.853	3.304	167.10	0.88	1.66
methane	95–189	0.996	21.475	190.72	0.17	0.32
ethane	131–302	1.685	17.393	209.43	3.14	1.50
propane	159–366	2.582	14.295	197.90	2.90	2.31
n-hexane	218–502	4.663	12.885	204.24	2.01	3.57
n-octane	244–563	5.915	12.721	207.79	4.15	4.03
1-hexene	217–499	4.491	13.072	205.49	2.93	3.55
1-octene	244–561	5.746	12.737	209.11	2.77	3.62

posed the square-well SAFT where they used the square-well fluid as the reference. In this work, we used the original SAFT of Huang and Radosz[11,12] that remains the most widely used EoS of this type.

In two recent studies (Economou and Tsonopoulos[24] and Yakoumis et al.[25]), the original SAFT and the CPA EoS were used to model liquid–liquid equilibria (LLE) of water/hydrocarbon mixtures along the three-phase equilibrium pressure. Economou and Tsonopoulos[24] concluded that SAFT cannot quantitatively correlate the hydrocarbon solubilities in the water-rich phase, even using the asymmetric mixing rules originally developed for the perturbed-hard-chain-theory (PHCT) (Donohue and Prausnitz[26]). On the other hand, Yakoumis et al.[25] using a rather limited database concluded that the two equations give comparable results for the correlation of water solubilities in the hydrocarbon, but CPA is in much better agreement with the experimental data for the correlation of hydrocarbon solubilities in water. Yakoumis et al.[25] attributed this improvement to the appropriate selection of the pure water parameters.

The scope of the present study is an investigation of the performance of SAFT and CPA for the correlation of pure water, n-alkanes (methane, ethane, propane, n-hexane, and n-octane), and 1-alkenes (1-hexene and 1-octene) phase equilibrium from approximately the triple point to very close to the critical point. Calculated vapor pressure, saturated liquid density, critical parameters, and second virial coefficient are compared against experimental data. Furthermore, and more importantly, the two EoS are used to predict the water/methane and water/ethane high-pressure phase equilibrium and the water/propane, /n-hexane, /n-octane, /1-hexene, and /1-octene phase equilibrium along the three-phase line. For all of the mixtures examined, the temperature is well below the pure water critical temperature.

Equations of State and Estimation of Pure Compound Parameters

The algebraic expressions for SAFT and CPA are briefly presented in the Appendix. Both models require three pure-component parameters for nonassociating fluids and five parameters for associating fluids. In the case of SAFT, these parameters are the number of segments per molecule, m, the segment volume, v^{00}, and the energy parameter, u^0/k, that accounts for the dispersion segment–segment interactions. The two hydrogen-bonding parameters are the energy (ϵ/k) and the volume (κ) of association. The CPA parameters for nonassociating compounds are a_0, c_1, and b parameters. The two additional parameters for associating compounds are the association energy of interaction between sites A and B on two different molecules, ϵ^{AB}, and the association volume of interaction, β^{AB}, between the two sites.

In the case of mixtures, both models use van der Waals one-fluid mixing rules with a single binary interaction parameter, k_{ij}, for the dispersion interactions that are fitted to experimental binary data.

Considerable effort has been devoted over the past few years concerning the number of hydrogen-bonding sites that should be attributed to water in a macroscopic model. Water molecules are known to form three-dimensional structures through hydrogen bonding. A water molecule has the two hydrogens and the two lone pairs of electrons that are able to form hydrogen bonds. As a result, each water molecule is capable of forming up to four hydrogen bonds. Some experimental results, however, suggest that only three hydrogen bonds per water molecule can be formed because of steric hindrance effects (Wei et al.[27]). Nevertheless, Economou and Tsonopoulos[24] and Yakoumis et al.[25] showed that the four-site model performs better with the SAFT and CPA EoS and, consequently, this approach was used in this study.

The parameters of pure water and hydrocarbons for both EoS are presented in Tables 1 and 2 and were regressed from experimental saturated vapor pressure and liquid density data taken from the DIPPR data compilation (Daubert and Danner[28]) over the temperature range $T_r = 0.43$–0.99 (only for methane the T_r range was from 0.5 to 0.99), i.e., from about the triple point to very close to the critical point of the compound. This is a much broader temperature range than the one

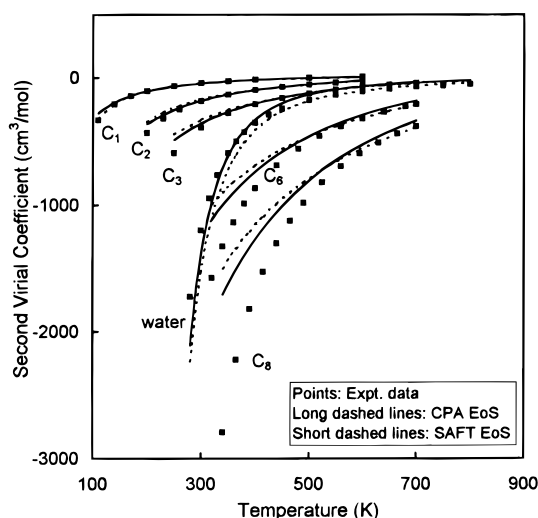**Table 3. Experimental and Predicted Pure Compound Critical Properties from the Two EoS**

| compound | T_c^{exp} (K) | T_c^{calc} (K) | | P_c^{exp} (bar) | P_c^{calc} (bar) | | ρ_c^{exp} (g/cm^3) | ρ_c^{calc} (g/cm^3) | |
		CPA	SAFT		CPA	SAFT		CPA	SAFT
water	647.13	659.74	690.85	220.55	246.40	342.19	0.322	0.324	0.304
methane	190.56	193.14	192.18	45.99	47.22	48.70	0.161	0.148	0.168
ethane	305.42	310.49	320.83	48.80	50.42	59.27	0.203	0.185	0.191
propane	369.82	376.49	388.71	42.49	44.94	52.10	0.217	0.199	0.200
n-hexane	507.43	516.34	529.71	30.12	33.96	36.20	0.233	0.211	0.202
n-octane	568.83	580.66	592.54	24.86	29.04	29.54	0.232	0.212	0.198
1-hexene	504.03	513.17	524.51	31.4	35.25	37.18	0.237	0.217	0.205
1-octene	566.60	577.76	589.65	25.5	29.32	30.57	0.237	0.215	0.202
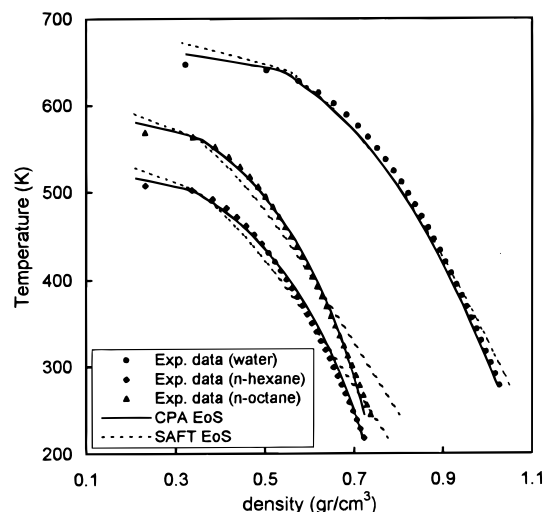
Figure 1. Saturated liquid density for water, n-hexane, and n-octane. Experimental data and CPA and SAFT correlation.

Figure 2. Second virial coefficient for water and n-alkanes. Experimental data (Tsonopoulos and Heidmann[38] for water and Tsonopoulos[39] for n-alkanes) and CPA and SAFT correlation.

used by Huang and Radosz[11] for the regression of SAFT parameters. In this way, the accuracy of the two EoS over a very wide temperature range is tested. It must be noted that in previous studies (Huang and Radosz[12] and Economou and Tsonopoulos[24]) only four of the five SAFT parameters for water were fitted and the segment volume parameter (v^{00}) was arbitrarily set equal to 10 cm^3/mol. Here, all five parameters were fitted to the experimental data. In this way, the resulting values were considerably different than before. A much higher m and a much lower v^{00} were obtained that correspond to the physical picture of water as a nonspherical molecule consisting of small spherical segments. Admittedly, the two parameters are highly correlated, resulting in a physically unrealistic picture for water. However, a more accurate description of pure water properties and, more importantly, of binary aqueous mixtures, as shown later, is obtained.

For the case of water, CPA and SAFT give similar results, which are in good agreement with the experimental data. On the other hand, CPA performs better than SAFT for hydrocarbons, with the exception of methane. Deviation values with SAFT reported in Table 2 for the vapor pressure and saturated liquid density of some of the hydrocarbons are higher than the corresponding values reported by Huang and Radosz[11] because of the much broader temperature range used here. In Figure 1, experimental data and the EoS correlation are shown for the saturated liquid density of water, n-hexane, and n-octane. The SAFT correlation for the two hydrocarbons deviates from the experimental data, especially at low temperature.

The critical properties of the pure compounds were calculated from the two EoS and are shown in Table 3. In general, CPA predictions are closer to the experi-

mental data than SAFT ones. This behavior is consistent with the fact that cubic EoS are more accurate in the vicinity of the pure-component critical point than mean-field perturbation theory based EoS. The higher T_c and P_c values obtained with SAFT for the hydrocarbons agree with the results of Blas and Vega[29] obtained with the soft-SAFT, one of the recent modifications of SAFT. Finally, the second virial coefficient of the pure components was calculated and is shown in Figure 2. Both CPA and SAFT are in reasonable agreement with the experimental data of pure water, but they overpredict the second virial coefficient of pure n-alkanes and 1-alkenes (very similar to n-alkanes, not shown here), especially at low temperatures.

Mixture Phase Equilibria

High-Pressure VLE of Water with Light Hydrocarbons. High-pressure VLE of water with hydrocarbons is very important in the case of natural gas reservoirs, because the solubility of gases in water is needed for estimating the true amount of gas in the reservoir. At high pressures the solubility of hydrocarbons in water is significant and, consequently, it cannot be neglected. The solubility data of hydrocarbons in water under high pressure are limited or nonexistent in some cases. For a recent review of such data, see Dhima et al.[30]

In this work we examined the high-pressure/high-temperature VLE for water/methane and water/ethane mixtures. For the water/methane mixture EoS calculations are compared with the data of Sage and Lacey[31] and of Sultanov et al.[32] The data of Sage and Lacey[31] include only solubilities of water in the hydrocarbon phase and cover the temperature range 311−511 K and

Table 4. High-Pressure VLE for Water (1)/Methane (2) and Water (1)/Ethane (2) Mixtures: Comparison of CPA and SAFT Predictions with Experimental Data (for CPA k_{ij} = 0.05 for Water/Methane and 0.04 for Water/Ethane; for SAFT k_{ij} = 0.495 for Water/Methane and 0.442 for Water/Ethane)

| system	T (K)	P (bar)	% AAD in y_1		% AAD in x_2	
			CPA	SAFT	CPA	SAFT
water (1)/methane (2)[a]	311–511	13.6–680.3	4.7	3.9		
water (1)/methane (2)[b]	423–603	98.1–981	7.0	11.6	23.7	20.9
water (1)/ethane (2)[a]	311–511	13.6–680.3	6.7	5.4		
water (1)/ethane (2)[c]	473–573	200–3500	27.8	37.6	46.0	45.6

[a] Experimental data from Sage and Lacey.[31] [b] Experimental data from Sultanov et al.[32] [c] Experimental data from Danneil et al.[33]
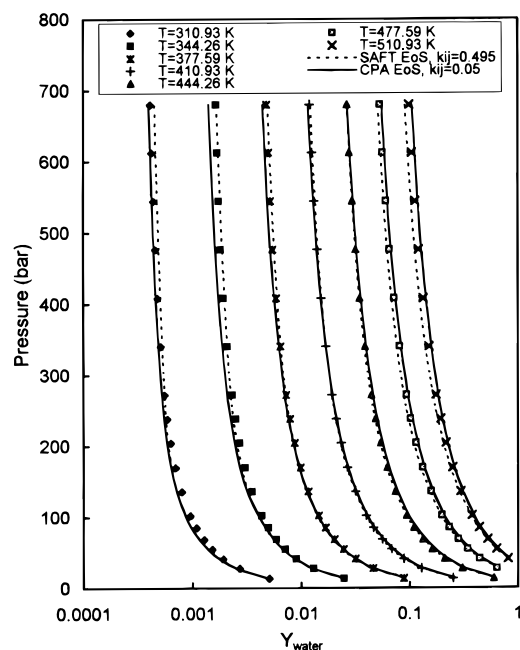
Figure 3. Solubility of water in methane. Experimental data (Sage and Lacey[31]) and CPA and SAFT correlations.

pressure range 13.6–680.3 bar. The data of Sultanov et al.[32] include solubilities in both phases and cover the temperature range 423–603 K and pressure range 98.1–980.7 bar. The two data sets are consistent with each other.

For the water/ethane mixture, EoS calculations are compared with the data of Sage and Lacey[31] and of Danneil et al.[33] The data of Sage and Lacey[31] include only solubilities of water in the hydrocarbon phase and cover the temperature range 311–511 K and the pressure range 13.6–680.3 bar. The data from Danneil et al.[33] include solubilities in both phases and cover the temperature range 473–573 K and the pressure range 200–3500 bar. The two data sets, however, seem to be inconsistent, especially for pressures above approximately 500 bar.

For engineering calculations, it is desirable to have an equation of state with a single temperature-independent k_{ij} value for a wide temperature range. In Table 4 and Figures 3–6 the VLE calculations with CPA and SAFT for water/methane and water/ethane, using a single temperature-independent k_{ij} value, are compared with the different sets of experimental data. SAFT and CPA give good predictions for the data of Sage and Lacey[31] for both binary mixtures and fair predictions for the data of Sultanov et al.[32] for the water/methane mixture. The correlation of Sage and Lacey data with SAFT presented here is very similar to the correlation with the Lennard-Jones SAFT presented by Kraska and Gubbins.[22]
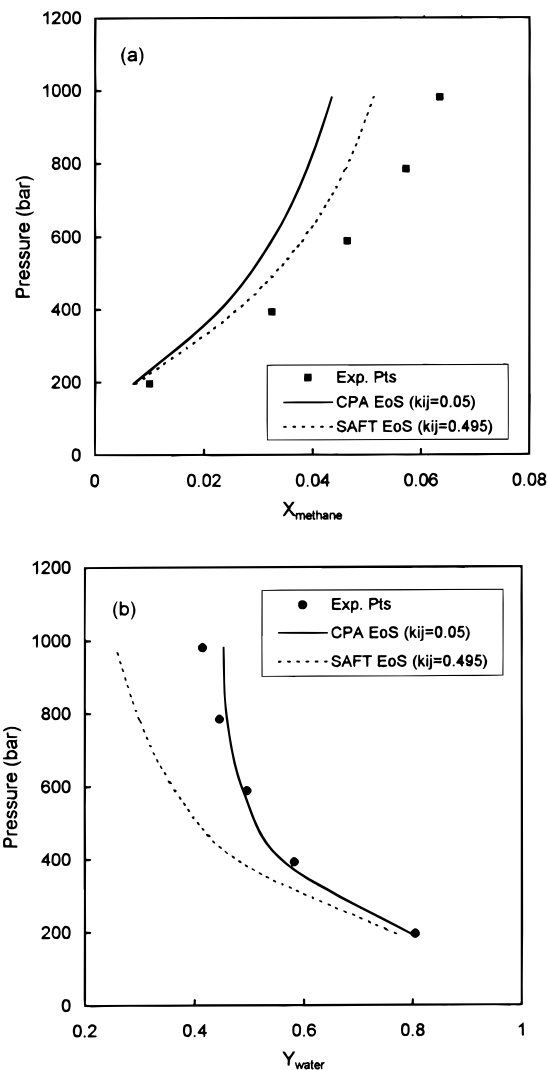
Figure 4. Water/methane VLE at 603 K. Experimental data (Sultanov et al.[32]) and CPA and SAFT correlations.

For the data of Danneil et al.[33] for the water/ethane mixture, the two EoS give poor predictions. In this case, the k_{ij} parameter was fitted to the data of Sage and Lacey[31] and, as a result, there is a relatively high deviation between predictions from the two models and these data. It should be noted here that both CPA and SAFT predict a maximum value for the ethane solubility in water around 700–1000 bar (depending on the temperature, Figure 6) unlike the experimental data that show a monotonic increase of the solubility. Very recently, Errington et al.[34] performed a Gibbs ensemble Monte Carlo simulation for the water/ethane mixture and observed behavior very similar to that obtained from the two EoS. Finally, it is worth noticing that the CPA k_{ij} value is close to zero, unlike SAFT where the k_{ij} value is much higher.
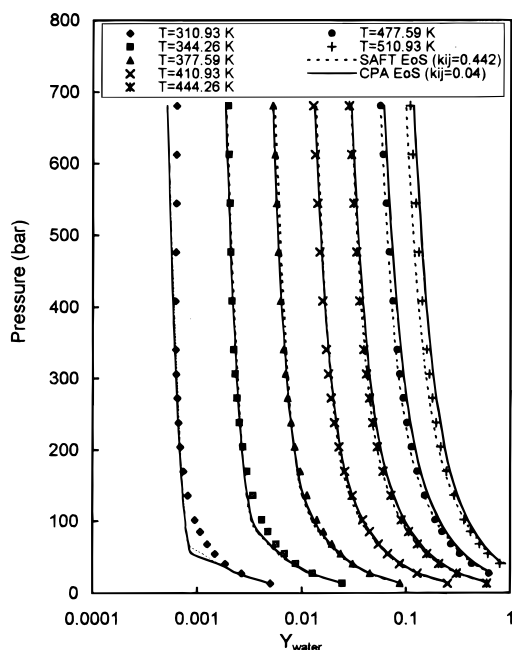
Figure 5. Solubility of water in ethane. Experimental data (Sage and Lacey[31]) and CPA and SAFT correlations.

LLE for Water/Alkane and Water/1-Alkene Mixtures. The LLE of water with propane, *n*-hexane, and *n*-octane from 298 K up to 10−20 K below the three-phase critical end point was modeled using the two EoS. The experimental data for the water/propane system are from Kobayashi and Katz,[35] for the water/*n*-hexane system from Tsonopoulos and Wilson[36] and for the water/*n*-octane system from Heidman et al.[37] For the water/*n*-hexane and the water/*n*-octane systems, the smoothed values reported by the authors for the mutual solubilities and the equilibrium pressure were used. A single temperature-independent k_{ij} value for each binary mixture was regressed from the experimental solubility of water in *n*-alkane and used to predict the solubility of *n*-alkanes in water. Table 5 presents the average absolute percent deviation of water solubility in *n*-alkane obtained by the two models along with the k_{ij} values. The two models are in good agreement with the experimental data. In Figure 7, experimental data and EoS predictions for the mutual solubilities for the three water/*n*-alkane binary mixtures are shown. In the case of the water/propane system, water vapor-phase compositions are also included. CPA predictions for the *n*-alkane solubilities in water are in fairly good agreement with the experimental data but not SAFT predictions. It is worth noting that the new parameters for SAFT result in improved predictions for the hydrocarbon solubilities in water compared to calculations presented previously by Economou and Tsonopoulos.[24] Even so, the SAFT model still cannot quantitatively correlate the hydrocarbon solubilities.

The LLE of water with 1-hexene and 1-octene from 298 K up to 10−20 K of the three-phase critical end point were modeled using the two EoS. The smoothed values reported by Economou et al.[4] for the mutual solubilities and the equilibrium pressures were used. Again a single temperature-independent k_{ij} value was used that was regressed from the experimental solubility of water in 1-alkenes.

In Table 5, the average absolute percent deviations of water solubility in 1-alkenes obtained from the two models are shown along with the k_{ij} values. Results are similar to those obtained for the *n*-alkane binaries. In
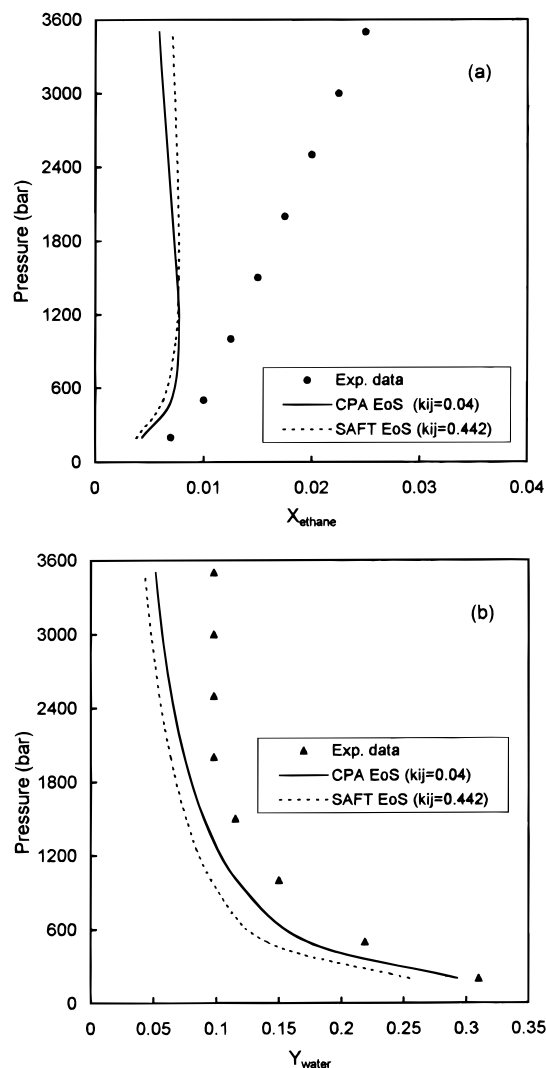

Figure 6. Water/ethane VLE at 523 K. Experimental data (Danneil et al.[33]) and CPA and SAFT predictions.

Table 5. Water/*n*-Alkane and Water/1-Alkene LLE: Comparison of CPA and SAFT Correlation with the Experimental Data for Water Solubility

	CPA		SAFT	
		% AAD in		% AAD in
hydrocarbon	k_{ij}	x_{water}	k_{ij}	x_{water}
propane	0.11	4.5	0.437	7.1
n-hexane	0.05	4.5	0.407	3.7
n-octane	−0.03	4.9	0.382	3.5
1-hexene	−0.125	6.8	0.307	3.2
1-octene	−0.135	6.7	0.325	8.3

Figure 8, experimental data and predictions from the two EoS are shown for the mutual solubilities of the two binary mixtures. CPA overpredicts the 1-alkene solubilities while SAFT gives better results than CPA for the case of water/1-hexene. It must be noted that for the case of water/1-alkene mixtures there is evidence for cross-association between the water and the 1-alkene molecules, which explains the higher 1-alkene solubilities in water compared to the *n*-alkane solubilities. Such treatment, however, is outside the scope of the present study.

Conclusions

In this work, two EoS, the SAFT and the CPA, that explicitly account for hydrogen bonding were used to
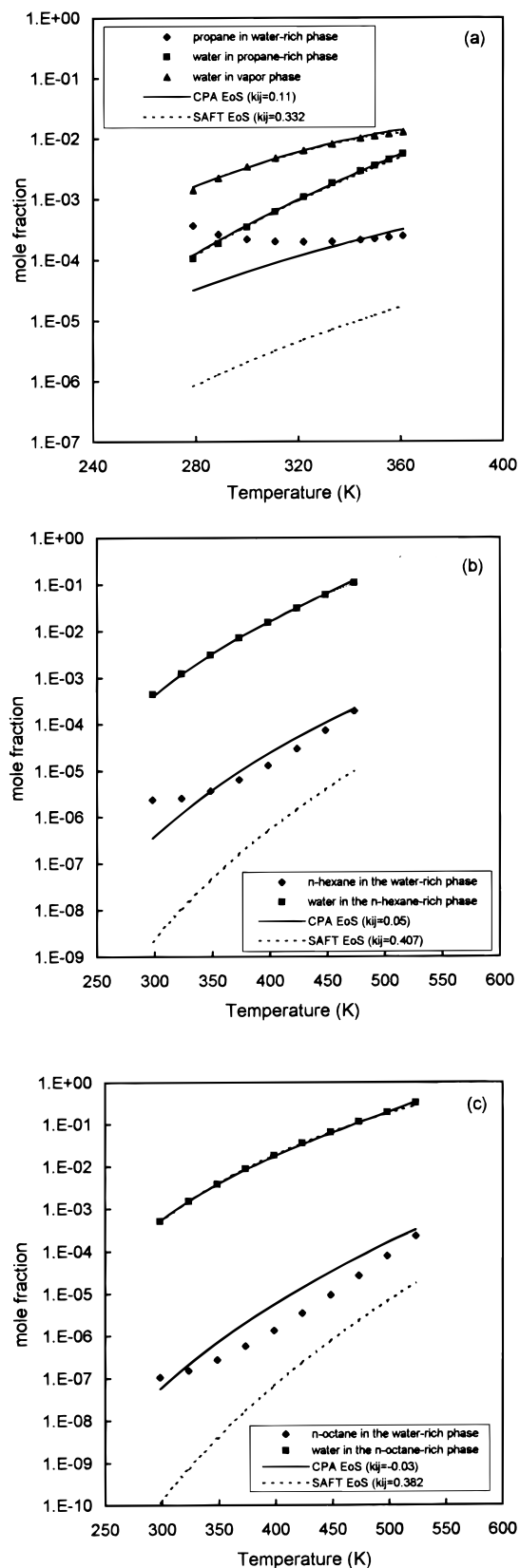
Figure 7. (a) Water/propane, (b) water/*n*-hexane, and (c) water/*n*-octane LLE. Experimental data and CPA and SAFT predictions.

model the phase equilibrium of pure water, pure hydrocarbons, and water/hydrocarbon binary mixtures at both low and high pressures. Pure compound parameters were estimated by fitting the two EoS to experimental data that cover temperatures from about the triple point to very close to the critical point. CPA is in
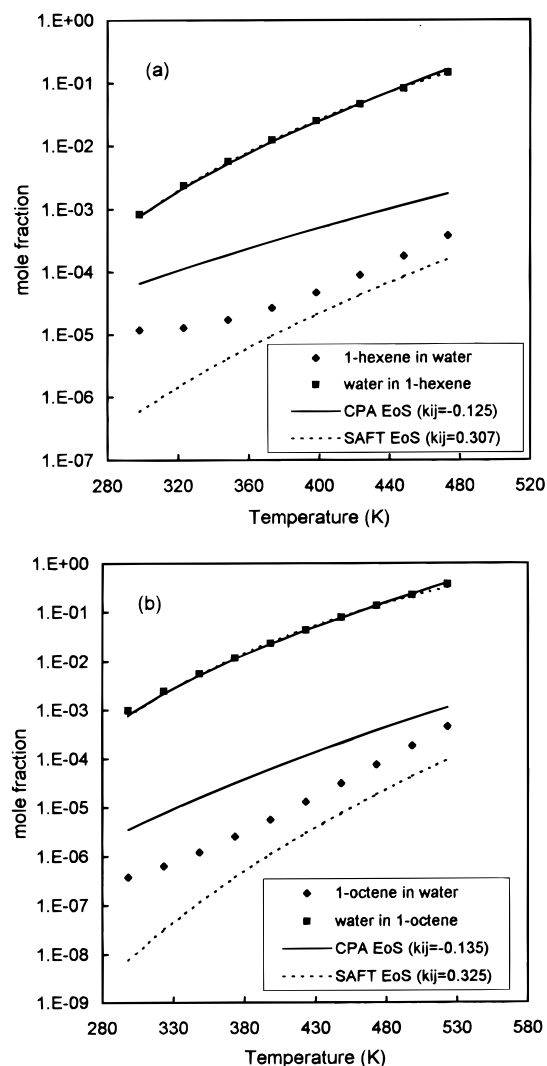

Figure 8. (a) Water/1-hexene and (b) water/1-octene LLE. Experimental data and CPA and SAFT predictions.

better agreement with the experimental data for the coexistence curves, especially in the critical region of the pure components and at low temperature.

Application of the two EoS to the correlation of water/methane and water/ethane VLE using a single temperature-independent k_{ij} in the temperature range 310−573 K and pressure range 13.6−3500 bar showed that both models perform satisfactorily over the entire range of conditions. Furthermore, solubilities of water in three *n*-alkanes and two 1-alkenes were accurately correlated with the two EoS using a single temperature-independent k_{ij}. At the same time, CPA predictions for the *n*-alkane solubilities in water are in fair agreement with the experimental data unlike SAFT predictions that are up to 3 orders of magnitude lower than the experimental data. For the case of 1-alkene solubilities in water, CPA predictions are above the experimental data and SAFT predictions below them by approximately the same magnitude.

It is apparent, in closing, that the physical term of the SAFT EoS, despite its complexity over a simple cubic EoS, does not offer any advantage over the latter, at least for the systems and the conditions examined here. This suggests the need for an improved physical term, which is further supported by the performance of SAFT in the correlation of vapor pressures and saturated liquid volumes and the prediction of critical properties

and second virial coefficients for nonassociating compounds. On the other hand, although the physical term of CPA is an oversimplification of reality, CPA represents better the systems examined here. This success is most probably due to cancellation of errors between the repulsive term and the dispersive term of the model. Interestingly, Kontogeorgis et al.[15] have shown that the pure compound parameter fitting procedure followed in CPA leads to a repulsive term that is close to the Carnahan−Starling equation for hard spheres. In any case, CPA represents a relatively simple tool for the modeling of systems involving associating compounds.

Appendix: The SAFT and CPA EoS

The original version of SAFT developed by Huang and Radosz[11,12] is used in this work. SAFT is an equation of state for pure components and fluid mixtures that accounts for repulsive, dispersive, and strong specific interactions such as hydrogen bonding. In terms of the compressibility factor, Z, SAFT can be expressed as

$$Z = \frac{P}{pRT} = 1 + Z^{seg} + Z^{chain} + Z^{assoc} = 1 + m(Z^{hs} + Z^{disp}) + Z^{chain} + Z^{assoc} \quad (A1)$$

where Z^{hs}, Z^{disp}, Z^{chain}, and Z^{assoc} account for hard-sphere repulsive interactions, dispersive interactions, chain connectivity, and hydrogen bonding. They are calculated from the expressions

$$Z^{hs} = \frac{4\eta - 2\eta^2}{(1 - \eta)^3} \quad (A2)$$

$$Z^{disp} = \sum_i \sum_j j D_{ij} \left(\frac{u}{kT}\right)^i \left(\frac{\eta}{0.74048}\right)^j \quad (A3)$$

$$Z^{chain} = (1 - m)\frac{2.5\eta - \eta^2}{(1 - \eta)(1 - 0.5\eta)} \quad (A4)$$

$$Z^{assoc} = \rho \sum_A \left[\frac{1}{X^A} - \frac{1}{2}\right]\frac{X^A}{\rho} \quad (A5)$$

where η is the packing fraction (a measure of reduced density), m is the number of segments per molecule, u/k is the dispersion energy, D_{ij} are universal constants, and X_A is the fraction of molecules not bonded at site A calculated from the expression

$$X_A = \frac{1}{1 + \rho \sum_{B=1}^{M} X_B \Delta_{AB}} \quad (A6)$$

where M is the total number of hydrogen-bonding sites per molecule and Δ_{AB} is the association strength calculated from the expression

$$\Delta^{AB} = g(d)^{seg}[\exp(\epsilon^{AB}/kT) - 1](\sigma^3 \kappa^{AB}) \quad (A7)$$

where ϵ/k is the energy and κ the volume of association. More details on the model can be found in the work of Huang and Radosz.[11,12]

The repulsive, chain, and hydrogen-bonding terms are extended to mixtures rigorously and so mixing rules are needed only for the dispersion term of the equation. In this work, the van der Waals one-fluid theory mixing rule of Huang and Radosz[12] was used with one temperature-independent binary interaction parameter.

The compressibility factor, Z, of the CPA is given by

$$Z^{CPA} = Z^{SRK} + Z^{assoc} \quad (A8)$$

where z^{SRK} is obtained by the classical SRK EoS:

$$Z^{SRK} = \frac{V}{V - b} - \frac{\alpha}{RT(V + b)} \quad (A9)$$

The contribution of the association term to the compressibility factor is given as in SAFT by eq A5. The only difference in CPA is that the association strength, Δ^{AB}, is given by the following expression:

$$\Delta^{AB} = g[\exp(\epsilon^{AB}/kT) - 1]\beta^{AB}b \quad (A10)$$

where ϵ^{AB} and β^{AB} are the association energy and volume of interaction between sites A and B of the molecule and g is the radial distribution function, which in CPA is given by

$$g = \frac{1 - n/2}{(1 - n)^3} \quad (A11)$$

The packing fraction, n, in CPA is given by the following expression:

$$n = b\rho/4 \quad (A12)$$

Extension of the CPA to mixtures requires explicit mixing rules only for the parameters of the physical part, while the extension of the association term to mixtures is straightforward. The classical van der Waals one-fluid mixing and combining rules are used for the parameters a and b.

More details on the CPA EoS can be found in Kontogeorgis et al.,[15] Yakoumis et al.,[25] and Voutsas et al.[40]

$$\Delta P \% = \frac{1}{NDAT} \sum_{i=1}^{NDAT} \left|\frac{P_i^{calc} - P_i^{exp}}{P_i^{exp}}\right| \times 100 \quad (A13)$$

$$\Delta \rho \% = \frac{1}{NDAT} \sum_{i=1}^{NDAT} \left|\frac{\rho_i^{exp} - \rho_i^{calc}}{\rho_i^{exp}}\right| \times 100 \quad (A14)$$

Nomenclature

a_0 = attractive-term parameter in CPA
b = covolume parameter in CPA
c_1 = parameter in the attractive term in CPA
k_{ij} = adjustable binary interaction parameter
m = number of segments per molecule in SAFT
P = pressure
R = gas constant
T = temperature
T_r = reduced temperature
u^0/k = temperature-independent energy parameter in SAFT
u/k = temperature-dependent energy parameter in SAFT
v^{00} = temperature-independent segment volume parameter in SAFT
v^0 = temperature-dependent segment volume parameter in SAFT
x = mole fraction in the liquid phase
y = mole fraction in the vapor phase

Greek Letters

β = parameter in the association term of CPA
ϵ^{AB} = energy of association in CPA
ϵ/k = energy of association in SAFT
κ = volume of association in SAFT
ρ = molar density

Subscripts and Superscripts

A, B = hydrogen-bonding sites on a molecule
assoc = association
disp = dispersion
c = critical property
calc = calculated
chain = chain
exp = experimental
hs = hard sphere
ij = property of $i-j$ interaction
seg = segment
r = reduced

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