

Extended Statistical Associating Fluid Theory (SAFT) Equations of State for Dipolar Fluids

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Polar forces have a considerable effect on the thermodynamic and phase equilibrium properties of pure and mixture fluids. In this work, the statistical associating fluid theory (SAFT) and perturbed chain-SAFT (PC-SAFT) are extended to explicitly account for dipole–dipole interactions. A recently proposed perturbation theory for pure dipolar fluids is incorporated in both models and further extended to mixtures. Polar SAFT (PSAFT) and PC-polar SAFT (PC-PSAFT) are applied to alcohols, ketones, water, and other dipolar fluids. Vapor pressure and saturated liquid densities are correlated over a wide temperature range from low temperature up to very near the critical point. Critical constants, second virial coefficients, and monomer fraction predictions are reported. Furthermore, the models are applied to correlate the vapor–liquid equilibria of binary mixtures. A temperature-independent binary interaction parameter is regressed from experimental data. Finally, model predictions for representative polar ternary mixtures are presented. In all cases, very good agreement with experimental data is obtained.

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Keywords: equation of state (EoS), dipolar fluids, SAFT, phase equilibria, perturbation theory

Introduction

Dipole–dipole interactions have a significant influence on the thermodynamic properties and phase behavior of several systems of industrial importance, such as water, alcohols, ketones, carboxylic acids, and their mixtures. A fundamental understanding of such interactions at the molecular level and subsequent development of engineering models is still a very challenging and only partially solved problem.^{1,2}

In contrast to the nonpolar fluids, whose structure primarily depends on the short-range repulsive interactions, it was earlier postulated that the microstructure and the macroscopic properties of strongly polar and associating fluids are governed by longer-range electrostatic (dipole–dipole, quadrupole–quadrupole, charge transfer, etc.) interactions.³ Only recently—and

thanks to the development of realistic pairwise potential models and extensive computer simulations—has it been possible to develop macroscopic models that quantitatively capture both repulsive and attractive interactions of very different origins.^{4,5}

Water is a typical fluid where the interplay between repulsive and strong orientation-dependent attractive interactions results in highly nonideal macroscopic thermodynamic properties. It was recently shown that the strong attractive interactions can be decomposed into short-range hydrogen bonding interactions and long-range electrostatic (primarily dipolar interactions) and that the former type of interactions together with the repulsive interactions determines almost exclusively the structure of the fluid and its thermodynamic properties.⁶

One of the earliest engineering models for real polar fluids based on perturbation theory was proposed by Gubbins and Twu.⁷ Their solution theory explicitly accounts for strong directional intermolecular forces and was found to be in excellent agreement with computer simulation results for strongly polar or quadrupolar fluids and also for real fluid properties.

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Donohue and coworkers further extended the Gubbins–Twu theory to chain polar (dipolar and quadrupolar) fluids by developing the perturbed anisotropic chain theory (PACT).⁸ PACT is a powerful equation of state (EoS) able to accurately predict the phase equilibria of both pure polar and mixture fluids.⁹ Despite its accuracy, PACT never gained wide acceptance for practical engineering calculations probably because of its considerably higher complexity.

An EoS family that has gained tremendous interest in academia and in industry is the *statistical associating fluid theory* (SAFT), rooted in Wertheim's thermodynamic perturbation theory (TPT).^{10,11} In SAFT's original formalism, the reference fluid is the hard sphere with short-range directional forces accounting for hydrogen bonding and the perturbation is the weak dispersion forces. In one of the most successful modifications of the original model, perturbed chain–SAFT (PC-SAFT) incorporated the hard chain fluid into the reference fluid, resulting in a more accurate model for long chain molecules (such as, polymers).¹²

The first attempt to extend SAFT to polar fluids was made by Walsh et al.,⁵ who combined Wertheim's theory with the u expansion for dispersion and multipolar interactions; for the latter the Padé approximant of Stell was used.¹³ In this model, each molecule is assumed to possess a nonspherical repulsive core with a Lennard–Jones attractive interaction, nonaxial multipole moments (dipole and quadrupole), and short-range square-well attraction sites for interactions leading to hydrogen bonding. Although some promising results were reported, it was recognized that a more accurate theory for associating liquids was necessary.⁵

A promising model for chain polar and associating fluids was proposed by Xu et al.¹⁴ that combines SAFT and PACT. Interestingly, this model does not contain an explicit term for association; hydrogen bonding is calculated through quadrupolar interactions. The main drawback of the model is its inadequate accuracy when it comes to associating polar molecules (for example, alcohols).¹⁴

Chapman and coworkers^{1,15,16} further extended SAFT to dipolar chains with multiple dipolar sites. In their model, it is assumed that a dipolar chain fluid can be formed by bonding nonpolar hard spheres to dipolar hard spheres, where the bonding contribution is identical to that for a hard-sphere fluid. Each segment has an ideal dipole at its center, perpendicular to the line connecting its center with the center of the immediately preceding segment. In this model, two more parameters in addition to the three nonassociating pure-component SAFT parameters are necessary: (1) the functional-group dipole moment; and (2) the fraction of dipolar segments per chain, which is an adjustable parameter. This model was shown to have substantial predictive capability for real fluids.^{1,15,16}

More recently, Liu et al.¹⁷ proposed a modified SAFT equation of state based on Yukawa and dipolar Yukawa potentials (referred to as YDD-SAFT). In YDD-SAFT dipolar interactions are explicitly calculated, although the model performance is worse than that of Lennard–Jones SAFT.¹⁸

The aim of this work is to extend SAFT and PC-SAFT to dipolar fluids using accurate but still simple expressions for dipolar interactions. For this purpose, the recently proposed model by Nezbeda and Pavlíček for water is used.^{19,20} Other models of higher accuracy but considerably increased complexity (as for example the model of Saager and Fischer²¹)

would result in a complex model that is not suitable for engineering calculations involving multiple components. The new models, referred to as polar SAFT (PSAFT) and PC-polar SAFT (PC-PSAFT), are applied to a variety of pure polar compounds. Phase equilibria, critical constants, second virial coefficients, and monomer fraction for associating dipolar fluids are calculated. Furthermore, mixture phase equilibria for representative binary and ternary mixtures are presented. In all cases, the comparison with experimental data is satisfactory.

Equation of State Development

In SAFT, fluids are modeled as chains of tangential spherical segments. The reference fluid in SAFT consists of the hard-core fluid with association sites (so that hydrogen bonding is explicitly calculated), whereas perturbation consists of weak dispersion interactions. In this work, an additional perturbation term is added to account for the dipole–dipole interactions. In this way, the EoS is written as the sum of contributions arising from hard sphere, chain formation, association, weak dispersion, and, finally, dipole–dipole interactions. PSAFT formulation for the residual Helmholtz free energy per mole is expressed as

$$\begin{aligned}\frac{\alpha^{\text{res}}(T, \rho)}{RT} &= \frac{a(T, \rho)}{RT} - \frac{a^{\text{ideal}}(T, \rho)}{RT} \\ &= \frac{a^{\text{ref}}(T, \rho)}{RT} + \frac{a^{\text{disp}}(T, \rho)}{RT} + \frac{a^{\text{dd}}(T, \rho)}{RT} \\ &= \frac{a^{\text{hs}}(T, \rho)}{RT} + \frac{a^{\text{chain}}(T, \rho)}{RT} + \frac{a^{\text{assoc}}(T, \rho)}{RT} + \frac{a^{\text{disp}}(T, \rho)}{RT} + \frac{a^{\text{dd}}(T, \rho)}{RT}\end{aligned}\quad (1)$$

where T and ρ are the temperature and density of the system, respectively, and the residual Helmholtz free energy is calculated with respect to the Helmholtz free energy for the ideal gas at the same T and ρ . Given the Helmholtz free energy of the fluid, all other thermodynamic properties (pressure, chemical potential, etc.) can be calculated using standard thermodynamic equations.²²

For the hard-sphere term of Eq. 1, the Carnahan–Starling²³ expression is used, so that

$$\frac{a^{\text{hs}}}{RT} = m \frac{4\eta - 3\eta^2}{(1 - \eta)^2} \quad (2)$$

where m is the number of spherical segments per molecule and η is the reduced density, evaluated from the following expression

$$\eta = \tau \rho m v^o \quad (3)$$

where $\tau = 0.74048$ and v^o is the close-packed hard-core volume of the fluid, which is calculated from the temperature-independent volume of the fluid, according to the following expression

$$v^o = v^{oo} [1 - C \exp(-3u^o/kT)]^3 \quad (4)$$

where u°/k is the dispersion energy per segment parameter and $C = 0.12$ (except for hydrogen, which is 0.241). m , v^{oo} [alternatively the segment diameter σ , calculated from the expression $v^{oo} = (\pi N_A/6\tau)\sigma^3$ can be used], and u°/k are the three characteristic nonassociating parameters for pure fluids.

For the chain term, the following expression is used, based on Wertheim's TPT

$$\frac{a^{\text{chain}}}{RT} = (1 - m) \ln \frac{1 - 0.5\eta}{(1 - \eta)^3} \quad (5)$$

and for association, the Helmholtz free energy is calculated from the expression

$$\frac{a^{\text{assoc}}}{RT} = \sum_{A=1}^M \left(\ln X^A - \frac{X^A}{2} \right) + 0.5M \quad (6)$$

where M is the number of association sites per molecule, and X^A is the mole fraction of molecules not bonded at site A . In Eq. 6, the sum is taken over all association sites of the molecule. The quantity X^A is calculated from the expression

$$X^A = \left(1 + \sum_{B=1}^M \rho X^B \Delta^{AB} \right)^{-1} \quad (7)$$

where Δ^{AB} is the association strength evaluated from the following expression

$$\Delta^{AB} = \sqrt{2} v^{oo} \frac{1 - 0.5\eta}{(1 - \eta)^3} [\exp(\varepsilon^{AB}/kT) - 1] \kappa^{AB} \quad (8)$$

In Eq. 8, the two pure-component parameters for association are introduced: the energy of association ε^{AB}/k and the volume of association, κ^{AB} . In this work, the Michelsen–Hendriks formulation²⁴ for the calculation of association interactions was used that substantially reduces the computational time required (up to 70%, depending on the number of components and the properties calculated).

For the dispersion term in Eq. 1, different expressions are used in SAFT and PC-SAFT models. In SAFT, the expression proposed by Alder,²⁵ based on molecular dynamics simulation data for the square-well fluid, is used

$$\frac{a^{\text{disp}}}{RT} = m \sum_{i=1}^4 \sum_{j=1}^9 D_{ij} \left(\frac{u}{kT} \right)^i \left(\frac{\eta}{\tau} \right)^j \quad (9)$$

where $u/k = (u^\circ/k)[1 + (e/kT)]$ and $e/k = 10$ K for all molecules except a few small molecules (for details see Huang and Radosz¹¹).

In PC-SAFT, the dispersion contribution to the Helmholtz free energy is given by¹²

$$\frac{a^{\text{disp}}}{RT} = -2\pi\rho I_1(n, m) m^2 \frac{u}{kT} \sigma^3 - \pi\rho m C_1 I_2(n, m) m^2 \left(\frac{u}{kT} \right)^2 \sigma^3 \quad (10)$$

where C_1 is the following compressibility expression

$$C_1 = \left\{ 1 + m \frac{8\eta - 2\eta^2}{(1 - \eta)^4} + (1 - m) \frac{20\eta - 27\eta^2 + 12\eta^3 - 2\eta^4}{[(1 - \eta)(2 - \eta)]^2} \right\}^{-1} \quad (11)$$

The integrals in the perturbation theory are evaluated from the following series expansions

$$I_1(\eta, m) = \sum_{i=0}^6 a_i(m) \eta^i \quad (12)$$

$$I_2(\eta, m) = \sum_{i=0}^6 b_i(m) \eta^i \quad (13)$$

where the coefficients a_i and b_i are functions of the chain length, expressed as

$$a_i(m) = a_{0i} + \frac{m-1}{m} a_{1i} + \frac{m-1}{m} \frac{m-2}{m} a_{2i} \quad (14)$$

$$b_i(m) = b_{0i} + \frac{m-1}{m} b_{1i} + \frac{m-1}{m} \frac{m-2}{m} b_{2i} \quad (15)$$

The coefficients a_{ji} and b_{ji} are given by Gross and Sadowski¹² and are not repeated here.

In this work, we introduce an explicit dipole–dipole term to SAFT and PC-SAFT. The aim of our work is to develop an accurate but yet simple model that can be extended to mixtures in a straightforward manner. For this reason, a relatively simple, but still accurate, perturbation model developed for spherical dipolar fluids^{19,20} is preferred over a more complicated 28-term expression²¹ that would be impractical for engineering calculations. As a result, the dipole–dipole term in PSAFT and PC-PSAFT for chain fluids has the form of a simple Padé approximant

$$\frac{a^{dd}}{RT} = m \frac{a_2}{1 - a_3/a_2} \quad (16)$$

where the terms a_2 and a_3 correspond to the following functions

$$a_2 = -\frac{4}{3} \left(\frac{u}{kT} \right)^2 \tilde{\mu}^4 \tilde{F}_2 \quad (17)$$

$$a_3 = \frac{10}{9} \left(\frac{u}{kT} \right)^3 \tilde{\mu}^6 \tilde{F}_3 \quad (18)$$

Table 1. Pure Component Parameters of the PSAFT Equation of State for Polar, Associating, and Nonassociating Compounds

Compound	Model*	m	ν^{oo} (mL/mol)	u/k (K)	ε^{hb}/k (K)	κ^{hb}	μ (D)	ν^{dd} (mL/mol)	% AAD**		T (K)
									P^{sat}	ρ^{liq}	
Alcohols											
Methanol	2B	1.779	11.8	207.03	2718.29	0.0537	1.70	44.2	0.74	1.30	288–508
Ethanol	2B	2.372	12.5	202.02	2873.11	0.0308	1.69	44.2	0.56	1.44	293–509
1-Propanol	2B	3.109	12.5	223.87	2671.29	0.0214	1.68	44.2	0.30	1.42	333–531
1-Butanol	2B	3.737	12.5	225.49	2608.32	0.0233	1.66	44.2	0.40	1.88	352–557
1-Pentanol	2B	4.267	12.5	209.88	2566.50	0.0656	1.70	44.2	1.02	2.35	346–580
1-Hexanol	2B	4.870	12.5	217.30	2766.50	0.0524	1.65	44.2	2.37	3.95	325–605
1-Heptanol	2B	5.592	12.5	233.27	2766.50	0.0079	1.74	44.2	1.76	3.81	335–626
1-Octanol	2B	6.304	12.5	227.69	2589.14	0.0158	1.65	44.2	1.55	4.50	328–646
1-Nonanol	2B	6.700	12.5	231.11	2766.50	0.0103	1.61	44.2	2.29	4.45	365–662
1-Decanol	2B	7.369	12.5	227.55	2766.50	0.0127	1.62	44.2	3.25	4.66	349–680
1-Undecanol	2B	7.930	12.5	222.88	2766.50	0.0191	1.67	44.2	7.28	6.19	344–696
1-Dodecanol	2B	8.527	12.5	227.95	2766.50	0.0121	1.69	44.2	2.17	4.53	374–712
1-Tridecanol	2B	9.093	12.5	227.86	2766.50	0.0127	1.65	44.2	3.26	4.99	365–727
Glycol											
Ethylene glycol	4C	3.394	9.4	319.92	1889.86	0.0228	2.31	45.2	2.40	2.29	403–713
Ketones											
Acetone		4.337	8.1	214.29			2.88	61.6	2.78	2.13	259–503
2-Butanone		5.175	8.0	206.10			2.76	33.4	1.53	1.88	316–530
2-Pentanone		5.569	8.7	209.14			2.77	32.3	1.41	2.49	337–555
3-Pentanone		5.708	8.5	205.55			2.82	16.3	1.32	2.44	331–555
2-Hexanone		5.890	9.7	215.29			2.68	15.9	3.35	2.80	305–581
Other Substances											
Water	4C	1.000	12.3	52.13	1982.33	0.0737	1.85	16.7	3.65	0.84	278–641
Ammonia	3B	1.743	7.0	120.67	1460.01	0.1607	1.47	9.7	2.91	0.54	199–402
Chloroform		3.795	10.2	235.67			1.01	31.3	1.72	3.15	252–531
Hydrogen sulfide	3B	1.570	12.9	255.48	287.28	0.0742	0.97	43.7	1.98	1.33	187–370
Acetic acid	1	2.022	14.3	266.69	6667.23	0.0016	1.74	87.9	0.74	1.89	349–586
Total average deviations									2.11	2.80	

* The bonding schemes here for association were taken from Huang and Radosz.¹¹

**% AAD = percentage average absolute deviation.

The reduced dipole moment is defined as

$$\tilde{\mu} = 85.12 \frac{\mu/m}{\sqrt{(u/k)\sigma^3}} \quad (19)$$

where μ is the dipole moment of the fluid (in D). The functions $\tilde{F}_i$ are obtained following the mean-spherical approximation and are of the form

$$\tilde{F}_2 = \frac{\eta}{K^3} \quad (20)$$

$$\tilde{F}_3 = \frac{\eta^2}{K^3} \quad (21)$$

Within this approximation, a short-range cutoff is introduced for the dipolar interactions, σ_d , and $K = \sigma_d/\sigma$. In the original formulation of the theory a switch function was introduced to ensure that a smooth transition is achieved between short-range hydrogen bonding and longer-range dipolar interactions in the expression for the potential energy. In this way, the range of dipolar interactions is extended beyond the first coordination shell of the polar molecule (where hydrogen bonding is dominant) and K should assume a value > 1 . Nezbeda and Pavlíček assigned a value of K equal to 1.5 for water.¹⁹ In this work, σ_d

[or equivalently, $\nu^{dd} = (\pi N_A \sqrt{6} \tau) \sigma_d^3$] is an adjustable parameter whose value is constrained to satisfy the limits discussed.

SAFT and PC-SAFT extension to mixtures is straightforward. Mixing rules are necessary only for the dispersion term. In the case of SAFT, they are as follows

$$m = \sum_i x_i m_i \quad (22)$$

$$\frac{u}{k} = \frac{\sum_i \sum_j x_i x_j m_i m_j \frac{u_{ij}}{k} \nu_{ij}^o}{\sum_i \sum_j x_i x_j m_i m_j \nu_{ij}^o} \quad (23)$$

$$\nu_{ij}^o = \left[\frac{1}{2} ((\nu_{ii}^o)^{1/3} + (\nu_{jj}^o)^{1/3}) \right]^3 \quad (24)$$

$$\frac{u_{ij}}{k} = \left(\frac{u_{ii}}{k} \frac{u_{jj}}{k} \right)^{1/2} (1 - k_{ij}) \quad (25)$$

where x_i is the mole fraction of component i , and k_{ij} is a binary adjustable parameter.

In the case of PC-SAFT, some additional mixing rules are used for mixture calculations¹²

Table 2. Pure Component Parameters of the PC-PSAFT Equation of State for Polar, Associating, and Nonassociating Compounds

Compound	Model*	m	ν^{oo} (mL/mol)	u/k (K)	ε^{hb}/k (K)	κ^{hb}	μ (D)	ν^{dd} (mL/mol)	% AAD		T (K)
									P^{sat}	ρ^{liq}	
Alcohols											
Methanol	2B	1.743	12.5	180.45	2766.50	0.0499	1.70	44.2	1.01	0.62	288–508
Ethanol	2B	2.549	12.5	188.06	2635.77	0.0419	1.69	44.2	0.55	0.63	293–509
1-Propanol	2B	3.442	12.5	224.75	2128.00	0.0171	1.68	44.2	0.41	0.78	333–531
1-Butanol	2B	4.112	12.5	231.00	2766.50	0.0011	1.66	44.2	1.30	1.34	352–557
1-Pentanol	2B	4.819	12.5	227.33	2540.81	0.0012	1.70	44.2	0.82	1.47	346–580
1-Hexanol	2B	4.967	14.0	234.11	2542.62	0.0012	1.65	44.2	1.87	2.07	324–605
1-Heptanol	2B	5.197	15.5	237.77	2589.08	0.0014	1.74	44.2	2.30	1.38	335–626
1-Octanol	2B	6.203	12.5	230.94	2766.50	0.0088	1.65	44.2	2.12	4.23	328–646
1-Octanol	2B	5.782	15.6	236.48	2528.71	0.0010	1.65	44.2	4.25	1.90	328–646
1-Nonanol	2B	6.275	15.4	236.37	2291.12	0.0012	1.61	44.2	4.84	2.63	365–662
1-Decanol	2B	6.419	17.0	240.50	2470.32	0.0013	1.62	44.2	4.72	2.00	349–680
1-Undecanol	2B	7.101	17.0	234.24	2566.50	0.0012	1.67	44.2	10.10	9.38	344–696
1-Dodecanol	2B	7.176	17.8	244.74	2505.76	0.0010	1.69	44.2	14.23	2.84	374–712
1-Tridecanol	2B	7.281	19.1	248.12	2658.79	0.0012	1.65	44.2	11.68	2.38	365–727
Glycol											
Ethylene glycol	4C	3.940	8.4	206.60	1657.81	0.2775	2.31	44.2	2.95	0.77	403–713
Ketones											
Acetone		2.797	14.9	246.99			2.88	41.4	1.54	2.91	259–503
2-Butanone		2.947	17.7	251.85			3.46	19.0	0.58	2.75	316–530
2-Pentanone		3.466	17.6	247.76			2.77	58.5	0.81	1.06	337–555
3-Pentanone		3.514	17.3	245.59			2.82	58.5	0.81	1.54	331–555
2-Hexanone		3.946	26.2	245.52			2.68	38.5	0.89	0.78	305–581
Other Substances											
Water	4C	1.000	12.8	42.77	1973.72	0.0706	1.85	16.7	3.64	0.84	278–641
Ammonia	3B	1.370	9.7	99.87	1499.44	0.1044	1.47	10.7	2.84	0.61	199–402
Chloroform		2.523	17.7	270.18			1.01	60.9	0.86	0.70	252–531
Hydrogen sulfide	3B	1.437	14.3	242.77	406.64	0.0099	0.97	32.8	0.15	0.41	187–370
Acetic acid	1	1.645	19.5	270.93	5184.32	0.0084	1.74	45.6	1.73	0.89	349–586
Total average deviations									3.21	1.95	

*The bonding schemes here for association were taken from Huang and Radosz.¹¹

$$m^2 \frac{u}{kT} \sigma^3 = \sum_i \sum_j x_i x_j m_i m_j \left(\frac{u_{ij}}{kT} \right) \sigma_{ij}^3 \quad (26)$$

$$m^2 \left(\frac{u}{kT} \right)^2 \sigma^3 = \sum_i \sum_j x_i x_j m_i m_j \left(\frac{u_{ij}}{kT} \right)^2 \sigma_{ij}^3 \quad (27)$$

$$\sigma_{ij} = \frac{1}{2} (\sigma_i + \sigma_j) \quad (28)$$

Finally, the following mixing rules are proposed for the dipolar interactions in PSAFT and PC-PSAFT

$$\tilde{\mu} = \frac{\sum_i \sum_j x_i x_j m_i m_j \tilde{\mu}_{ij}}{\left(\sum_i x_i m_i \right)^2} \quad (29)$$

$$\tilde{\mu}_{ij} = \sqrt{\tilde{\mu}_i \tilde{\mu}_j} \quad (30)$$

$$K^3 = \frac{\sum_i x_i m_i \left(\frac{\sigma_d}{\sigma} \right)_i^3}{\sum_i x_i m_i} \quad (31)$$

Results and Discussion

Pure component parameter estimation: correlation of vapor pressure and saturated liquid density

PSAFT and PC-PSAFT as developed above contain six pure component parameters: three for nonassociating nonpolar components (that is, the segment number m , the segment volume v^{oo} , and the segment energy parameter u/k); two additional parameters for association (that is, the association energy ε^{hb}/k and the association volume κ^{hb}); and an additional parameter for the dipolar term (that is, the characteristic segment volume of dipole–dipole interactions, v^{dd}). For nonpolar compounds, PSAFT and PC-PSAFT reduce to SAFT and PC-SAFT, respectively. In this work, PSAFT and PC-PSAFT are applied to various polar and associating, as well as to polar and nonassociating fluids including primary alcohols, ethylene glycol, water, ammonia, ketones, chloroform, hydrogen sulfide, and acetic acid. Parameters are estimated by fitting the models to experimental vapor pressure and saturated liquid density data

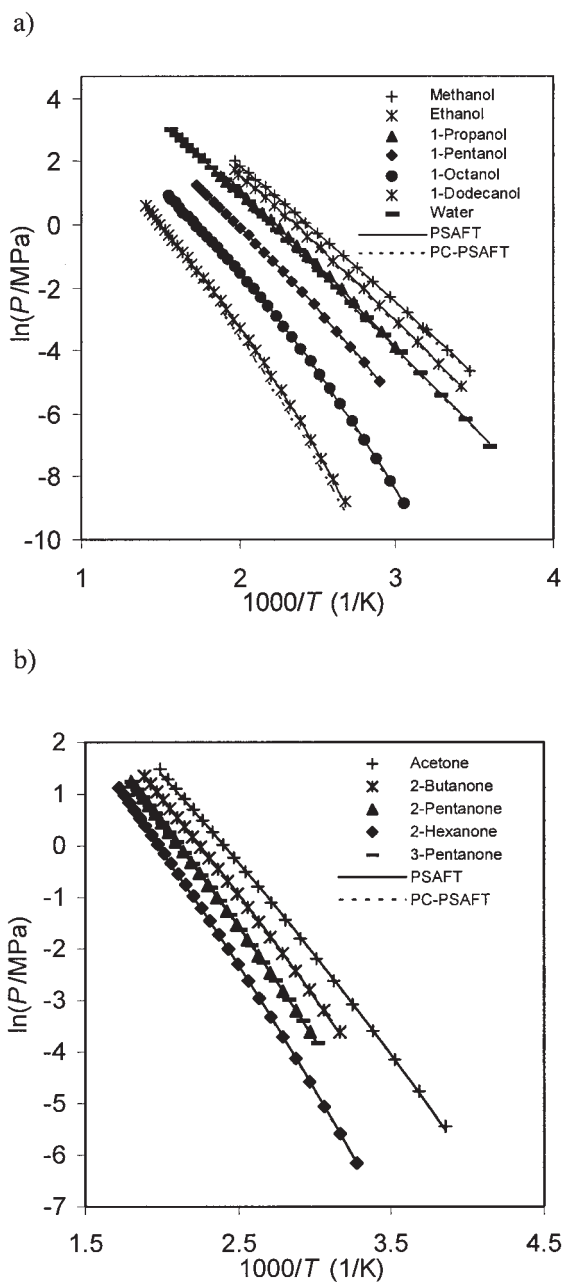


Figure 1. Experimental data²⁶ (points) and EoS correlation (lines) for the vapor pressure of (a) alcohols and water, and (b) ketones.

over a very wide range of temperature, typically from $1.2T_{ir}$ up to $0.99T_c$. Experimental data were taken from the DIPPR data compilation.²⁶ Such pseudo-experimental data should always be carefully treated because some systematic deviation from real experimental data may occur. In Tables 1 and 2, the values of the four (for nonassociating compounds) or six (for associating compounds) parameters, the temperature range used for the parameter estimation, and the average absolute deviations between experiment and theory for vapor pressure and saturated liquid density are presented. For the associating fluids, the association models indicated are based on the bonding schemes introduced by Huang and Radosz.¹¹

Considering the wide temperature range used for the parameter estimation, extended up to very close to the critical point, model correlations are very good in all cases. In the course of parameter estimation, it was found that more than one set of parameters may provide accurate correlation of the experimental data. This is not unusual and has also been frequently reported in the literature for other EoS.²⁷ The parameter values that are finally selected satisfy the following constraints: they are physically meaningful (some discussion for v^{dd} was provided above; similar arguments for other parameters are given below) and, furthermore, for a homologous series it is ensured that parameters vary smoothly with molecular weight (that is, segment number m) or are set constant, for the case of segment volume parameters (that is, segment volume v^{oo} and dipolar segment volume v^{dd}).

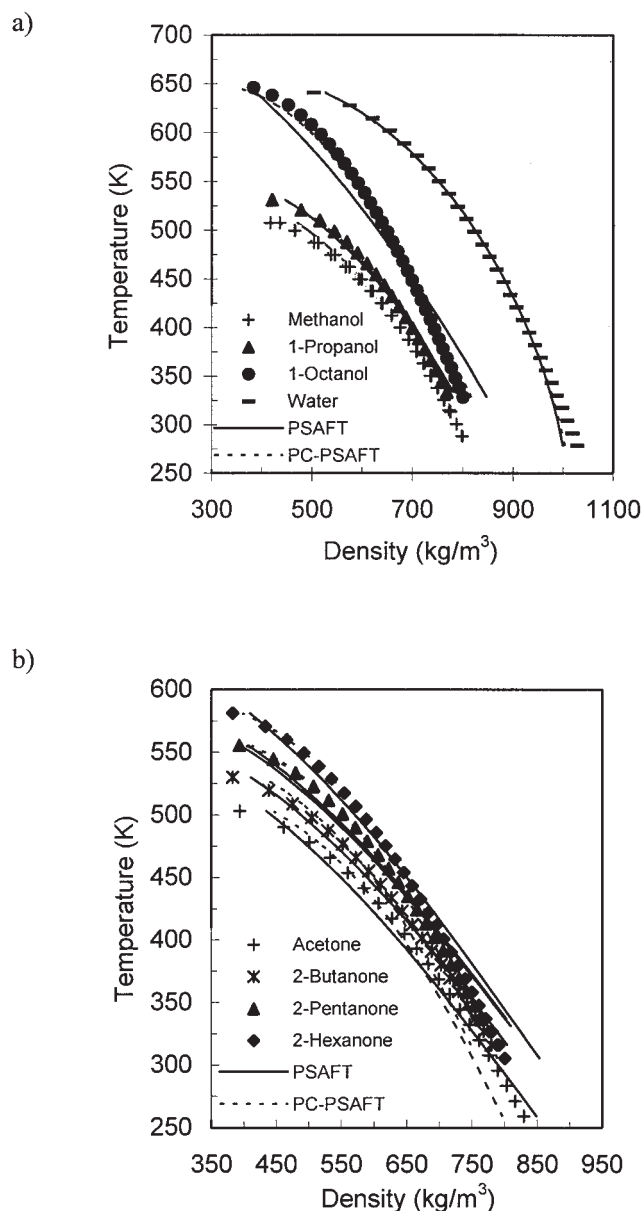


Figure 2. Experimental data²⁶ (points) and EoS correlation (lines) for the saturated liquid density of (a) alcohols and water, and (b) ketones.

In Figure 1, the vapor pressure for several 1-alcohols and water (top) and ketones (bottom) is shown at different temperatures. Good agreement between experimental data and model correlations is obtained. For the higher 1-alcohols examined, the deviation increases with carbon number, especially for PC-PSAFT. It is not clear whether the accuracy of the model decreases or the DIPPR experimental data contain some systematic error.

In Figure 2, experimental data and EoS correlations are shown for the saturated liquid density of the selected compounds. The results are generally good, except from the correlation for the heavier alcohols and ketones, especially at low temperatures. Such failure has been reported previously for SAFT, as well.²⁸

A more detailed analysis of the model performance, the association scheme assumed (for the associating fluids) and the parameter values estimated is given below for each of the various fluids examined.

1-Alcohols. Alcohols are very important organic solvents widely used in various industrial chemical processes. Accurate calculation of their thermodynamic properties is essential for optimum process design. The hydroxyl group in the molecule has a hydrogen and two lone pairs of electrons and so hydrogen bonds are formed between alcohol molecules. Spectroscopic measurements have revealed that alcohols form linear oligomers through hydrogen bonding.^{29,30} Furthermore, most of the theoretical models developed for alcohols explicitly account for hydrogen bonding assuming formation of linear oligomers.^{31–33} The 2B association scheme (a proton-donor site and a proton-acceptor site) in SAFT¹¹ used here accounts exactly for such behavior.

Molecular parameters m , mv^{oo} , and mul/k vary linearly with molecular weight in both PSAFT and PC-PSAFT, thus allowing reliable extrapolation of the parameter values to higher 1-alcohols. In this work, alcohols only up to 1-tridecanol were examined because the uncertainty in the experimental data increases substantially for the higher unstable alcohols.³⁴

An optimum value of 44.2 cm³/mol for the characteristic dipole–dipole interactions volume, v^{dd} , was found for all alcohols. This corresponds to an effective dipole–dipole interaction diameter (σ_d) about 1–2 Å greater than the hard-sphere diameter of the corresponding molecules. Interestingly, in polar SAFT¹ a different approach is used where an average molecular dipole moment for a homologous series is used, and the second polar parameter (that is, the fraction of polar segments x_p) assumes different values for different components.¹

Finally, the association energy parameter (ϵ^{hb}/k) for alcohols assumes values within the range of the experimentally measured enthalpy of hydrogen bonding, $\Delta H_{\text{assoc}}/R$, of 2500–3000 K.³⁵

Ketones. Many naturally occurring substances, such as the components of essential oils, terpenes, steroids, and sugars, all products of great industrial and biological importance, contain ketones. Ketones are nonassociating dipolar compounds. However, they form weak complexes when mixed with proton-donor compounds, such as chloroform. In the so-called chemical theories, ketones are treated as cross-associating compounds.³² A number of different ketones are examined here (see Tables 1 and 2) and parameters m , mv^{oo} , and mul/k vary linearly with molecular weight, both for PSAFT and PC-PSAFT. For this family of compounds, PC-PSAFT is more

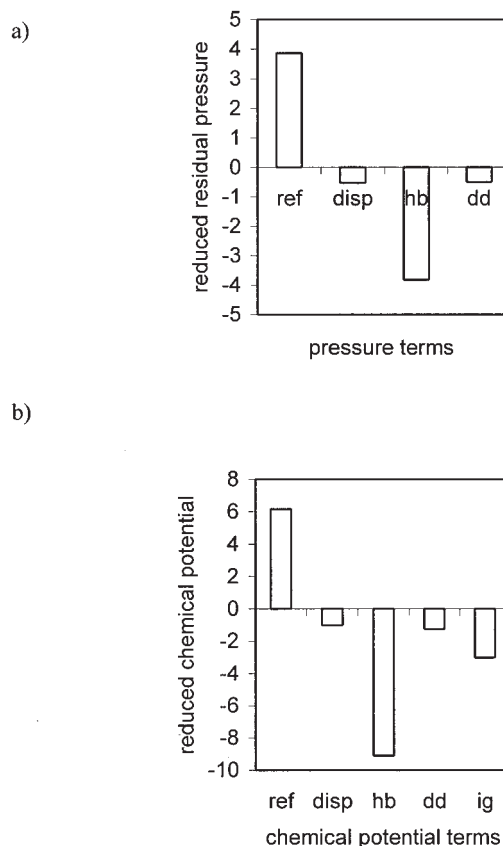


Figure 3. Contribution of the reference term, the dispersion term, the hydrogen bonding term, the dipole–dipole term, and the ideal gas term in (a) pressure and (b) chemical potential of saturated liquid water at 460 K from PSAFT.

accurate than PSAFT. Both models presented here are of comparable accuracy with the polar SAFT proposed by Sauer and Chapman.¹

Water. Water is of immense importance for biological and industrial processes and has been studied extensively for decades. A large number of molecular force fields³⁶ and statistical mechanics–based EoS^{37–39} have been proposed to calculate structure, thermodynamic, thermal, transport, and other properties. Nevertheless, the accurate representation of water properties over a wide range of conditions is still open.

In EoS for associating fluids, the number of hydrogen-bonding sites per water molecule should be defined. In SAFT, water is modeled either as a three-site fluid or a four-site fluid. Extensive analysis of the performance of both models was presented by Economou and Tsonopoulos.⁴⁰ In this work, the 4C model is used both in PSAFT and PC-PSAFT. In both models, water is treated as a spherical molecule ($m = 1$). Explicit calculation of hydrogen bonding and dipole–dipole interactions results in relatively low weak dispersion interactions, in agreement with realistic molecular models^{41,42} and primitive models for water.⁶ The dispersion energy parameter u/k assumes a value of 52.13 K for PSAFT and 42.77 K for PC-PSAFT, whereas in TIPS, a widely used force field for liquid water, the value is 59.7 K,⁴¹ and in MSPC/E, a recently developed force field for water phase equilibria over a wide

Table 3. Experimental and Predicted Pure Component Critical Properties for Water, Alcohols, and Ketones from PSAFT and PC-PSAFT*

Compound	T_c^{exp} (K)	T_c^{calc} (K)		P_c^{exp} (MPa)	P_c^{calc} (MPa)		ρ_c^{exp} (g/cm ³)	ρ_c^{calc} (g/cm ³)	
		PSAFT	PC-PSAFT		PSAFT	PC-PSAFT		PSAFT	PC-PSAFT
Water	647.13	662.36	680.04	22.06	25.60	27.42	0.322	0.314	0.320
Methanol	512.64	527.78	519.41	8.10	10.01	8.98	0.272	0.278	0.265
Ethanol	513.92	524.56	522.37	6.15	7.42	6.85	0.276	0.100	0.100
1-Pentanol	586.15	590.76	590.20	3.88	4.34	4.09	0.270	0.254	0.267
Acetone	508.20	516.42	520.64	4.70	4.89	5.53	0.278	0.257	0.268
2-Butanone	535.50	540.44	544.33	4.15	4.26	4.57	0.270	0.248	0.266

*Experimental values from Daubert and Danner.²⁶

temperature range, the value is 74.5 K.⁴² In SAFT and PC-SAFT, u/k for water is unrealistically high and equal to 350 and 366.5 K, respectively.^{11,12} Furthermore, the energy of association (ϵ^{hb}/k) is 1982.33 K for PSAFT and 1973.72 K for PC-PSAFT, in good agreement with the experimentally measured enthalpy of hydrogen bonding of 1813 K.⁴³ Such an agreement between parameter values in molecular models and parameter values in macroscopic models is an additional justification that the expression of the partition function into contributions from various types of intermolecular forces or, correspondingly, of the Helmholtz free energy in the various terms of Eq. 1 is meaningful.

To further ensure that the effect of dipole–dipole interactions on the thermodynamic properties is not negligible, the contribution of each term in the PSAFT perturbation expansion for pressure and chemical potential for saturated liquid water at 460 K was calculated. As shown in Figure 3, the dipole–dipole interaction contribution is similar to the contribution of the weak dispersion forces. Similar results were also obtained from PC-PSAFT under the same conditions.

Despite the physically realistic model and parameter values, both PSAFT and PC-PSAFT predict a monotonic variation of saturated liquid water density with temperature, failing to capture the maximum value in density, at about 4°C. Work is under way to correct such deficiency using a newly developed statistical mechanical model for water.³⁸

Ammonia. Ammonia is one of the most heavily produced inorganic chemicals, widely used as an intermediate in the production of fertilizers, plastics, explosives, dyes, pharmaceuticals, and so forth. Here, ammonia is modeled as an associating molecule with two proton-donor sites and a proton-acceptor site (3B model). Alternatively, the 4B scheme with three proton-donor sites (the three hydrogens) and a proton-acceptor site can be used.¹⁷ However, the 3B model is in better agreement with the microstructure of liquid ammonia as recently calculated from molecular simulation.⁴⁴

The tetrahedral sp^3 structure of the ammonia molecule corresponds to the structure of the hydronium ion, H_3O^+ (with one lone pair available to form a hydrogen bond). Because water is assigned the value of m equal to 1.0, a realistic value for ammonia should be in the range between 1 and 2, which is the case for both PSAFT and PC-PSAFT. In SAFT,¹¹ v^{oo} was arbitrarily set as 10 cm³/mol. In this work, this parameter is fitted to experimental data. Consequently, the molecular volume, given by the product of the number of segments per molecule and the segment volume (mv^{oo}), which assumes a value of 12.2 cm³/mol in PSAFT and 13.3 cm³/mol in PC-PSAFT, is in close agreement to ammonia van der Waals

volume of 13.8 cm³/mol.⁴⁵ The dispersion energy parameter u/k assumes approximately the same value for both PSAFT and PC-PSAFT, that is 55–65% lower than that in SAFT. Finally, the calculated ϵ^{hb}/k values in both models are close to the literature value of 1409 K, obtained from detailed quantum mechanics calculations.⁴⁶

Hydrogen Sulfide. Hydrogen sulfide is a highly toxic sub-

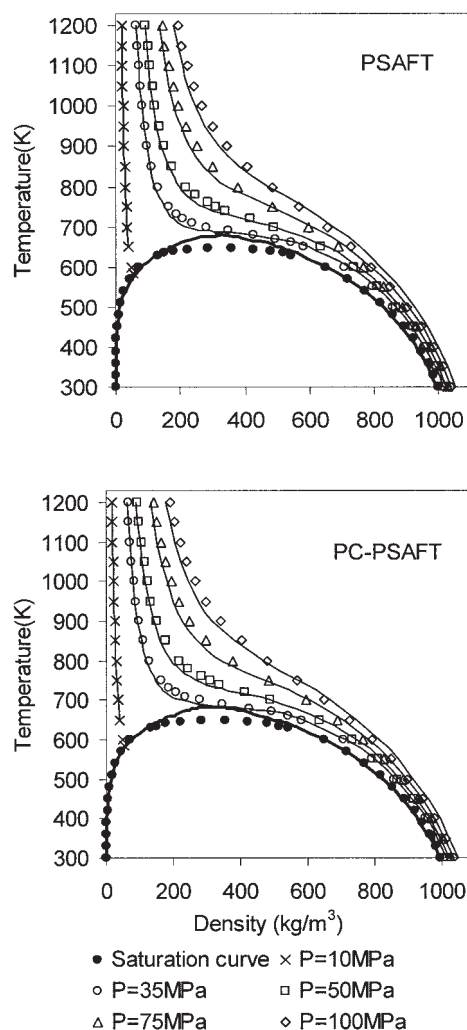


Figure 4. Experimental data⁵³ (points) and PSAFT (lines, top) and PC-PSAFT (lines, bottom) prediction of water density at saturation, subcritical, and supercritical conditions.

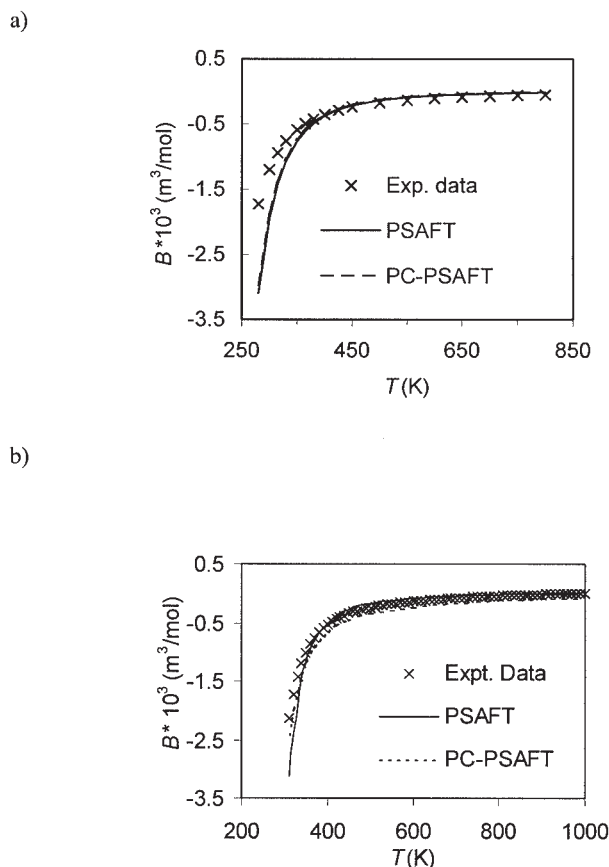


Figure 5. Experimental data,²⁶ PSAFT and PC-PSAFT predictions for the second virial coefficient of (a) water and (b) ethanol.

stance, even in traces, and is found in natural gas and oil. Removal of hydrogen sulfide is necessary before natural gas and oil are used further, so the accurate knowledge of its thermodynamic properties is necessary for the design of the relevant processes. In PSAFT and PC-PSAFT, hydrogen sulfide is modeled with the 3B association scheme, and the energy of association is considerably lower than the corresponding values for water and similar to the dispersion energy value. This behavior is in agreement with experimental data for this component.^{47,48}

Acetic Acid. Acetic acid is used extensively in a variety of industrial processes, such as in food and textile industries. Acetic acid is known to form strong dimers both in the liquid phase and in the vapor phase,²² resulting in strong deviations from ideality even at low pressure.⁴⁹ In this work, acetic acid is modeled assuming dimer formation in both phases and so the association scheme 1 was used. The hydrogen bond energy values obtained are comparable with the values reported by Wolbach and Sandler, derived using molecular orbital calculations.⁵⁰ On the other hand, the bonding volume values are close to the value 0.0019, derived by the expression $K^{hb} = K = 1.485 \times 10^{-4} \sigma^3$ [$\kappa^{hb} = (4\pi/\sigma^3)K^{hb}$] suggested by Jackson et al.⁵¹ for systems with one bonding site, developed so as to ensure that only dimer formation was possible in molecular simulations.

Ethylene Glycol (EG). EG is used extensively in the pet-

rochemical industry to prevent gas hydrate formation (in transportation lines for gas and crude oil). It is also used for the production of poly(ethylene glycol), a widely used polymer in pharmaceutical and other applications. EG has two hydroxyl groups per molecule and so the 4C association scheme is used. The DIPPR correlation used to generate pseudo-experimental vapor pressure and saturated liquid density data is not very accurate for the glycols, as shown by Kontogeorgis and co-workers.⁵² Consequently, parameters for this component reported in Tables 1 and 2 should be treated with caution.

Chloroform. Chloroform does not self-associate but forms strong hydrogen bonds with ketones. The acetone/chloroform mixture exhibits a strong negative deviation from Raoult's law forming an azeotrope over a wide temperature range.²² In fact, this mixture is often used as a benchmark to test new theories.³² The deviation of PSAFT and PC-PSAFT correlation from the experimental data reported in Tables 1 and 2 is lower from the corresponding deviation for the case of SAFT¹¹ and YDD-SAFT.¹⁷

Critical property prediction

Mean-field EoS including SAFT do not account for critical phenomena, such as local density fluctuations. As a result, the coexistence curve in the vicinity of the critical point predicted

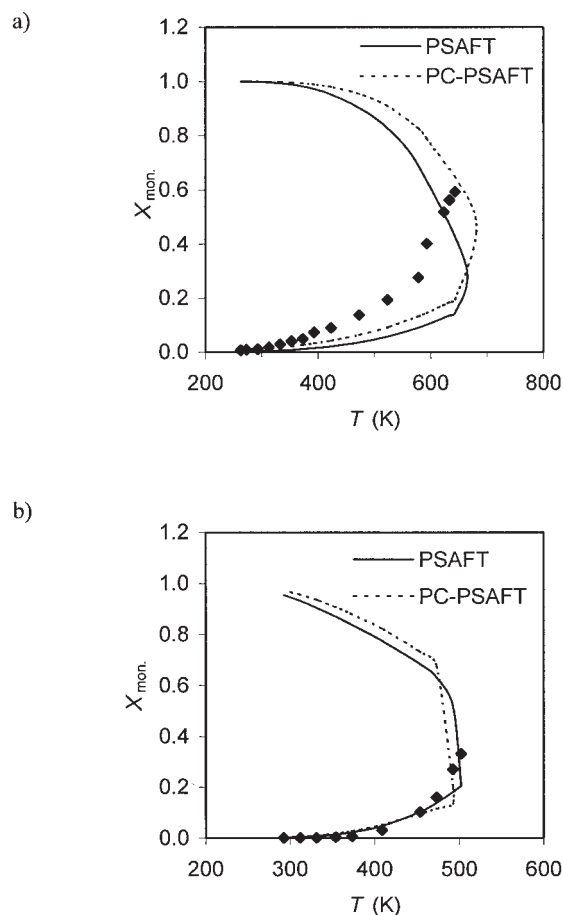


Figure 6. Fraction of (a) water and (b) ethanol monomer molecules, X_{mon} , at saturation. Experimental data (points)⁵⁴ and model predictions (lines).

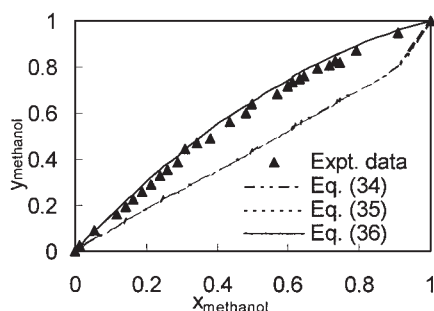


Figure 7. Methanol/ethanol VLE.

Experimental data (points) and PC-PSAFT correlation (lines) at atmospheric pressure (0.101325 MPa) with different combining rules for the association parameters.

by such an EoS is narrower than the experimentally measured curve. In this way, the critical constants predicted by mean-field theories are higher than the experimental values.²⁸ In this work, the accuracy of the newly proposed models in the critical region was assessed by calculating the critical constants of some representative polar compounds. In Table 3, the calculated critical temperature, critical pressure, and critical density are presented together with the experimental values. Both PSAFT and PC-PSAFT overpredict the critical temperature by only 5–15 K (with the exception of PC-PSAFT for water). Such a relatively small deviation should be attributed to the fact that the temperature range used to regress the pure component parameters was extended up to very near the critical temperature ($0.99T_c$).

Supercritical properties

An EoS with strong theoretical basis is expected to accurately predict the thermodynamic properties of fluids over a wide range of conditions, away from the region used for

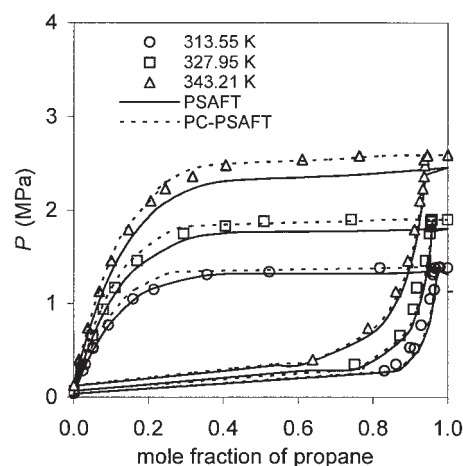


Figure 8. Propane/methanol VLE.

Experimental data (points) and model correlations (lines).

parameter regression. The *PVT* properties in the supercritical region of several fluids are of interest both scientifically and technologically. In Figure 4, experimental data⁵³ and PSAFT and PC-PSAFT predictions at subcritical and supercritical conditions of water over a wide temperature (300–1200 K) and pressure (up to 100 MPa) range are shown. Model predictions are very accurate in all cases away from the critical point.

Second virial coefficient

The second virial coefficient *B* accounts directly for the intermolecular forces and as a result it is widely used to test new theories. Early theories for the second virial coefficient of strongly polar and associating fluids assumed that *B* can be expressed as a contribution arising from weak dispersion forces (physical term) and a contribution arising from polar and/or

Table 4. Binary Interaction Parameter and Deviation in *K*-Factor between Experimental Data and Model Calculations for Binary Mixture Vapor–Liquid Equilibria

System	PSAFT			PC-PSAFT			$T(K)$	Ref.*
	k_{ij}	% AAD		k_{ij}	% AAD			
		K_1	K_2		K_1	K_2		
Methanol/ethanol	0.010	19.5	26.2	−0.013	8.6	6.7	273.15–353.15	1
Methanol/1-propanol	−0.011	7.4	7.6	−0.017	7.6	4.4	273.15–333.15	1
Methanol/1-butanol	0.015	5.5	25.1	−0.030	3.8	17.0	344.55–376.00	1
Methanol/propane	0.058	14.0	7.1	0.057	18.9	16.0	313.55–343.21	2
Ethanol/1-propanol	0.0064	3.2	1.8	−0.001	2.7	1.4	323.15–367.00	1
Ethanol/1-butanol	0.008	3.6	2.7	−0.021	3.3	4.3	353.15–388.15	1
Ethanol/1-pentanol	0.019	7.7	10.7	−0.025	3.4	8.9	353.45–405.55	1
Ethanol/propane	0.039	8.2	3.1	0.022	12.1	5.9	313.58–349.78	2
1-Propanol/1-pentane	0.023	10.7	8.0	0.025	28.9	11.7	313.10–317.10	3
Chloroform/benzene	−0.010	1.1	0.9	−0.009	0.2	0.9	335.53–350.92	4
Chloroform/acetone	−0.025	6.7	6.3	−0.053	1.7	7.1	330.68–335.26	4
Chloroform/2-butanone	−0.025	6.7	6.3	−0.053	1.7	7.1	336.05–352.85	1
Benzene/acetone	0.028	6.5	5.7	−0.002	12.2	6.6	330.49–345.38	4
Methanol/acetone	−0.003	9.7	3.7	−0.050	5.0	8.7	331.27–335.42	1
Ethanol/acetone	−0.034	15.2	3.5	−0.063	20.9	22.9	330.97–342.85	1
Methanol/CO ₂	0.023	28.9	3.5	0.015	41.4	10.7	313.2	5
Ethanol/CO ₂	0.051	45.2	7.6	0.042	22.8	3.5	313.2	5
Acetone/2-butanone	−0.005	11.7	7.2	−0.026	8.1	11.5	331.55–395.15	1

*(1) Gmehling and Onken. *Vapor–Liquid Equilibrium Data Collection*; DECHEMA Chemistry Data Series; Vol. I, Part 2a. Frankfurt, Germany: DECHEMA; 1977; (2) Joung et al. *J Chem Eng Data*. 2004;49:426; (3) Rice et al. *Fluid Phase Equilib*. 1990;56:303; (4) Kojima et al. *J Chem Eng Data*. 1991;36:343; (5) Yoon et al. *J Chem Eng Data*. 1993;38:53.

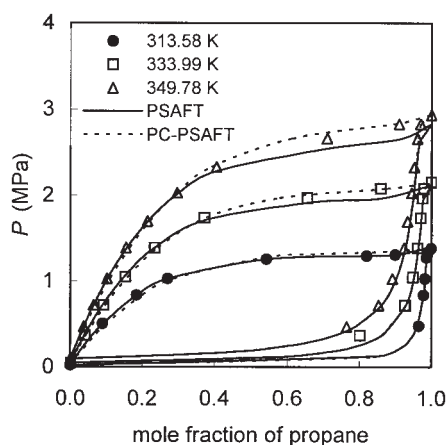


Figure 9. Propane/ethanol VLE.

Experimental data (points) and model correlations (lines).

association forces (chemical term).²² Such an approach was successfully used for the correlation of experimental data for pure fluids and mixtures. Alternatively, the second virial coefficient can be calculated directly from the EoS based on the expression $B = (1/2RT)(\partial^2 P/\partial \rho^2)|_{\rho=0}$, and so it can be expressed as a perturbation expansion, similar to the expression used for the Helmholtz free energy (Eq. 1). In this case, the contribution attributed to dipolar interactions both in PSAFT and PC-PSAFT is

$$B^{dd} = \frac{a_2 m}{\rho} \quad (32)$$

Second virial coefficient calculations were performed for representative polar fluids and results are presented in Figure 5 for water (top) and ethanol (bottom) together with experimental data.²⁶ Deviations between model predictions and experimental data increase at lower temperatures, especially for water.

Monomer fraction

Hydrogen bonding results in the formation of oligomer species. The fraction of these species (monomers, dimers, etc.) depends on temperature and density (or pressure) and is an

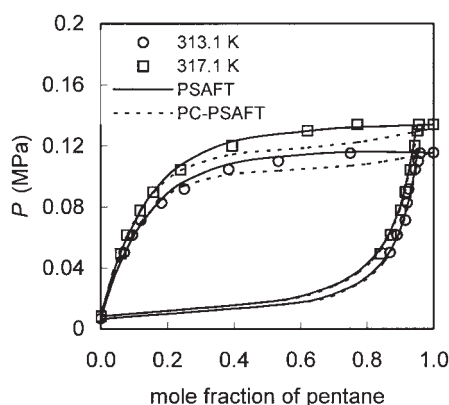


Figure 10. *n*-Pentane/1-propanol VLE.

Experimental data (points) and model correlations (lines).

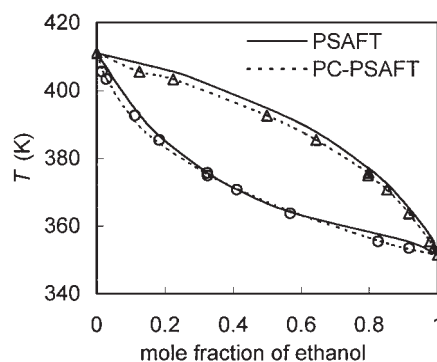
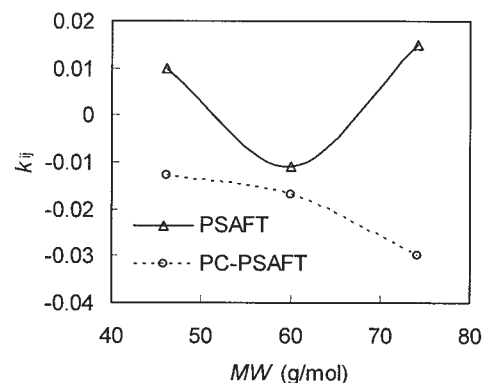


Figure 11. Ethanol/1-pentanol VLE.

Experimental data (points) and model correlations (lines).

important microscopic property of the fluid. Monomer fraction can be measured spectroscopically and/or calculated from an EoS that explicitly accounts for hydrogen bonding or from molecular simulation. For the case of first-order perturbation theories such as SAFT, where multiple bonding sites are assumed per molecule, and bonding on each site is treated inde-

a)



b)

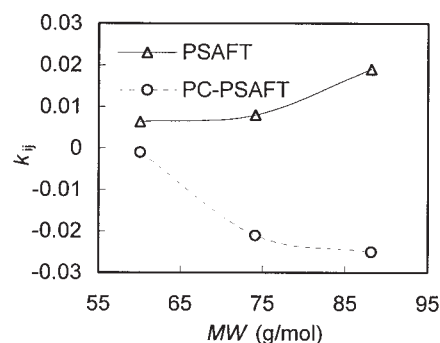


Figure 12. Binary interaction parameter for (a) methanol/1-alcohol (ethanol to 1-butanol) and (b) ethanol/1-alcohol (1-propanol to 1-pentanol) for PSAFT and PC-PSAFT.

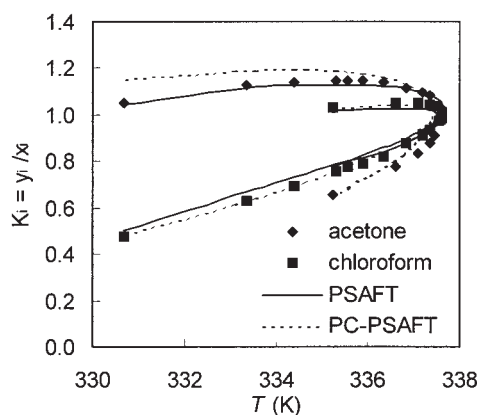


Figure 13. Experimental data (points) and model correlation (lines) for the K -factor in acetone/chloroform mixture.

pendently of the remaining sites, the monomer fraction X_{mon} is calculated as the product over all M sites of the fraction of molecules not bonded at each site A :

$$X_{\text{mon}} = \prod_{A=1}^M X^A \quad (33)$$

In this work, model predictions for X_{mon} are compared against experimental data for water and for ethanol at saturation at various temperatures.⁵⁴ As shown in Figure 6, calculations from PSAFT and PC-PSAFT are similar and in good agreement with experimental values, with the exception of water at elevated temperatures. Certainly, an improved association model is needed for water. Such an improved model should account for cooperativity effects when multiple hydrogen bonds are formed by a water molecule. The first-order thermodynamic perturbation theory used in SAFT does not account for this. Debenedetti and coworkers³⁸ developed a simple yet accurate model that accounts for local density and entropic effects when hydrogen bonds are formed. This can be the basis for further extending PSAFT and PC-PSAFT.

Mixture phase equilibria

PSAFT and PC-PSAFT were used extensively to model binary and ternary polar mixture vapor–liquid equilibria (VLE). A temperature-independent binary interaction parameter, k_{ij} , was fitted to experimental data.

The objective function OF , used for fitting the k_{ij} values, involves either the mixture equilibrium pressure data, when bubble-point calculations are performed, or the K -factor for each component i , $K_i = y_i/x_i$, when flash calculations are performed. In the former case, it is

$$OF_b = \frac{1}{Ndata} \sum_{i=1}^{Ndata} \left| \frac{P_i^{\text{exp}} - P_i^{\text{cal}}}{P_i^{\text{exp}}} \right|$$

where $Ndata$ is the number of data points used in the regression, whereas in the latter case it is

$$OF_f = \frac{1}{Ndata} \frac{1}{Ncomps} \sum_{i=1}^{Ndata} \sum_{j=1}^{Ncomps} \left| \frac{K_{ij}^{\text{exp}} - K_{ij}^{\text{cal}}}{K_{ij}^{\text{exp}}} \right|$$

where $Ncomps$ is the number of components in the mixture.

For the case of mixtures with multiple association components appropriate combining rules are necessary for the calculation of cross-association parameters, that is the association energy and the association volume. Considerable work has been reported in recent years on the development of combining rules that have a strong theoretical basis and result in accurate predictions.^{17,50,55}

The following combining rules were considered in this work:

$$\varepsilon^{A_i B_j} = \sqrt{\varepsilon^{A_i B_i} \varepsilon^{A_j B_j}} \quad \kappa^{A_i B_j} = \frac{\kappa^{A_i B_i} + \kappa^{A_j B_j}}{2} \quad (34)$$

$$\varepsilon^{A_i B_j} = \frac{\varepsilon^{A_i B_i} + \varepsilon^{A_j B_j}}{2} \quad \kappa^{A_i B_j} = \sqrt{\kappa^{A_i B_i} \kappa^{A_j B_j}} \quad (35)$$

Table 5. PSAFT and PC-PSAFT Model Predictions for Ternary and Corresponding Binary Mixture Vapor–Liquid Equilibria of Acetone/Chloroform/Benzene in the Temperature Range 330.85–351.00 K and Methanol/Ethanol/Carbon Dioxide at 313.2 K

% AAD													
	Acetone/Chloroform			Chloroform/Benzene			Benzene/Acetone			Acetone/Chloroform/Benzene*			
	y_1	y_2	P	y_1	y_2	P	y_1	y_2	P	y_1	y_2	y_3	P
PSAFT	4.92	4.90	2.67	1.15	1.60	0.54	21.41	8.35	12.21	11.42	12.85	15.55	3.90
PC-PSAFT	9.79	14.14	4.87	0.35	0.77	0.24	17.92	5.12	9.82	8.35	4.53	4.60	3.45
	Methanol/Ethanol			Ethanol/Carbon Dioxide			Methanol/Carbon Dioxide			Methanol/Ethanol/Carbon Dioxide**			
	y_1	y_2	P	y_1	y_2	P	y_1	y_2	P	y_1	y_2	y_3	P
PSAFT	14.08	10.99	4.19	47.76	0.67	2.14	40.14	0.77	2.34	39.84	41.06	0.47	8.33
PC-PSAFT	5.90	7.56	0.90	23.67	0.32	2.99	22.97	0.40	1.85	20.67	58.72	0.34	7.96

Note: y_i = vapor phase mole fraction.

* Experimental data taken from Kojima et al. *J Chem Eng Data*. 1991;36:343.

**Experimental data taken from Yoon et al. *J Chem Eng Data*. 1993;38:53.

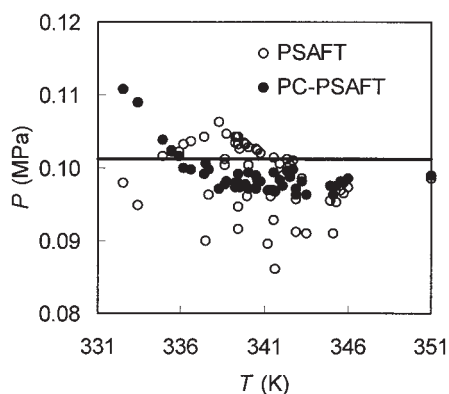


Figure 14. Predicted equilibrium pressure for the mixture acetone/chloroform/benzene from PSAFT and PC-PSAFT at temperatures 330.85–351.00 K.

In all cases, the experimental pressure is 0.101325 MPa (atmospheric) (solid line).

$$\varepsilon^{A_i B_j} = \frac{\varepsilon^{A_i B_i} + \varepsilon^{A_j B_j}}{2} \quad k^{A_i B_j} = \sqrt{k^{A_i B_i} k^{A_j B_j}} \left(\frac{\sqrt{\sigma_{ii} \sigma_{jj}}}{\sigma_{ij}} \right)^3 \quad (36)$$

All three sets of combining rules were used to model the VLE of the methanol/ethanol mixture. Experimental data at atmospheric pressure and model calculations using a k_{ij} value are shown in Figure 7. It is clear that the Eq. 36 system constitutes the most accurate set of combining rules. This set of rules is based on molecular orbital calculations and was also used by Gross and Sadowski⁵⁶ in modeling mixtures of associating fluids with PC-SAFT. Furthermore, the k_{ij} for Eq. 36 assumes the smallest absolute value compared to the other two: $k_{ij} = -0.0616$ (Eq. 34), $k_{ij} = -0.0618$ (Eq. 35), $k_{ij} = -0.0116$ (Eq. 36). All calculations presented in the rest of this paper are based on this combining rule, unless otherwise stated.

In Table 4, a summary of the calculations with PSAFT and PC-PSAFT for the various binary mixtures is presented. The binary parameter was optimized using the OF_f function (flash calculations). Both models provide accurate correlation of VLE for binary mixtures of non-self-associating nonpolar/self-associating polar fluids as shown in Figures 8 through 10. Similarly, mixtures of compounds of the same homologous series (for example, alcohols) are accurately correlated. In Figure 11 experimental data and model correlations with PSAFT and PC-PSAFT are presented for the ethanol/1-pentanol system. A series of methanol and ethanol mixtures with heavier alcohols were examined and k_{ij} was plotted as a function of the molecular weight of the second alcohol. As shown in Figure 12, a systematic change in this parameter is observed, thus allowing reliable extrapolation of the theories to similar mixtures where no experimental data are available. The increase in the absolute value of k_{ij} in all cases indicates that for highly asymmetric mixtures both theories become less accurate.

In this work, self-associating compound/non-self-associating compound mixtures—such as methanol/acetone and ethanol/acetone—where cross-associating species are formed, were examined (Table 4). Both PSAFT and PC-PSAFT provide good correlation of the experimental data.

Finally, mixtures of nonassociating but highly cross-associating compounds were examined. A typical mixture is acetone/chloroform. Strong dipole–dipole interactions account for such complexation. Model correlation with PSAFT and PC-PSAFT and experimental data presented in Figure 13 for the K -factor are in very good agreement. In all the binary mixtures examined, the k_{ij} values are relatively small. This is an indication of the accuracy of the models.

An even stricter test of the new models is their ability to accurately predict multicomponent phase equilibria using only pure-component and binary parameters. Representative calculations for two such mixtures (acetone/chloroform/benzene and methanol/ethanol/carbon dioxide) are presented in Table 5 and Figures 14 and 15. In both cases, bubble pressure calculations were performed. Model predictions are in satisfactory agreement with experimental data. It should be pointed out, however, that carbon dioxide has a substantial quadrupole moment not explicitly accounted for here. A further development of the model can account for higher multipolar interactions and is expected to be more accurate.

Conclusions

In this work, SAFT and PC-SAFT were extended to PSAFT and PC-PSAFT, respectively, to explicitly treat dipolar interactions using a recently developed simple perturbation theory for dipolar fluids.^{19,20} In PSAFT and PC-PSAFT, dispersion

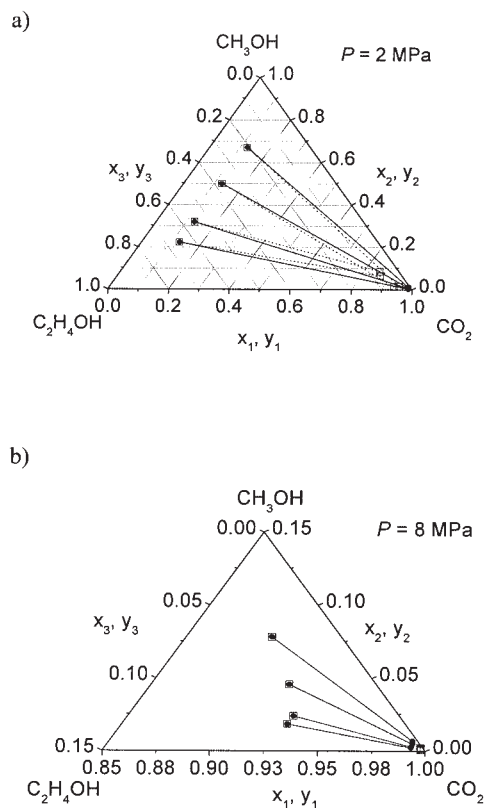


Figure 15. Tie lines for the VLE compositions of methanol/ethanol/carbon dioxide mixture at 2 MPa (top) and 8 MPa (bottom).

Experimental data (solid lines and black circles) and PSAFT prediction (dotted lines and open squares).

interactions, hydrogen bonding, and dipolar interactions are all explicitly taken into account. Both models were used to regress vapor pressure and saturated liquid density of various polar associating and polar nonassociating fluids over a wide temperature range. Furthermore, other thermodynamic properties (such as the critical constants and the second virial coefficient) and microscopic properties (such as the monomer fraction of associating fluids) were calculated. In all cases, the agreement between experimental data and model calculations was very good.

Both polar models were extended to mixtures using standard mixing and combining rules. A temperature-independent binary interaction parameter was fitted to experimental VLE data. Mixture calculations were in reasonably good agreement with experimental data. Furthermore, accurate multicomponent phase-equilibrium predictions were obtained.

Overall, the performance of the two models is similar, at least for the fluids (pure components and mixtures) examined here. In some cases PSAFT is more accurate than PC-PSAFT and vice versa.

Despite the success of the new models, further additional work is needed so that secondary effects on the formation of hydrogen bonds (that is, cooperativity effects, steric hindrances, and so on) are explicitly taken into account to improve model predictions. Such an additional increase in the complexity of the models is certainly necessary to model accurately the saturation curve of species such as water and their mixture properties. Work in this area is currently under way.

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Literature Cited

- Sauer SG, Chapman WG. A Parametric study of dipolar chain theory with applications to ketone mixtures. *Ind Eng Chem Res.* 2003;42:5687–5696.
- Kettler M, Nezbeda I, Chialvo AA, Cummings PT. Effect of the range of interactions on the properties of fluids: Phase equilibria in pure carbon dioxide, acetone, methanol, and water. *J Phys Chem B.* 2002;106:7537–7546.
- Gray CG, Gubbins KE. *Theory of Molecular Fluids: Fundamentals*. Vol. 1. Oxford, UK: Oxford Univ. Press; 1984.
- Kolafa J, Nezbeda I, Lísál M. Effect of short- and long-range forces on the properties of fluids. III. Dipolar and quadrupolar fluids. *Mol Phys.* 2001;99:1751–1764.
- Walsh JM, Guedes HJR, Gubbins KE. Physical theory for fluids of small associating molecules. *J Phys Chem.* 1992;96:10995–11004.
- Nezbeda I, Lísál M. Effect of short and long range forces on the thermodynamic properties of water. A simple short range reference system. *Mol Phys.* 2001;99:291–300.
- Gubbins KE, Twu CH. Thermodynamics of polyatomic fluid mixtures—I. Theory. *Chem Eng Sci.* 1978;33:863–878.
- Vimalchand P, Donohue MD, Celmins I. Thermodynamics of multipolar molecules: The perturbed-anisotropic-chain theory. In: Chao KC, Robinson RL Jr, eds. *Equations of State: Theories and Applications*. Washington, DC: American Chemical Society; 1985:297–313.
- Vimalchand P, Celmins I, Donohue MD. VLE calculations for mixtures containing multipolar compounds using the perturbed anisotropic chain theory. *AIChE J.* 1986;32:1735–1738.
- Chapman WG, Gubbins KE, Jackson G, Radosz M. New reference equation of state for associating liquids. *Ind Eng Chem Res.* 1990;29:1709–1721.
- Huang SH, Radosz M. Equation of state for small, large, polydisperse, and associating molecules. *Ind Eng Chem Res.* 1990;29:2284–2294.
- Gross J, Sadowski G. Perturbed-chain SAFT: An equation of state based on a perturbation theory for chain molecules. *Ind Eng Chem Res.* 2001;40:1244–1260.
- Stell G, Rasaiah JC, Narang H. Thermodynamic perturbation theory for simple polar fluids. II. *Mol Phys.* 1974;27:1393–1414.
- Xu K, Li Y, Liu W. Application of perturbation theory to chain and polar fluids. Pure alkanes, alkanols and water. *Fluid Phase Equilib.* 1998;142:55–66.
- Jog PK, Chapman WG. Application of Wertheim's thermodynamic perturbation theory to dipolar hard sphere chains. *Mol Phys.* 1999;97:307–319.
- Jog PK, Sauer SG, Blaessing J, Chapman WG. Application of dipolar chain theory to the phase behavior of polar fluids and mixtures. *Ind Eng Chem Res.* 2001;40:4641–4648.
- Liu Z-P, Li Y-G, Chan K-Y. Equation of state for nonpolar, polar, chain, and associating fluids based on the dipolar Yukawa potential. *Ind Eng Chem Res.* 2001;40:973–979.
- Kraska T, Gubbins KE. Phase equilibria calculation with a modified SAFT equation of state. 1. Pure alkanes, alkanols and water. *Ind Eng Chem Res.* 1996;35:4727–4737.
- Nezbeda I, Pavlíček J. Application of primitive models of association: A simple theoretical equation of state of water. *Fluid Phase Equilib.* 1996;116:530–536.
- Nezbeda I, Weingerl U. A molecular-based theory for the thermodynamic properties of water. *Mol Phys.* 2001;99:1595–1606.
- Saager B, Fischer J. Construction and application of physically based equations of state. *Fluid Phase Equilib.* 1992;72:67–88.
- Prausnitz JM, Lichtenthaler RN, Gomes de Azevedo E. *Molecular Thermodynamics of Fluid-Phase Equilibria*. 3rd Edition. Englewood Cliffs, NJ: Prentice Hall; 1999.
- Carnahan NF, Starling KE. Equation of state for nonattracting rigid spheres. *J Chem Phys.* 1969;51:635–636.
- Michelsen ML, Hendriks EM. Physical properties from association models. *Fluid Phase Equilib.* 2001;180:165–174.
- Alder BJ, Young DA, Mark MA. Studies in molecular dynamics. X. Corrections to the augmented van der Waals theory for the square well fluid. *J Chem Phys.* 1972;56:3013–3029.
- Daubert TE, Danner RP. *Physical and Thermodynamic Properties of Pure Compounds: Data Compilation*. New York, NY: Hemisphere; 2001.
- Kontogeorgis GM, Voutsas EC, Yakoumis IV, Tassios DP. An equation of state for associating fluids. *Ind Eng Chem Res.* 1996;35:4310–4318.
- Voutsas EC, Boulougouris GC, Economou IG, Tassios DP. Water/hydrocarbon phase equilibria using the thermodynamic perturbation theory. *Ind Eng Chem Res.* 2000;39:797–804.
- Liddel U, Becker ED. Infrared spectroscopic studies of hydrogen bonding in methanol, ethanol, and *t*-butanol. *Spectrochim Acta.* 1957;10:70–84.
- Becker ED. Infrared studies of hydrogen bonding in alcohol-base systems. *Spectrochim Acta.* 1961;17:436–447.
- Ikononou GD, Donohue MD. Thermodynamics of hydrogen-bonded molecules: The associated perturbed anisotropic chain theory. *AIChE J.* 1986;32:1716–1725.
- Economou IG, Ikononou GD, Vimalchand P, Donohue MD. Thermodynamics of Lewis acid–base mixtures. *AIChE J.* 1990;36:1851–1864.
- Panayiotou CG. Applications of the LFAS theory to VLE and volumetric properties in 1-alkanol + normal alkane mixtures. *Pure Appl Chem.* 1989;61:1453–1460.
- Gude M, Teja AS. Vapor–liquid critical properties of elements and compounds. 4. Aliphatic alkanols. *J Chem Eng Data.* 1995;40:1025–1036.
- Pimentel GC, McClellan AL. *The Hydrogen Bond*. San Francisco, CA: Freeman; 1960.
- Guillot B. A reappraisal of what we have learnt during three decades of computer simulations on water. *J Mol Liq.* 2002;101:219–260.
- Economou IG, Donohue MD. Equations of state for hydrogen bonding systems. *Fluid Phase Equilib.* 1996;118:518–529.
- Truskett TM, Debenedetti PG, Sastry S, Torquato S. A single-bond approach to orientation-dependent interactions and its implications for liquid water. *J Chem Phys.* 1999;111:2647–2656.

39. Truskett TM, Dill KA. A simple statistical mechanical model of water. *J Phys Chem B*. 2002;106:11829–11842.
40. Economou IG, Tsionopoulos C. Associating models and mixing rules in equations of state for water/hydrocarbon mixtures. *Chem Eng Sci*. 1996;52:511–525.
41. Jorgensen WL. Transferable intermolecular potential functions for water, alcohols, and ethers. Application to liquid water. *J Am Chem Soc*. 1981;103:335–340.
42. Boulougouris GC, Economou IG, Theodorou DN. Engineering a molecular model for water phase equilibrium over a wide temperature and pressure range. *J Phys Chem B*. 1998;102:1029–1035.
43. Koh CA, Tanaka H, Walsh JM, Gubbins KE, Zollweg JA. Thermodynamic and structural properties of methanol–water mixtures: Experiment, theory and molecular simulation. *Fluid Phase Equilib*. 1993;83:51–58.
44. Thompson H, Wasse JC, Skipper NT, Hayama S, Bowron DT, Soper AK. Structural studies of ammonia and metallic lithium–ammonia solutions. *J Am Chem Soc*. 2003;125:2572–2581.
45. Bondi A. van der Waals volumes and radii. *J Phys Chem*. 1964;68:441–451.
46. Gao J. Computation of intermolecular interactions with a combined quantum mechanical and classical approach. *ACS Symp Ser*. 1993;No. 569:8–21.
47. de Oliveira G, Dykstra CE. Weakly bonded clusters of H₂S. *J Mol Struct (THEOCHEM)*. 1996;362:275–282.
48. Wormald CJ. (Water + hydrogen sulphide) association. Second virial cross coefficients for (water + hydrogen sulphide) from gas phase excess enthalpy measurements. *J Chem Thermodyn*. 2003;35:1019–1030.
49. Tsionopoulos C, Prausnitz JM. Fugacity coefficients in vapor-phase mixtures of water and carboxylic acids. *Chem Eng J*. 1970;1:273–278.
50. Wolbach JP, Sandler SI. Using molecular orbital calculations to describe the phase behavior of cross-associating mixtures. *Ind Eng Chem Res*. 1998;37:2917–2928.
51. Jackson G, Chapman WG, Gubbins KE. Phase equilibria of associating fluids. Spherical molecules with multiple bonding sites. *Mol Phys*. 1988;65:1–31.
52. Derawi SO, Michelsen ML, Kontogeorgis GM, Stenby EH. Application of the CPA equation of state to glycol/hydrocarbons liquid–liquid equilibria. *Fluid Phase Equilib*. 2003;209:163–184.
53. *NIST Chemistry Webbook*. NIST standard reference database, Number 69, February 2000 Release.
54. Luck WAP. A model for hydrogen-bonded liquids. *Angew Chem Int Ed Engl*. 1980;19:28–41.
55. Von Solms N, Michelsen ML, Kontogeorgis GM. Applying association theories to polar fluids. *Ind Eng Chem Res*. 2004;43:1803–1806.
56. Gross J, Sadowski G. Application of the perturbed-chain SAFT equation of state to associating systems. *Ind Eng Chem Res*. 2002;41:5510–5515.

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