

An equation of state for property prediction of alcohol–hydrocarbon and water–hydrocarbon systems

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Abstract

Equations of state have been widely used in the petroleum and chemical industries for thermodynamic property calculation. In the presence of polar substances that self-associate through hydrogen bonding (such as water or alcohol), equations of state are of very limited use. One way to account for the association is to consider the equation of state to be formed of two contributions: physical and chemical. In this work, we develop an equation of state consisting of two terms as proposed by Andrecko [Fluid Phase Equilib. 65 (1991) 89], a chemical and a physical term, for correlation of thermodynamic properties of mixtures containing an associating species. This equation of state is used to correlate vapor pressure data for a number of associating molecules, such as alcohol and water, as well as bubble point pressure data for binary water–hydrocarbon and alcohol–hydrocarbon systems. The results obtained are in good agreement with the experimental data and requiring the use of only one adjustable parameter for each binary system. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The correct prediction of thermodynamic properties and phase equilibrium is an important step in the design of any industrial process. These properties are also necessary for petroleum production from natural hydrocarbon reserves. Of fundamental importance in compositional numerical simulation of hydrocarbon reservoirs is the set of equations that represent the distribution coefficients of components between equilibrium phases within the porous medium, together

with the physical and thermodynamic properties of the fluids in the reservoir. In these simulations, equations of state are commonly employed for the determination of physical and thermodynamic properties and phase equilibrium calculations. For enhanced oil recovery methods where water, gas, polymer, alcohol or surfactants are injected into the reservoir, and where complex reservoir–injected fluid systems are formed, predictions using the available equations of state are not of sufficient accuracy.

For equations of state to be able to deal with such complex systems where deviations from ideality are large, changes in the attractive forces related terms (mainly through modifications in mixing rules) are often suggested. Alterations in the terms representing

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Table 1
Parameters for the equation of state

	Water	Methanol	Ethanol	1-Propanol
T^* (K)	252.25	140.68	173.64	186.79
v^* (cc/gmol)	10.26	18.06	29.46	38.69
c	1.000	1.285	1.253	1.256
ΔH^0 (kJ/mol)	-19.44	-23.70	-23.58	-25.81
ΔS^0 (J/mol K)	-94.00	-93.05	-98.13	-100.90
α	5.06	0.06507	0.1358	0.01148
	$\times 10^{-8}$			

repulsive forces in these equations have also been implemented. From the mathematical point of view, these modifications often lead to rather complex models.

Hard sphere-based perturbation and variational theories of statistical mechanics have been successful in the prediction of properties of nonassociating molecular fluids (Mansoori and Canfield, 1969, 1970). With the development of an accurate hard sphere equation of state for mixtures (Mansoori et al., 1971), the perturbation and variational equations could be applied for fluids and mixtures with various intermolecular potential energy functions with success (Ali and Mansoori, 1974; Lan and Mansoori, 1975; Alem and Mansoori, 1984; Hamad and Mansoori, 1987). The Perturbed Hard Sphere Expansion Theory (PHSET) of mixtures made it possible to apply the perturbation and variational theories analytically for fluids and fluid mixtures of both scientific and industrial interest (Mansoori and Leland, 1972; Lan and Mansoori, 1977; Chen et al., 1987).

For the calculation of densities of systems containing hydrocarbons for which sufficient molecular characterization data are not available, Riazi and Mansoori (1993) proposed a simple but accurate cubic equation of state. For prediction of the vapor pressure of hydrocarbons and other compounds, Edalat et al. (1993,

Table 2
Deviations in calculated vapor pressure and liquid volumes

Substance	(% Deviation in)	PRE	This work
Water	Pressure	4.32	4.73
	Liquid volume	22.03	2.85
Methanol	Pressure	7.48	1.47
	Liquid volume	21.59	6.87
Ethanol	Pressure	3.42	1.38
	Liquid volume	9.96	2.33
1-Propanol	Pressure	9.62	1.32
	Liquid volume	4.63	3.01

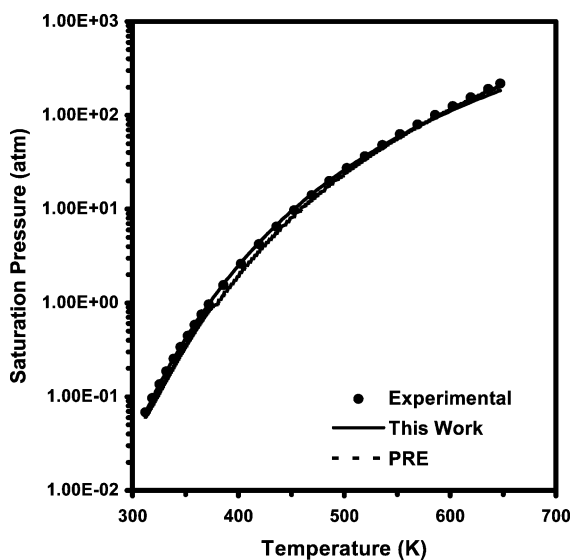


Fig. 1. Experimental and calculated saturation pressures of water.

1997) have produced an accurate generalized correlation. Mohsen-Nia et al. (1993, 1994, 1995) proposed cubic equations of state which could predict the phase behavior, as well as densities, of hydrocarbon mixtures with other compounds more accurately than other cubic equations of state in its class. A new analytic

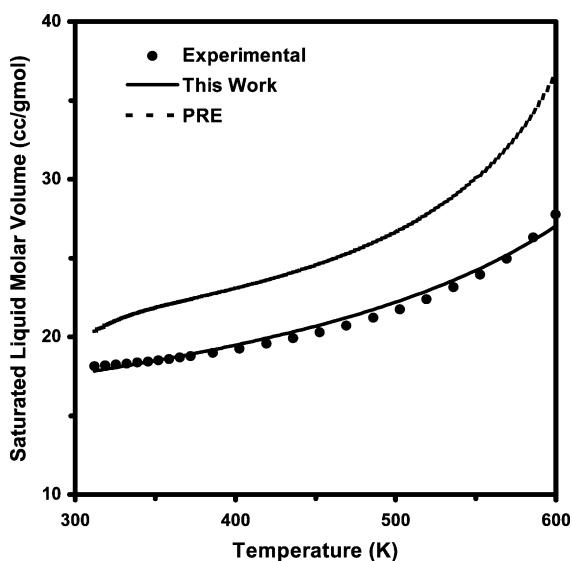


Fig. 2. Experimental and calculated saturated liquid molar volumes of water.

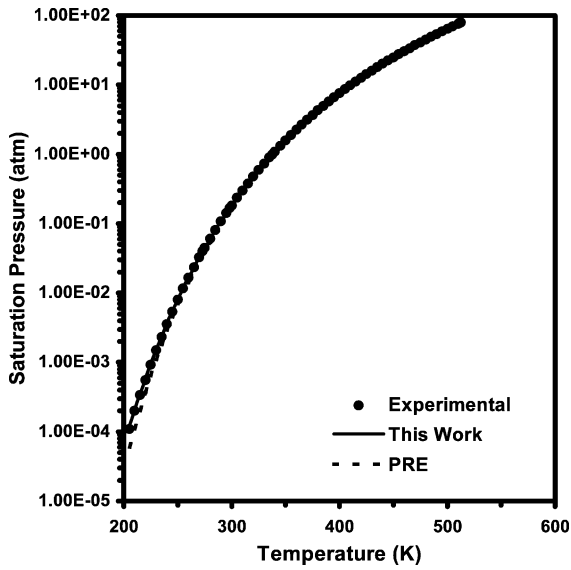


Fig. 3. Experimental and calculated saturation pressures of methanol.

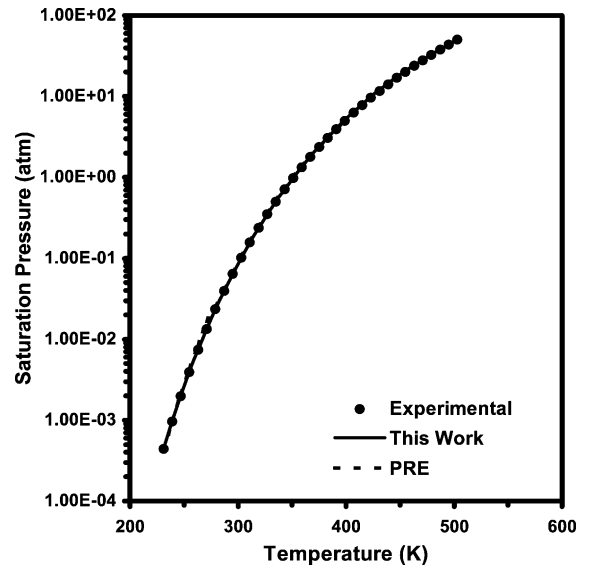


Fig. 5. Experimental and calculated saturation pressures of ethanol.

technique for petroleum fluid characterization using molar refraction was recently proposed by Touba et al. (1997). This technique has substantial potential applications for petroleum fluids for which conventional characterization data are not available. For petroleum

fluids with limited characterization data, a robust and accurate phase behavior prediction calculation technique which requires minimum amount of characterization data was recently proposed by Manafi et al. (1999). This technique was also successfully applied

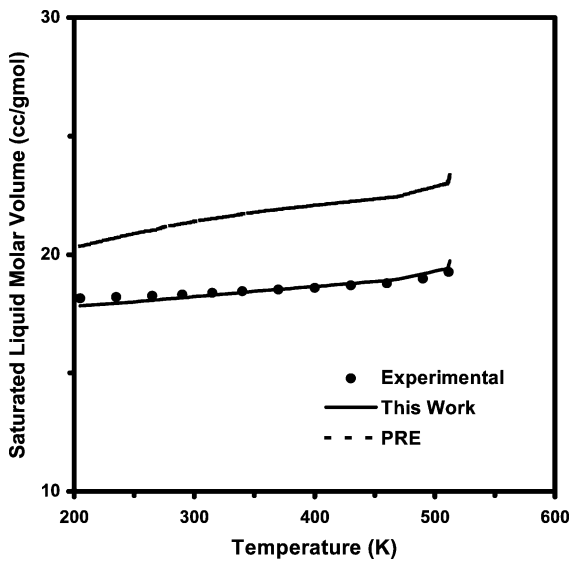


Fig. 4. Experimental and calculated saturated liquid molar volumes of methanol.

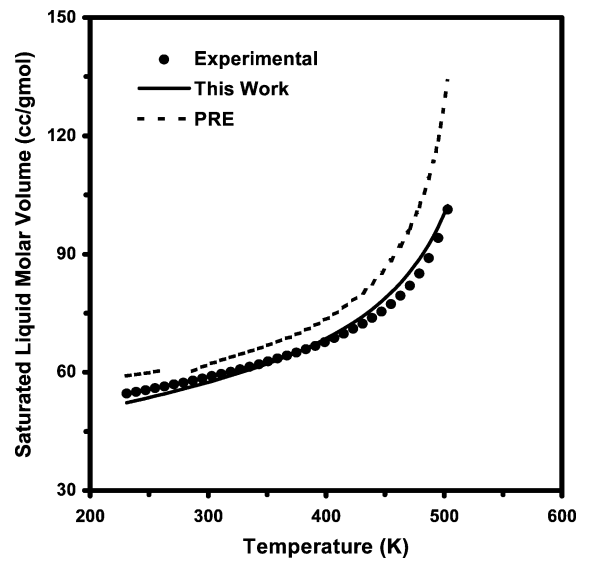


Fig. 6. Experimental and calculated saturated liquid molar volumes of ethanol.

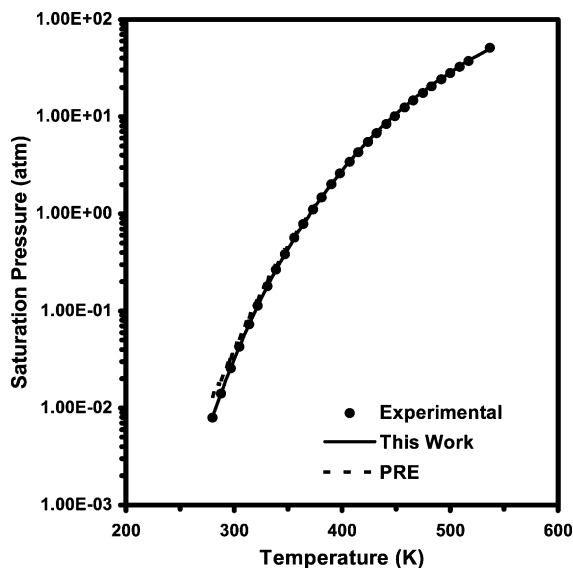


Fig. 7. Experimental and calculated saturation pressures of 1-propanol.

by Fazlali et al. (2001) to predict the phase behavior of complex petroleum fluids.

All these analytical and statistical mechanics-based equations of state have improved the prediction of systems containing hydrocarbons and other fluids whether polar or nonpolar, but their application to associating substances required joining them with an association theory (Aghamiri et al., 1998). Molecules, such as water or alcohols, self-associate forming clusters or aggregates.

There are several possible ways to deal with the presence of associating molecules in mixtures.

(i) One may start with empirical equations of state which have been successful in dealing with associating fluids and improve upon them by applying statistical mechanical approaches, as was done by Benmekki and Mansoori (1987).

(ii) One may treat the associating species as reactant monomers and simultaneously solve the chemical and physical equilibria situation (Aghamiri et al., 1996; Touba and Mansoori, 1996, 1998). This implies the determination of products and reactants in the reactions considered, as well as the extent of such reactions. Normally, a reaction is assumed and its extent is treated through various chemical association theories. The work on this direction has been successful and it is still in progress in various laboratories.

(iii) Al-Mutawa et al. (1993) proposed the use of continuous thermodynamics to solve the association problem. Using the gamma function to simulate the distribution of different sizes and geometric forms of the associating species, they developed a model based on the Van der Waals equation of state. Their method can be generalized to any equation of state. Touba and Mansoori (1996, 1998) and Aghamiri et al. (1996) were able to develop a theory which could generate continuous thermodynamic distributions from the format of the chemical association without any need for an empirical distribution function.

(iv) The fluctuation theory of statistical mechanics has been quite successful in predicting the behavior of variety of associating fluid mixtures (Hamad and Mansoori, 1990a,b; Hamad et al., 1992; Matteoli et al., 2000). Extension of this work towards multi-component mixtures and petroleum fluids is still in progress in various laboratories.

(v) Anderko (1991) has shown that for systems containing one associating component, an equation of state can be developed consisting of two separate parts, a chemical part and a physical part. His results depended on the kind of mixing rules used for the different sizes of molecules of the associating specie. If a self-associating fluid, such as water, forms clus-

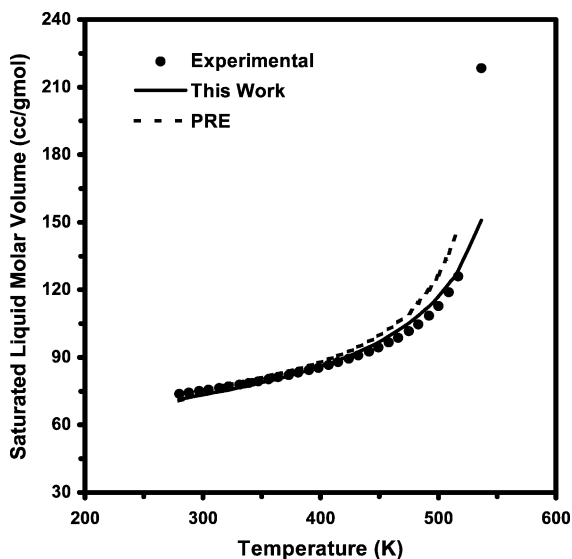


Fig. 8. Experimental and calculated saturated liquid molar volumes of 1-propanol.

ters, there are no published theoretical models to describe this chemical association. Anderko (1991) developed an empirical expression for the chemical contribution of the equation of state and with the Yu and Lu (1987) equation of state representing the physical part, analyzed and performed phase equilibrium calculations for some binary water–hydrocarbon systems. Shinta and Firoozabadi (1995) used this method with the Peng and Robinson (1976) equation representing the physical contribution and they included a new adjustable parameter in the chemical contribution in the global equation.

With the objective of finding a model that can accurately predict thermodynamic properties in systems containing large hydrocarbon molecules and associating species, such as water or alcohols, a situation that could be encountered during steam or alcohol injection for enhanced oil recovery in petro-

leum reservoirs, we propose a new thermodynamic model that uses the chemical term proposed by Anderko (1991), together with the Wang and Guo (1993) equation of state for systems containing self-associating and large hydrocarbon molecules. The model is used to calculate the saturation pressure and saturated liquid molar volumes of some associating fluids, such as water, methanol, ethanol and 1-propanol. Subsequently, the model is used to calculate bubble and dew point pressures in binary systems containing associating compounds and hydrocarbon molecules.

2. Thermodynamics modelling

Following the treatment presented by Anderko (1991), we may separate an equation of state for as-

Table 3
Binary systems containing water

Substance	T (K)	Equation	ΔP (%)	Δy_w (%)	δ	Reference to data used
Methane	323.15	This work	1.64	45.80	−0.06979	Gillespie and Wilson (1982)
		PRE	2.62	87.76	−0.2312	
	348.15	This work	2.19	43.40	−0.04936	
		PRE	3.56	65.51	−0.1651	
	423.15	This work	1.65	20.07	−0.01128	
		PRE	0.27	21.23	0.004602	
	477.59	This work	0.08	10.39	−0.002255	
		PRE	0.75	10.96	0.1062	
	533.15	This work	0.08	4.37	−0.005240	
		PRE	0.16	9.26	0.2033	
588.71	This work	4.81	9.88	0.05811		
	PRE	5.47	2.28	0.4777		
<i>n</i> -Decane	573.20	This work	4.56	8.35	0.2983	Wang and Chao (1990)
		PRE	7.01	20.15	0.5393	
	593.20	This work	7.01	8.84	0.3043	
		PRE	9.10	34.24	0.5875	
	613.20	This work	1.01	67.21	0.3221	
		PRE	0.85	22.56	0.6680	
<i>n</i> -Dodecane	603.60	This work	3.57	6.13	0.2427	Stevenson et al. (1994)
		PRE	1.35	5.96	0.5068	
	633.00	This work	2.35	22.47	0.2394	
		PRE	1.89	6.00	0.6031	
Carbon dioxide	304.21	This work	5.83	14.06	0.1365	Gillespie and Wilson (1982)
		PRE	5.76	14.75	−0.1145	
	348.15	This work	7.87	8.74	0.1468	
		PRE	5.12	73.06	−0.06473	
	366.48	This work	5.06	5.52	0.1475	
		PRE	3.75	50.35	−0.04666	
	394.26	This work	4.83	5.31	0.1474	
		PRE	2.93	28.85	−0.02176	

sociating fluids into a chemical and a physical term (Pires et al., 1996). The compressibility factor of an associating fluid may be calculated by the expression:

$$z = z^{\text{CH}} + z^{\text{PH}} - 1 \quad (1)$$

In the above equation, z^{PH} and z^{CH} represent the physical and chemical contributions to the compressibility factor, respectively. A similar expression can then be written for the pressure:

$$P = P^{\text{CH}} + P^{\text{PH}} - \frac{NRT}{V} \quad (2)$$

and

$$\left(\frac{\partial P}{\partial N_i}\right)_{T,V,N_{j|i}} = \left(\frac{\partial P^{\text{CH}}}{\partial N_i}\right)_{T,V,N_{j|i}} + \left(\frac{\partial P^{\text{PH}}}{\partial N_i}\right)_{T,V,N_{j|i}} - \frac{RT}{V} \quad (3)$$

From the definition of the fugacity coefficient (Modell and Reid, 1983; Prausnitz et al., 1986), it can be shown that:

$$RT \ln(\phi_i z) = - \int_{\infty}^V \left[\left(\frac{\partial P^{\text{CH}}}{\partial N_i}\right)_{T,V,N_{j|i}} - \frac{RT}{V} \right] dV - \int_{\infty}^V \left[\left(\frac{\partial P^{\text{PH}}}{\partial N_i}\right)_{T,V,N_{j|i}} - \frac{RT}{V} \right] dV \quad (4)$$

Defining

$$RT \ln(\phi_i^{\text{CH}} z^{\text{CH}}) = - \int_{\infty}^V \left[\left(\frac{\partial P^{\text{CH}}}{\partial N_i}\right)_{T,V,N_{j|i}} - \frac{RT}{V} \right] dV \quad (5)$$

and

$$RT \ln(\phi_i^{\text{PH}} z^{\text{PH}}) = - \int_{\infty}^V \left[\left(\frac{\partial P^{\text{PH}}}{\partial N_i}\right)_{T,V,N_{j|i}} - \frac{RT}{V} \right] dV \quad (6)$$

We get the expression:

$$\ln(\phi_i z) = \ln(\phi_i^{\text{CH}} z^{\text{CH}}) + \ln(\phi_i^{\text{PH}} z^{\text{PH}}) \quad (7)$$

With the CSPHC equation of state to model the physical part of the equation of state (Wang and Guo, 1993), we have the following expression for the compressibility factor:

$$z^{\text{PH}} = 1 + \langle c \rangle \left[\frac{1.11574 \langle b \rangle}{(v - 0.44744 \langle b \rangle)} - \frac{Z_m a_m}{(v + a_m)} \right] \quad (8)$$

where:

$$\langle c \rangle = \sum_i x_i c_i \quad (12)$$

$$\langle b \rangle = 4\tau \langle v^* \rangle \quad (13)$$

$$\langle v^* \rangle = \sum_i x_i v_{ii}^* \quad (14)$$

$$v^* = \frac{N_A s \sigma^3}{\sqrt{2}} \quad (15)$$

$$a_m = \sum_i \sum_j x_i x_j v_{ji}^* \left[\exp\left(\frac{\langle T^* \rangle_i}{2T}\right) - 1 \right] \quad (16)$$

$$v_{ij}^* = \frac{N_A \sigma_{ij}^3 s_j}{\sqrt{2}} \quad (17)$$

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \quad (18)$$

$$\langle T^* \rangle_j = \frac{\sum_i x_i c_i T_{ij}^*}{\sum_i x_i c_i} \quad (19)$$

$$T_{ij}^* = \frac{\varepsilon_{ij} q_i}{c_i k} \quad (20)$$

$$\varepsilon_{ij} = \sqrt{(\varepsilon_i \varepsilon_j)} (1 - \delta_{ij}) \quad (21)$$

Using the above equation of state, the following expression is obtained for the physical part of the fugacity coefficient of a component in a mixture:

$$\begin{aligned} \ln(\phi_i^{\text{PH}} z^{\text{PH}}) &= \left(\frac{d_1}{d_2}\right) c_i \ln\left(\frac{v}{v - 4\tau d_2 \langle v^* \rangle}\right) \\ &+ \frac{\langle c \rangle 4\tau d_1 v_i^*}{(v - 4\tau d_2 \langle v^* \rangle)} \\ &- c_i Z_m \ln\left(\frac{v + a_m}{v}\right) \\ &- \langle c \rangle Z_m \left(\frac{\beta}{v + a_m}\right) \end{aligned} \quad (22)$$

and

$$\begin{aligned} \beta &= \sum_j x_j \langle v^* \rangle_j \\ &\times \left[\frac{\left(\langle c \rangle c_i T_{ij}^* - c_i \sum_k x_k c_k T_{kj}^* \right)}{(2 \langle c \rangle^2 T)} \right] \exp\left(\frac{\langle T^* \rangle_j}{2T}\right) \\ &+ \sum_j x_j (v_{ij}^* y_j + v_{ji}^* y_i) - a_m \end{aligned} \quad (23)$$

$$y_j = \exp\left(\frac{\langle T^* \rangle_j}{2T}\right) - 1 \quad (24)$$

For infinite linear association, it is possible to obtain an analytical model for the chemical contribution of the equation of state (Ikonomou and Donohue, 1986):

$$z^{\text{CH}} = \frac{2}{1 + \left(1 + \frac{4KRTx_a}{v}\right)^{1/2}} \quad (25)$$

where K is the equilibrium constant, given by:

$$\ln(K) = \frac{1}{R} \left(-\frac{\Delta H^0}{T} + \Delta S^0 \right) \quad (26)$$

with $\Delta C_p^0 = 0$, ΔH^0 and ΔS^0 representing the enthalpy and entropy of association, respectively.

As the association between water molecules is not linear, Anderko (1991) proposed the following model:

$$z^{\text{CH}} = \frac{x_a}{1 + \frac{RTKx_a}{v} + \alpha \left(\frac{RTKx_a}{v}\right)^2} + (1 - x_a) \quad (27)$$

In the above equation, x_a is the apparent mole fraction of the self-associating compound and α is an adjustable parameter. The entropy and enthalpy of association are also treated as adjustable parameters, but their values must be compatible with those already published in the literature.

With the last equation, it is possible to derive an expression for the term that represents the chemical part of the fugacity:

$$\begin{aligned} \ln(\phi_i^{\text{CH}} z^{\text{CH}}) &= - \left[0.5 \ln(E) - \frac{AD}{C^{1/2}} + \frac{(E-1)}{E} \right] \end{aligned} \quad (28)$$

if $C > 0$, and

$$\begin{aligned} \ln(\phi_i^{\text{CH}} z^{\text{CH}}) &= - \left[0.5 \ln(E) - \frac{A}{2C^{1/2}} \ln\left(\frac{F - x_a C^{1/2}}{F + x_a C^{1/2}}\right) + \frac{(E-1)}{E} \right] \end{aligned} \quad (29)$$

in the case $C < 0$.

In these expressions, we have:

$$A = RTK \quad (30)$$

$$B = \alpha(RTK)^2 \quad (31)$$

$$C = 4B - A^2 \quad (32)$$

$$D = \arctg\left(\frac{2v + Ax_a}{x_a C^{1/2}}\right) - 2\arctg 1 \quad (33)$$

$$E = 1 + \frac{Ax_a}{v} + \frac{Bx_a^2}{v^2} \quad (34)$$

$$F = 2v + Ax_a \quad (35)$$

With the chemical and physical contributions obtained, we have the expressions for a new equation of state for mixtures of associating and nonassociating fluids. In what follows, we demonstrate the applicabil-

ity of this equation of state for calculation of thermodynamic properties of alcohol–hydrocarbon and water–hydrocarbon systems of interest in petroleum industry.

Table 4
Binary systems containing alcohols

System	T (K)	Equation	ΔP (%)	Δy_{alc} (%)	δ	Reference to data used
Methanol/butane	323.15	This Work	4.23	11.28	–0.07191	Gmehling et al. (1979)
		PRE	13.71	33.49	0.04109	
Methanol/ <i>n</i> -pentane	372.7	This Work	2.86	6.80	–0.07542	Wilsak et al. (1987)
		PRE	11.98	22.07	0.09735	
	397.7	This Work	1.01	5.47	–0.07288	
		PRE	9.82	21.65	0.1327	
422.6	This Work	0.57	4.03	–0.07193		
	PRE	8.92	15.64	0.1543		
Methanol/hexane	298.15	This Work	10.67	13.38	–0.09633	Gmehling et al. (1979)
		PRE	19.22	26.92	–0.001577	
333.15	This Work	6.80	10.11	–0.08969		
	PRE	16.59	26.80	0.02790		
Ethanol/pentane	283.15	This Work	16.40	26.08	0.07113	Gmehling et al. (1979)
		PRE	25.97	48.15	0.02422	
293.15	This Work	15.36	24.95	0.07575		
	PRE	25.02	46.23	0.03812		
Ethanol/hexane	298.15	This Work	6.20	9.28	0.08710	Gmehling et al. (1979)
		PRE	11.91	24.81	0.02693	
313.15	This Work	7.33	11.25	0.08391		
	PRE	14.20	30.48	0.03964		
323.15	This Work	4.56	7.84	0.08457		
	PRE	11.25	31.48	0.04853		
Ethanol/heptane	313.15	This Work	5.59	10.83	0.09523	Gmehling et al. (1979)
		PRE	7.13	15.96	0.02581	
333.15	This Work	6.50	8.41	0.09007		
	PRE	8.84	13.38	0.04079		
Ethanol/octane	318.15	This Work	9.65	6.73	0.08930	Gmehling et al. (1979)
		PRE	15.17	12.87	0.002160	
328.15	This Work	10.58	11.03	0.09378		
	PRE	16.24	18.98	0.009570		
338.15	This Work	9.31	8.89	0.09224		
	PRE	14.23	14.71	0.01856		
348.15	This Work	10.07	10.84	0.09101		
	PRE	14.64	16.12	0.03879		
1-Propanol/propane	354.75	This Work	2.41	34.00	0.0001374	Muhlbauer and Raal (1993)
		PRE	5.31	67.77	0.04767	
	378.15	This Work	4.21	19.15	–0.004890	
		PRE	7.14	10.98	0.05466	
393.15	This Work	2.75	18.28	–0.01093		
	PRE	5.70	31.22	0.05495		
1-Propanol/hexane	293.15	This Work	20.27	15.79	0.1181	Gmehling et al. (1979)
		PRE	20.61	30.68	0.05823	
323.15	This Work	8.02	12.19	0.08465		
	PRE	10.51	28.94	0.03761		
1-Propanol/heptane	333.15	This Work	10.54	17.25	0.1094	Gmehling et al. (1979)
		PRE	9.73	25.96	0.05121	

3. Results and analyses

The parameters of the equation of state for pure substances, namely the energy and entropy of vaporization, were obtained by calculating the best fit of experimental vapor pressure and liquid volume data. The following function was minimized for the data set available for each associating substance:

$$\text{O.F.} = \frac{\sum_{i=1}^{n_p} \left[\left(\left| \frac{V_{ei} - V_{ci}}{V_{ei}} \right| + \left| \frac{P_{ei} - P_{ci}}{P_{ei}} \right| \right) \right]}{2n_p} \quad (36)$$

where V_e is the experimental saturated liquid molar volume, V_c is the calculated saturated liquid molar volume, P_e is the experimental saturation pressure, P_c is the calculated saturation pressure and n_p is the number of experimental points.

Experimental data from the triple to the critical point (Smith and Van Ness, 1975; Smith and Srivastava, 1986) were used to obtain the parameters for water, methanol, ethanol and 1-propanol.

Table 1 presents the pure component parameters obtained for the chemical and physical terms of the equation. The average deviations in pressure and liquid molar volumes for methanol, ethanol, 1-propanol and water, obtained with this model, and the corresponding values obtained by the Peng and Robinson (1976)

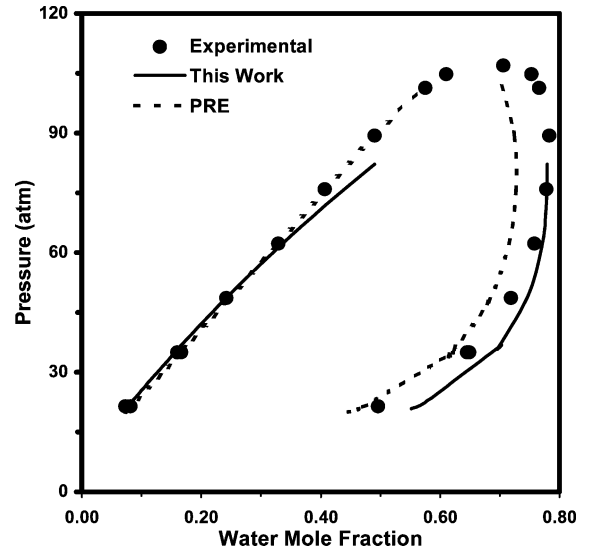


Fig. 10. Water/*n*-dodecane system at 603.6 K.

equation (PRE) of state are presented in Table 2. For all the four systems, the superiority of the new model in the correlation of experimental vapor pressure and saturated volume data is evident (Figs. 1–8). The new equation of state presents excellent correlation of experimental data, particularly at low temperatures, where molecular association is more pronounced.

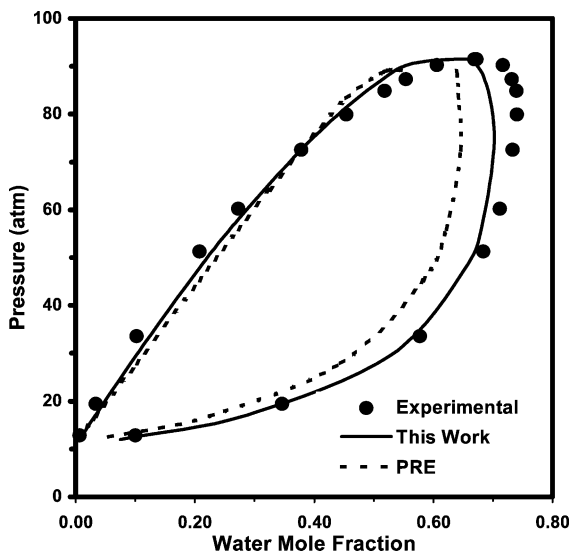


Fig. 9. Water/*n*-decane system at 573.2 K.

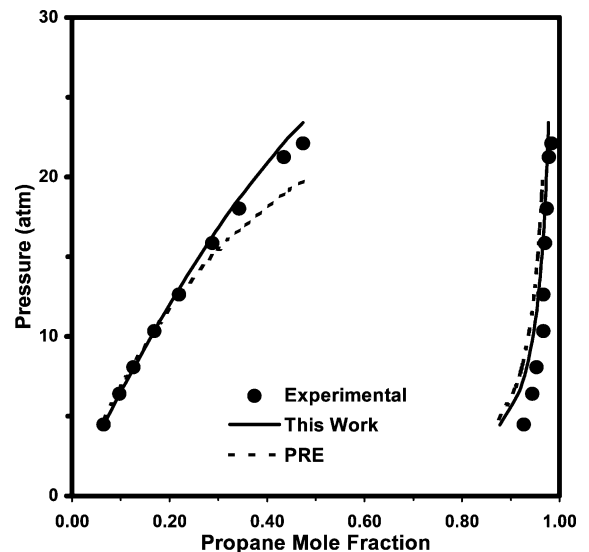


Fig. 11. Propane/1-propanol system at 354.75 K.

For binary mixtures, bubble point pressure calculations were used to obtain the best binary interaction parameter that would minimize the difference between the calculated and experimental saturation pressure values for each binary system. The average deviations in pressure and vapor phase compositions and the binary interaction parameters obtained are presented in Tables 3 and 4 for water–hydrocarbon and alcohol–hydrocarbon systems, respectively. The system water–carbon dioxide was included for its importance in gas-based enhanced oil recovery processes, with the CO₂ parameters used being those established by Wang and Guo (1993). The results are presented in Table 3.

The ability of the developed equation to correlate vapor–liquid equilibrium data, as compared to that of the Peng–Robinson equation (PRE), is shown in Figs. 9–13, for a number of the binary systems. As could be seen in these figures, the calculated values with this new model were in good agreement with experimental data and much superior to those obtained with the Peng and Robinson (1976) equation.

In general, the binary interaction parameters are relatively small (compared to those needed for the Peng–Robinson equation). Interaction parameters needed for the correlation of the water–hydrocarbon systems are, however, much larger than those obtained for the alcohol–hydrocarbon systems. This can be

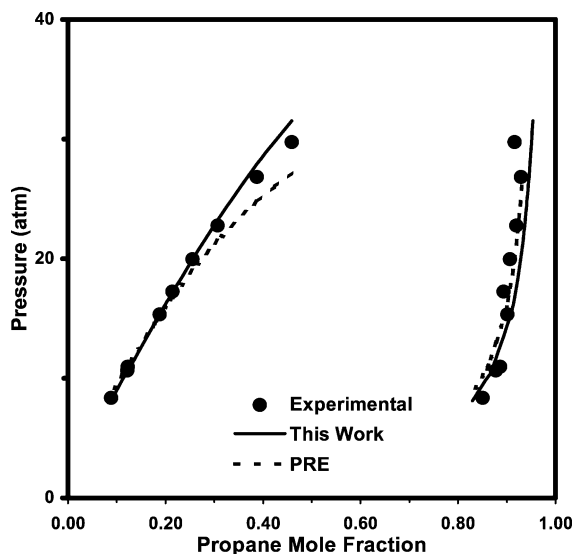


Fig. 12. Propane/1-propanol system at 378.15 K.

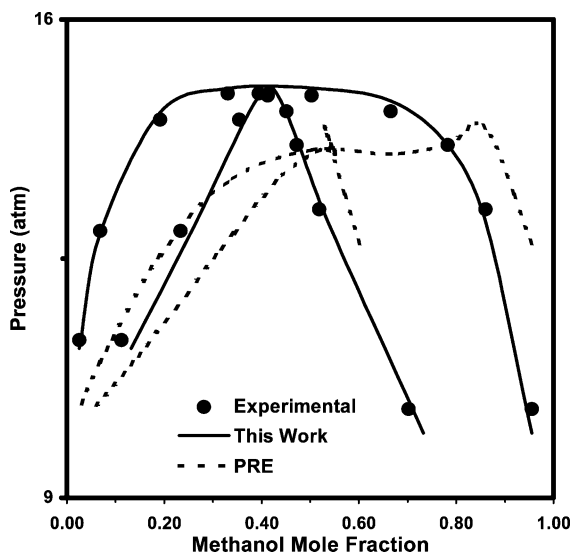


Fig. 13. *n*-Pentane/methanol system at 397.70 K.

attributed to the more complex, nonlinear association of water molecules as compared to the linear association in alcohols, the latter is better represented in the developed model.

4. Conclusions

A new equation of state for self-associating compounds was developed by adopting the separation of chemical and physical contributions in two independent terms, as suggested in the literature, and the use of a convenient chemical contribution and the Cubic Simplified Perturbed Hard Chain Theory for the physical contribution.

The new model was successful in correlating saturation pressure and liquid molar volumes data of pure water and pure alcohols with good accuracy. The equation was also successful in the correlation of phase equilibria in binary water–hydrocarbon and alcohol–hydrocarbon systems using relatively smaller binary interaction parameters than needed with the Peng–Robinson equation. For the correlation of binary alcohol–hydrocarbon systems, interaction coefficients were much smaller than observed in water–hydrocarbon systems, due, perhaps, to the more complex association of water molecules as compared to the linear association in alcohols.

Nomenclature

<i>a</i>	attractive parameter of the equation of state
<i>A</i>	equation parameter
<i>b</i>	volumetric or repulsive parameter of the equation of state
<i>B</i>	second virial coefficient or parameter of equation
<i>c</i>	1/3 of the external degrees of freedom of a molecule
<i>C</i>	equation parameter
<i>C_p</i>	heat capacity at constant pressure (J/mol K)
<i>d</i>	universal constant ($d_1 = 1.11574$ and $d_2 = 0.44744$)
<i>D</i>	equation parameter
<i>E</i>	equation parameter
<i>f</i>	fugacity (atm)
<i>F</i>	parameter of equation
<i>H</i>	enthalpy (kJ/mol)
<i>k</i>	Boltzmann's constant (1.381×10^{-23} J/K)
<i>K</i>	equilibrium constant of chemical reactions or distribution coefficient of a compound in equilibrium
<i>N</i>	number of moles
<i>N_A</i>	Avogadro's number (6.023×10^{23} molecules/mol)
<i>n_p</i>	number of points
O.F.	objective function
<i>P</i>	pressure (atm)
<i>q</i>	normalized surface area per molecule (cm ² /molecule)
<i>R</i>	gas universal constant (82.0567 atm cm ³ /gmol K)
<i>s</i>	number of segments in a molecule
<i>S</i>	entropy (J/mol K)
<i>T</i>	temperature (K)
<i>T*</i>	characteristic temperature of intermolecular interactions (K)
<i>v</i>	molar volume (cm ³ /gmol)
<i>v*</i>	characteristic molar volume (cm ³ /gmol)
<i>z</i>	compressibility factor
<i>Z_m</i>	maximum coordination number (36)

Greek Letters

α	parameter of equation
β	parameter of equation
δ	binary interaction coefficient

ϕ	fugacity coefficient
σ	diameter of the hard nucleus of a segment of a chain like molecule (cm)
ε	characteristic energy per external surface unit area (J/cm ²)
ε^*	characteristic energy for the interaction between segments (J)
τ	constant (0.7405)

Subscripts

a	associating compound
b	bubble point
c	calculated property
e	experimental property
<i>ij</i>	relative to the pair of molecules, segments or compounds <i>i</i> – <i>j</i>

Superscripts

CH	chemical
PH	physical

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