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Correlation and prediction of liquid–liquid equilibria for alcohol/hydrocarbon mixtures using PC-SAFT equation of state at high pressure up to 150 MPa

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ABSTRACT

In this paper, we present a systematic study of the ability of the PC-SAFT equation of state to predict of liquid–liquid equilibria (LLE) for alcohol/hydrocarbon mixtures at high pressure on the basis of LLE data at 0.1 MPa. The adjustable temperature-independent binary interaction parameters, k_{ij}, in the PC-SAFT model were determined from LLE data at 0.1 MPa. The new proposed parameters set for methanol and ethanol with the two-site association scheme reproduce vapor pressures and liquid density with the same accuracy of PC-SAFT original parameters but show a better representation of the LLE data. In addition to using pure component PC-SAFT parameters derived from the standard method of fitting to liquid density and saturated vapor pressure, the new PC-SAFT parameters set for methanol and ethanol are determined from experimental association energy. The new association energy parameter of methanol and ethanol shows better agreement with the experimental results at approximately 298 K compared to all previously published PC-SAFT parameters.

Different binary methanol + hydrocarbon and ethanol + hydrocarbon systems at high pressure up to 150 Mpa were tested using the PC-SAFT. LLE calculations and prediction show good agreement with experimental data for almost considered systems.

1. Introduction

The reliable correlation and prediction of liquid–liquid equilibrium (LLE) data plays an important role in many kinds of separation technologies. Recently, LLE data for wide pressure and temperature ranges have become necessary because of the diversification of separation processes. However, collecting data on LLE is time consuming and especially at elevated pressures not easy to perform.

Most of PC-SAFT parameters were determined for methanol/ethanol using LLE data at 0.1 MPa. However, it would be useful if the correlated results of the LLE data at 0.1 MPa using the PC-SAFT model could be used directly to predict the results for high pressure. In this work, an attempt was made to apply the PC-SAFT EoS to predict the LLE for high pressures using only the binary interaction parameter (k_{ij}) determined from LLE data at 0.1 MPa. The model was tested on the methanol + hydrocarbon and ethanol + hydrocarbon systems for which the LLE data are available over a wide pressure range.

2. Previous applications of SAFT to alcohol containing systems

Several studies with SAFT-type models have been published for alcohol-containing mixtures, these applications have focused on methanol + hydrocarbon and ethanol + hydrocarbon VLE and LLE using the PC-SAFT [1–4], simplified PC-SAFT (sPC-SAFT) [5–8], or SAFT-γ [9]. These literature investigations illustrated that PC-SAFT are promising model, e.g. they can predict well methanol–alkane VLE including the azeotrope [7], as well as simultaneous VLE and LLE at low [3] and high pressures [2]. Overall the performance of PC-SAFT is similar but no systematic studies with PC-SAFT for methanol + hydrocarbons and ethanol + hydrocarbons systems at high pressure have been presented.

3. PC-SAFT equation of state

The equation employed in this work is the original PC-SAFT model developed by Gross and Sadowski [10]. In PC-SAFT,

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Table 1
The association energy of methanol and ethanol calculated from PC-SAFT variants compared to the experimental value.

	Association energy ε^{AB}		Experimental data
Methanol dimer	2090 K [26]	(sPC-SAFT)	2630 K [30]
	2102 K [27]	(PCSAFT-D)	2634 K [31]
	2304 K [7]	(sPC-SAFT)	2785 K [32]
	2750 K this work	(PC-SAFT)	
	2761 K [14]	(GC-PC-SAFT)	
	2836 K [28]	(tPC-PSAFT)	
	2847 K [1]	(PC-SAFT)	
	2899 K [11,29]	(PC-SAFT)	
Ethanol dimer	2222 K this work	(PC-SAFT)	2033 K [35]
	2653 K [1]	(PC-SAFT)	2114 K [36]
	2655 K [11,29]	(PC-SAFT)	2297 K [31]
	2799 K [33]	(sPC-SAFT)	2320 K [37]
	2811 K [34]	(sPC-SAFT)	2432 K [38]
	3306 K [14]	(GC-PC-SAFT)	

molecules are formed by chains of freely jointed spherical segments, being expressed in terms of the reduced residual Helmholtz energy, which consists in of the following contributions:

$$a^{res} = a^{hc} + a^{dis} + a^{asso} \tag{1}$$

The first term, a^{hc} is used to describe the formation of the chain. The second term, a^{disp}, is called “dispersive” accounting for the London-type attractive interactions between segments. For these contributions, three PC-SAFT parameters are necessary: the number of segments (m), the segment diameter (σ), and the segment dispersion energy (ε/k). For associating molecules, additional parameters are needed to describe these interactions. The contribution a^{assoc}, which comes from Wertheim theory, is used to consider the associating interactions and depends on two additional parameters: energy of association (ε^{AB}/k) and volume of association (κ^{AB}). The interested reader is referred to the original papers for more details [10,11].

PC-SAFT applies to mixtures using the van der Waals one-fluid model [11], as well as modified Lorentz–Berthelot mixing rules that relate the potential parameters ε_{ij} and σ_{ij} between segments of molecules i and j.

$$\varepsilon_{ij} = \left(1 - k_{ij}\right)\sqrt{\varepsilon_{ii}\varepsilon_{jj}} \tag{2}$$

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \tag{3}$$

For mixtures considered in this work only one interaction parameter is used (k_{ij}) and results will often be compared to those obtained with other published parameters set for methanol and ethanol.

4. PC-SAFT pure compound parameters

4.1. Hydrocarbons

Pure component parameters used in this study are taken from the literature [12]. For such specific compounds that PC-SAFT parameters are not available yet, they are treated as a specific nonpolar non-associative compound, possessing its own parameters determined on the pure compound liquid density and vapor pressure, these data were taken from the DIPPR database [13]. The relative deviations obtained on the vapor pressures and saturated liquid phase volumes are presented in Table 2.

4.2. Methanol and ethanol

There are some investigations on the choice of an association scheme for alcohols. Most studies use either the two-site (2B) or the three-site (3B) scheme [2,3,5,7,8,14], but the best phase equilibrium results are obtained when the 2B scheme is used [5,7]. Good VLE results are obtained for mixtures of alcohols with alkanes as well as for cross-associating systems, often better than those when all SAFT parameters are fitted to vapor pressures and liquid densities, but in some case using additional properties (than vapor pressures and liquid densities) in the parameter estimation yields improved pure compound parameters in association equations of state [7]. It is concluded from these investigations that it is possible using quantum chemistry to eliminate one of the two association parameters of SAFT, but typically not both [2,15]. The remaining parameters must be fitted to vapor pressure and liquid density data. Still, in this way the deviations in vapor pressures and liquid densities are similar to those obtained when all five parameters of association models (PC-SAFT) are fitted to experimental data. Moreover, it is found that it makes little difference to use the more advanced quantum chemical method [2].

A number of investigators [16–21] working on association models based on Wertheim’s theory have concluded that, while there are several sets of pure-compound parameters which can provide good representation of pure-compound properties, careful choice among them is needed for the simultaneous representation of mixtures and pure-compound properties [7,18,22].

In this work, we tried to determine a new appropriate set of pure-compound properties for methanol and ethanol. Prior to parameter estimation, an association scheme must be chosen, for methanol and ethanol, the 2B schemes was used, in agreement with previous investigations [5,7]. Throughout this manuscript the following notation will be used:

- G&S: 2B parameters set taken from Gross and Sadowski [11]
- L&K: 2B parameters set taken from Lee and Kim [1]
- This work: new 2B parameters set obtained in this work

Table 2
Pure-component parameters of the PC-SAFT equation of state.

Component	m	σ (A)	ε/k (K)	ε^{AB}/k (K)	κ^{AB}	Δ P^{sat}	Δ ρ^{liq}	Tr	ref
2,2,4-trimethyl-pentane	3.1331	4.0953	250.02			0.36	0.56	0.33–0.99	This work
2,2,5-trimethyl-hexane	3.6871	4.0142	243.90			1.68	0.27	0.35–0.99	This work
methyl-cyclopentane	2.4651	3.9141	273.13			3.04	0.78	0.34–1	This work
methanol	1.5255	3.2300	188.90	2899.50	0.03518	2.36	2.01	0.39–1	[11,29]
	1.5143	3.2564	193.76	2847.81	0.03522	0.79	0.42	0.5–0.99	[1]
	1.6538	3.1555	193.82	2750.27	0.04613	1.87	1.12	0.45–0.99	This work
ethanol	2.3827	3.1771	198.24	2653.40	0.03238	0.99	0.79	0.45–1	[11,29]
	2.3862	3.1698	198.00	2655.01	0.03242	0.4	0.13	0.5–0.99	[1]
	3.1139	2.8913	189.92	2222.27	0.08388	1.00	0.64	0.35–0.99	This work

The percentage deviation of a property (Pressure) ΔP^{sat} and (liquid density) $\Delta\rho^{liq}$ is defined as: $\Delta P^{sat}(\%) = 100\cdot \sum_{data} \frac{|P_{sat,\exp} - P_{sat,calc}|}{n_{data}\cdot P_{sat,\exp}}$ $\Delta\rho^{liq}(\%) = 100\cdot \sum_{data} \frac{|v_{liq,\exp} - v_{liq,\exp}|}{n_{data}\cdot v_{liq,\exp}}$.