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Modified Soave-Redlich-Kwong Equations of State Applied to Mixtures Containing Supercritical Carbon Dioxide

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Abstract−The well-known equation of state Soave-Redlich-Kwong and two of its modifications are applied to describe vapor-liquid equilibrium in binary asymmetric mixtures, which contain supercritical carbon dioxide and a heavy component. Several mixing rules including the classical van der Waals mixing rules with one and two interaction parameters, non-quadratic mixing rules, and the used of a Gibbs free energy model, are used with these equations. Seven mixtures containing supercritical carbon dioxide are considered in the study. The experimental data were obtained from literature sources and the adjustable parameters were found by minimizing the errors between predicted and experimental data of the concentration of the solute in the liquid phase. The work allows concluding on the advantages, disadvantages and expected accuracy of these equations of state and mixing rules for correlating vapor-liquid equilibrium data in asymmetric systems as those studied.

Key words: Equations of State, SRK Equation, Supercritical Fluids, Vapor-liquid Equilibrium

INTRODUCTION

The most common method used for the correlation and prediction of phase equilibria in mixtures involves the use of equations of state (EoS). Common and industrially important EoS are the cubic equations derived from the van der Waals equation of state (VdW). Among the many cubic EoS of VdW type nowadays available, those of Redlich and Kwong [1949], of Soave [1972], of Peng and Robinson [1976], of Patel and Teja [1981], and the generalized PTV equation proposed by one of the authors [Valderrama, 1990], among others, have proven to combine the simplicity and accuracy required for the prediction and correlation of volumetric and thermodynamic properties of fluids [Wilson, 1966; Mihajlov et al., 1981; Trebble and Bishnoi, 1986; Valderrama and Rojas, 1999].

The Soave-Redlich-Kwong EoS (SRK) is probably the most widely employed model to correlate and predict fluid properties and phase equilibria in the process industry. The SRK equation can be written in a general form as follows:

$$P = \frac{RT}{(V-b)} + \frac{a_c \alpha(T_r)}{V(V+b)} \tag{1}$$

The parameters a and b for pure substances are determined by using the critical properties and the acentric factor. For mixtures, the parameters a and b are also concentration dependent (a_m and b_m), dependency expressed through defined mixing rules, as described later here.

From 1970 to 1980, most of the applications of EoS to mixtures used the classical van der Waals mixing rules (VdW). An interaction parameter has been introduced into the force parameter "a" to improve predictions of mixture properties [Zudkevitch and Joffe, 1970]. It has been recognized, however, that even with the use of an interaction parameter the classical VdW mixing rules give accurate results for simple fluid mixtures only [Adachi and Sugie, 1985; Trebble, 1988; Shibata and Sandler, 1989].

During the last twenty-five years, efforts have been made to extend the applicability of cubic equations of state to obtain accurate representation of phase equilibria in many industrially important mixtures. The different approaches presented in the literature include the use of multiple interaction parameters in the mixing rules [Kwak and Mansoori, 1986; Trebble and Bishnoi, 1988], the introduction of the local-composition concept [Heyen, 1983], the connection between excess Gibbs free energy models and equations of state [Huron and Vidal, 1979], and the use of non-quadratic mixing rules [Panagiotopoulus and Reid, 1986; Stryjek and Vera, 1986; Adachi and Sugie, 1986].

The SRK equation has been considered for very many applications and has been many times extended and modified in different ways. Two of these modifications are those of Chang et al. [1987], known as the Extended SRK equation (TSRK), and of Holderbaun and Gmehling [1991], known as the predictive SRK equation (PSRK). The original SRK equation and these two modifications are applied and conveniently modified in this work to correlate vapor-liquid equilibria in mixtures containing supercritical carbon dioxide.

MIXING RULES FOR THE SRK EQUATION

As expressed above, classical mixing rules of van der Waals type were used in the past for most applications. These mixing rules can be expressed as:

$$a_m = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j a_{ij} \qquad b_m = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j b_{ij} \tag{2}$$

Customarily, the geometric mean is used for the force parameter

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a_{ij}, while the arithmetic mean is used for the volume parameter b_{ij}:

$$a_{ij}=a_i a_j \qquad b_{ij}=\frac{b_i+b_j}{2} \tag{3}$$

Concentration-independent interaction parameters have been introduced into a_{ij}, and b_{ij} to improve correlation of phase equilibria. This has been done as follows:

$$a_{ij}=a_i a_j(1-k_{ij}) \qquad b_{ij}=\frac{b_i+b_j}{2}(1-\beta_{ij}) \tag{4}$$

These modifications retain the quadratic form of the mixing rules and the quadratic concentration dependence of the second virial coefficient. Some more basic modifications to these equations have been proposed in the literature, introducing concepts such as Volume Dependent mixing rules, Non-Quadratic mixing rules, and combination of EoS+Gibbs free energy models.

The quadratic mixing rules [Eq. (2)], are usually sufficient for the correlation of phase equilibrium in simple systems. To improve correlation of phase equilibrium in complex systems, Panagiotopoulos and Reid [1985] introduced a second interaction parameter. This was done by making the k_{ij} parameter in Eq. (4) concentration dependent, transforming the mixing rule into a non-quadratic form.

$$a_{ij}=\sqrt{a_i a_j}[1-k_{ij}+(k_{ij}-k_{ji})x_i] \text{ with } k_{ij}\neq k_{ji} \tag{5}$$

Expressions similar to that of Panagiotopoulus and Reid have been presented by Adachi and Sugie [1986] and by Sandoval et al. [1989]. The classical and the non-quadratic mixing rules can be summarized in one general form, named "*general non-quadratic mixing rule*" [Arce et al., 2001]:

$$k_{ij}=\delta_{ij}x_i+\delta_{ji}x_j \tag{6}$$

Here, δ_{ij} and δ_{ji} are the two parameters to be calculated from experimental phase equilibrium data. This general non-quadratic mixing rule has also been considered in his study.

Another attractive way, which has been proposed to develop more accurate mixing rules, has been the combination of an EoS with a model for the excess Gibbs free energy (or activity coefficient model). Two main approaches have been used for applying these models. In the first approach the link between the EoS and the excess Gibbs free energy model is done at infinite pressure [Huron and Vidal, 1979; Wong and Sandler, 1992]. In the second approach the link between the EoS and the excess Gibbs free energy model is done at low or zero pressure [Dahl and Michelsen, 1990; Holderbaum and Gmehling, 1991]. A good description of these methods is given in the literature [Huron and Vidal, 1979; Holderbaun and Gmehling, 1991; Wong and Sandler, 1992; Orbey and Sandler, 1998].

EQUATIONS OF STATE AND MIXING RULES USED

Three SRK equations of state were used: i) the original SRK equation with classical van der Waals mixing rules and with non-quadratic mixing rules; ii) the TSRK equation with non-quadratic mixing rules; and the PSRK equation which includes the UNIFAC model in the mixing rule. Original UNIFAC molecular parameters are considered and new parameters are proposed to improve correlations. All the EoS used obey the general following general expression:

$$P=\frac{RT}{V-b}-\frac{a_c\alpha(T_r)}{V(V+b)} \tag{7}$$

The SRK equation

$$\begin{aligned}
&a_c=0.42748\frac{R^2T_c^2}{P_c}\\
&b=008664\frac{RT_c}{P_c}\\
&\alpha(Tr)=[1+m(1-T_r^{0.5})]^2\\
&m=0.48+1.574\omega-0.176\,\omega^2
\end{aligned} \tag{8}$$

Mixing rules (SRK1)

$$\begin{aligned}
&a_m=\sum\sum x_i x_j a_{ij}\\
&b_m=\sum\sum x_i x_j b_{ij}\\
&a_{ij}=(a_i a_j)^{0.5}(1-k_{ij})\\
&b_{ij}=[(b_i+b_j)/2]
\end{aligned} \tag{9}$$

Mixing rules 2 (SRK2)

$$\begin{aligned}
&a_m=\sum\sum x_i x_j a_{ij}\\
&b_m=\sum\sum x_i x_j b_{ij}\\
&a_{ij}=(a_i a_j)^{0.5}(1-\delta_{ij}x_i+\delta_{ji}x_j)\\
&b_{ij}=[(b_i+b_j)/2]
\end{aligned} \tag{10}$$

Mixing rules 3 (SRK3)

$$\begin{aligned}
&a_m=\sum\sum x_i x_j a_{ij}\\
&b_m=\sum\sum x_i x_j b_{ij}(1-\beta_{ij}) \quad \text{con} \quad \beta_{ij}=\beta_{ji}\\
&a_{ij}=(a_i a_j)^{0.5}(1-\delta_{ij}x_i+\delta_{ji}x_j)
\end{aligned} \tag{11}$$

Mixing rules 3M (SRK3M)

$$a_m=\sum\sum x_i x_j a_{ij}$$

Table 1. Properties of the pure substances included in the mixtures studied

Substance	Formula	M	Tc (K)	Pc (MPa)	ω	Zc
Carbon dioxide	CO_2	44.01	304.2	7.38	0.231	0.271
1-Octanol	$C_8H_{18}O$	130.2	652.5	2.86	0.595	0.310
1-Decanol	$C_{10}H_{22}O$	158.3	684.4	2.37	0.661	0.249
2-Metil-1-pentanol	$C_6H_{14}O$	102.2	582.0	3.40	0.726	0.267
Lauric acid	$C_{12}H_{24}O$	200.3	743.0	1.94	0.880	0.221
Palmitic acid	$C_{16}H_{32}O_2$	256.4	776.0	1.51	1.061	0.215
α-Pinene	$C_{10}H_{16}$	136.2	632.6	2.76	0.286	0.267
Limonene	$C_{10}H_{16}$	136.2	660.0	2.75	0.312	0.252

Table 2. Experimental data for the systems considered in this study. In the table the temperature and pressure values have been rounded to the closest integer. In the Table, "x" and "y" refer to the concentration of the solute

System CO_2+	T (K)	Range of pressure (MPa)	Range of x	Range of y	Reference
1-Decanol	348	7-19	0.260-0.640	0.0002-0.0298	Weng et al., 1994
	403	6-19	0.250-0.750	0.0018-0.0135	
1-Octanol	403	6-18	0.360-0.750	0.0055-0.0269	Weng et al., 1994
	453	6-19	0.400-0.770	0.0210-0.0520	
2m-1-Pentanol	348	6-12	0.370-0.660	0.0033-0.0166	Weng et al., 1994
	403	6-15	0.418-0.760	0.0195-0.0482	
	453	6-18	0.430-0.790	0.0802-0.1110	
Lauric acid	423	1-5	0.740-0.950	0.0001-0.0004	Yau et al., 1992
	473	1-5	0.780-0.960	0.0018-0.0049	
Palmitic acid	423	1-5	0.736-0.940	0.0001-0.0002	Yau et al., 1992
	473	1-5	0.780-0.950	0.0002-0.0011	
α-Pinene	313	3-8	0.093-0.700	0.0024-0.0057	Pavlicek et al., 1993
	323	4-10	0.050-0.640	0.0027-0.0160	
	328	5-10	0.205-0.628	0.0029-0.0108	
Limonene	313	6-8	0.112-0.418	0.0011-0.0031	Iwai et al., 1996
	323	4-10	0.166-0.712	0.0018-0.0078	
	333	5-10	0.230-0.650	0.0027-0.0078	

$$b_m = \sum\sum x_i x_j b_{ij}(1-\beta_{ij}) \quad \text{con} \quad \beta_{ij} \neq 0 \text{ for the solvent only}$$

$$a_{ij} = (a_i a_j)^{0.5}(1-\delta_{ij} x_i + \delta_{ji} x_j) \tag{12}$$

The PSRK equation

$$P = \frac{RT}{V-b} - \frac{a_c \alpha(T_r)}{V(V+b)} \tag{13}$$

$$a_c = 0.42748 \frac{R^2 T_c^2}{P_c}$$

$$b = 0.08664 \frac{RT_c}{P_c} \tag{14}$$

$$\text{Para } T_r<1\text{: } \alpha(T_r) = [1+c_1(1-T_r^{0.5})+c_2(1-T_r^{0.5})^2+c_3(1-T_r^{0.5})^3]^2$$

$$\text{Para } T_r>1\text{: } \alpha(T_r) = [1+c_1(1-T_r^{0.5})]^2$$

c_1, c_2 and c_3 are empirical constants given in the literature [Chemstations, 2000].

1. Mixing rule 1 (PSRK-ORIG)

$$a = b\left[\frac{g_0^E}{A_1} + \sum x_1 \frac{a_i}{b_i} + \frac{RT}{A_i}\sum x_i \ln\frac{b}{b_i}\right] \tag{15}$$

$$b = \sum_{i=1} x_i b_i \tag{16}$$

In Eq. (15), $A_1 = -0.64663$ and the Gibbs free energy g_0 is calculated by using UNIFAC, with molecular parameters: r=1.3 and q=0.982, as given in the literature [Chemstations, 2000]. The UNIQUAC model and its application can be found in standard books [Walas, 1986; Prausnitz et al., 1999].

2. Mixing rule 2 (PSRK-MOD)

The same as above but the molecular parameters for carbon dioxide in the UNIFAC model for g_0 are considered as adjustable parameters. These are calculated as explained later here.

The TSRK equation

$$P = \frac{RT}{V-b} - \frac{a_c \alpha(T_r)}{V(V+b)} \tag{17}$$

$$a_c = 0.42748 \frac{R^2 T_c^2}{P_c}$$

$$b = 0.08664 \frac{RT_c}{P_c} \tag{18}$$

$$\alpha(T_r) = [1+m(1-T_r^{0.5}) - p(1-T_r)(0.7-T_r) \qquad \text{p is an empirical parameter}$$

$$m = 0.48508 + 1.55171\omega - 0.15613\omega^2$$

Mixing rule

$$a = \sum\sum x_i x_j a_{ij} \qquad a_{ij} = (a_i a_j)^{0.5}(1-k_{ij})$$

$$b = \sum\sum x_i x_j b_{ij} \qquad b_{ij} = (b_{ij}+b_j)(a-c_{ij})/2$$

Table 3. Deviations in the predicted pressure and vapor phase solute concentration using three equations of state. The TSRK is without interaction parameters

System CO_2+	T (K)	SRK		PRSK		TRSK	
		%ΔP	$\%\Delta y_2$	%ΔP	$\%\Delta y_2$	%ΔP	$\% \Delta y_2$
1-Octanol	403	29.3	27.8	33.8	34.8	26.5	26.5
	453	19.2	17.9	25.2	21.9	16.2	12.4
1-Decanol	348	40.3	73.1	36.2	74.1	33.6	58.4
	403	18.1	10.5	18.7	19.4	14.3	17.6
2m-1-Pentanol	348	29.5	42.6	32.2	48.2	28.7	42.0
	403	26.7	23.8	33.9	29.4	23.6	22.6
Lauric acid	423	6.7	165.0	8.2	147.0	3.8	158.5
	473	5.7	45.2	9.2	29.1	4.4	37.5
Palmitic acid	423	7.3	49.0	12.6	53.0	1.9	49.0
	473	8.4	66.9	14.2	52.6	2.43	58.2
α-Pinene	313	30.0	57.8	3.9	21.8	30.2	55.9
	323	21.8	57.8	3.3	18.7	21.7	57.5
Limonene	313	22.6	62.9	4.2	28.6	13.9	92.6
	323	28.9	66.0	5.9	86.5	20.3	91.6

$$k_{ij}=k^0_{ij}+k^1_{ij}T(K) \qquad c_{ij}=c^0_{ij}+c^1_{ij}T(K)$$

$$z=\frac{PV}{RT} \qquad A=\frac{aP}{R_2T_2} \qquad B=\frac{bP}{RT} \tag{19}$$

APPLICATIONS

In this work, seven gas+liquid binary systems containing supercritical carbon dioxide were selected for study. The experimental data were taken from the literature. Calculations were performed using the SRK equation (with quadratic and non-quadratic mixing rules), the TSRK equation (with three interaction parameters), and the PSRK equation (with original and with new modified UNIFAC parameters). Table 1 shows the basic properties of the fluid substances involved in the study. In the Table, M is the molecular weight, T_b is the normal boiling temperature, T_c is the critical temperature, P_c is the critical pressure, ω is the acentric factor and Z_c is the critical compressibility factor. The data was obtained from Daubert et al. [1996] and Chemstations [2000]. Table 2 gives details on the experimental vapor-liquid equilibrium data for the seven mixtures studied. The literature source for each mixture is indicated in the table.

RESULTS AND DISCUSSION

Results of the application of the different equations and mixing rules are presented in Tables 3 to 6. The results are shown as the deviations given by the different models for predicting the pressure (%ΔP) and the solute concentration in the gas phase (%Δy_2).

In Table 3, the SRK and the TSRK equations were used without interaction parameters, while for the PSRK equation average values for the molecular parameters for carbon dioxide in all mixtures were used: r=0.982 and q=1.3, [Chemstations, 2000]. In Table 4

Table 4. Deviations in the predicted pressure and vapor phase solute concentration using the SRK equation and the no-quadratic mixing rules. The mixing rules SRK2, SRK3 and SRK3M correspond to Eqs. (10), (11) and (12), respectively

System		SRK2				SRK3					SRK3M				
CO_2+	T(K)	δ_{ij}	δ_{ji}	%P	%y_2	δ_{ij}	δ_{ji}	β_{ij}	%P	%y_2	δ_{ij}	δ_{ji}	β_{ij}	%P	%y_2
1-Octanol	403	0.089	0.139	0.5	28.9	0.079	0.135	0.052	0.7	26.2	0.057	0.104	0.052	0.5	24.7
	453	0.079	0.099	0.9	11.8	0.105	0.100	-0.034	1.2	17.3	0.056	0.079	0.026	0.9	11.9
1-Decanol	313	0.098	0.179	1.4	31.5	0.093	0.181	0.030	1.3	29.5	0.095	0.179	0.007	1.5	25.1
	403	0.039	0.152	1.9	35.1	0.034	0.138	0.048	1.8	18.7	-0.027	0.101	0.103	1.2	40.6
2-Methyl-1-pentanol	348	0.070	0.156	3.8	14.0	0.050	0.200	-0.099	0.9	90.4	0.050	0.147	0.037	3.5	23.4
	403	0.081	0.144	0.4	9.2	0.086	0.143	-0.017	0.6	10.2	0.074	0.135	0.010	0.5	10.5
Lauric acid	423	-0.050	0.050	2.5	582.6	0.001	0.153	-0.300	2.5	236.8	0.000	0.147	-0.150	2.8	136.4
	473	-0.050	0.050	1.9	247.4	0.002	0.145	-0.150	1.8	215.7	0.150	0.153	-0.150	4.3	158.3
Palmitic acid	423	-0.050	0.052	1.9	32.9	0.002	0.007	0.150	1.1	94.7	0.300	0.450	-0.600	1.7	26.3
	473	-0.050	0.050	1.9	214.8	0.003	0.150	-0.150	1.5	373.4	0.150	0.139	-0.150	2.4	76.1
α-Pinene	313	0.110	0.167	0.7	25.9	0.096	0.184	-0.058	1.2	35.4	0.092	0.158	0.051	0.4	20.6
	323	0.111	0.173	0.4	51.2	0.104	0.215	-0.038	1.1	44.72	0.103	0.169	0.022	0.5	8.6
Limonene	313	0.103	0.160	0.2	6.7	0.101	0.151	0.005	0.9	8.4	0.093	0.162	0.032	0.1	24.4
	323	0.105	0.192	0.8	37.5	0.106	0.202	0.001	1.4	37.5	0.094	0.185	0.034	0.7	26.3

Table 5. Parameters in the TSRK equation and deviations in the predicted vapor phase solute concentration for the seven systems studied

System	T(K)	TSRK parameters				
		k^0_{ij}	k^1_{ij}	c^0_{ij}	c^1_{ij}	% Δy_2
1-Octanol	403	−3.55E-02	4.01E-04	−2.18E-02	−1.87E-04	21.4
	453	−2.89E-02	2.31E-03	−7.62E-03	−6.53E-05	10.4
1-Decanol	348	−4.59E-02	6.58E-02	−4.47E-01	3.85E-04	24.9
	403	1.22E-01	6.82E-04	3.29E-01	2.34E-05	11.7
2m-1-pentanol	348	−4.98E-02	5.80E-04	−9.27E-02	−4.43E-04	12.7
	403	−5.29E-02	4.56E-04	−1.88E-02	−2.41E-04	10.4
Lauric acid	423	1.40E-01	−2.66E-04	4.84E-02	−1.62E-04	60.0
	473	−2.17E-01	5.19E-04	−2.38E-01	−1.62E-04	29.9
Palmitic acid	423	−4.32E-02	1.28E-04	−1.34E-04	1.55E-04	20.0
	473	−2.02E-01	4.93E-04	−2.12E-01	−5.03E-05	32.7
α-Pinene	313	4.95E-02	3.60E-04	−3.11E-01	4.17E-04	25.9
	323	−3.61E-02	5.55E-04	−4.50E-02	−1.19E-04	20.5
Limonene	313	−2.72E-02	4.57E-04	−1.89E-01	−2.21E-04	75.8
	323	−2.39E-02	5.48E-04	−2.75E-01	−2.72E-04	67.6

Table 6. Deviations in the predicted pressure and vapor phase solute concentration using the PSRK and the modified model (PSRKmod). In the PSRK model the UNIFAC parameters are r=0.982 y q=1.3

System	T(K)	PSRK		PSRKmod			
		%ΔP	$\%\Delta y_2$	r	q	%ΔP	%Δy
1-Octanol	403	33.8	34.8	1.4	0.98	25.7	30.1
	453	25.2	21.9			16.6	18.5
1-Decanol	348	36.2	74.1	1.4	0.98	27.7	65.2
	403	18.7	19.4			14.5	11.9
2m-1-Pentanol	348	32.2	48.2	1.6	0.98	10.0	21.7
	403	33.9	29.4			6.6	15.7
Lauric acid	423	8.2	97.0	1.4	0.98	19.7	94.5
	473	9.2	29.1			22.4	21.5
Palmitic acid	423	12.6	53.	1.4	0.98	27.1	53.0
	473	14.2	52.6			27.7	53.3
α-Pinene	313	3.9	21.8	1.3	0.98	3.9	21.8
	323	3.3	18.7			3.3	18.7
Limonene	313	4.2	28.6	1.0	0.98	4.0	15.6
	323	5.9	86.5			8.6	25.2

results using the SRK equation with the classical mixing rule (one interaction parameter) and the non-quadratic mixing rule (two interaction parameters) are presented. Table 5 presents results using the TSRK equation with non-quadratic mixing rule, including four parameters.

Table 6 shows results with the PSRK equation with different UNIFAC molecular parameters for carbon dioxide in the different mixtures. The original parameters used were those reported by Chemstations [2000] for CO_2 (r=0.982 and q=1.3). These parameters were recalculated for each mixture resulting in different values for r and q, as shown in Table 6. The calculations were done by trial and error, searching for the minimum deviations in the solute concentration in the gas phase. On the basis of these results new average values for r and q are proposed: r=1.4 and q=0.98.

An overall picture of the accuracy of the models employed in this work is presented in Fig. 1. The figure shows the overall deviation given by the different models for the seven mixtures studied. As seen in the figure, the TSRK equation gives the lowest deviation (30%). Important to notice is also the relative low deviation given by the two PSRK models. The predictive PSRK equation of state gives 44% and the modified PSRK model gives 33%. The lower deviation given by the TSRK model is probably due to the greater number of parameters [four, as shown in Eq. (9)], included in the model.

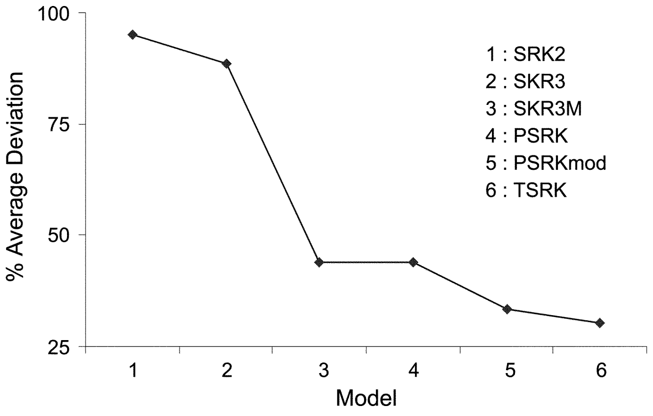

Fig. 1. Overall deviation given by the different models for the data used, for all systems.

It should be noticed that the deviation in the gas phase concentration of the solute is normally high, as usually reported in the literature for similar type of calculations. Yakoumis et al. [1996], for instance, reported absolute errors of the order of 0.001 for the solute concentration in the gas phase for some mixtures containing a supercritical component. This value, if expressed as percent deviation, is of the order of 130%. Zou et al. [1990] presented similar results, while Coniglio [1995] and Gamse [2000] reported results with deviations greater than 200%. For all these cases and for the systems considered in this study, deviation in the solvent concentration in the gas phase is below 1%. However, considering that in supercritical fluid extraction one is usually interested in the solute being extracted, a severe test of the accuracy of a model must be the correct correlation of the solute concentration in the gas phase. Using the solvent concentration in the gas phase is at least a misleading way of analyzing the capabilities of a given model.

CONCLUSIONS

1. The concentration of the solvent in the gas phase can be obtained with good accuracy even with the classical van der Waals mixing rules with one or two interaction parameters.

2. Solute concentration in the gas phase in gas+liquid systems is predicted with high and, in several cases, with unacceptable accuracy. This is a deficiency of most methods proposed in the literature until today.

3. Considering that in supercritical fluid extraction one is usually interested in the solute being extracted, a correct and severe test of the accuracy of a model must be correct correlation of the solute concentration in the gas phase.

4. Equations such as SRK with simple mixing rules are not recommended for correlating gas-liquid systems. Despite some comments usually found in the literature, in which conclusions are drawn by analyzing the concentration of the solvent (carbon dioxide), this in the gas phase only.

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NOMENCLATURE

a, b : parameters in an EoS
a_c : parameter in the general EoS [Eq. (1)]
a_i, b_i : EoS parameters for pure components
a_{ij}, b_{ij} : EoS interaction coefficients between components “i” and “j” in a mixture

A_1 : constant number for the PSRK EoS [Eq. (16)]
A_i : auxiliary parameters in an EoS
k_{ij}, k_{ji} : binary interaction parameters in an EoS
c_1, c_2, c_3 : parameters in the PSRK EoS
c_{ij}^0, c_{ij}^1 : interaction parameters for the TSRK EOS
k_{ij}^0, k_{ij}^1 : interaction parameters for the TSRK EOS
m : parameter in the α(T) function an Eq. (1)
N : number of points in a data set
M : molecular weight
p : parameter in the PSRK EoS
P : pressure
P_c : critical pressure
P_r : reduce pressure ($P_r = P/P_c$)
R : ideal gas constant
r, q : UNIFAC parameters
T : temperature
T_c : critical temperature
T_r : reduced temperature ($T_r = T/T_c$)
V : volume
y_2 : vapor phase mole fraction of the solute
x_i, x_j : liquid phase mole fraction of components i, j
Z_c : critical compressibility factor

Abbreviations

EoS : equation of state
PSRK : predictive SRK EoS
SRK1 : one-parameter mixing rule for the PSRK EoS
SRK2 : two-parameter mixing rule for the PSRK EoS
SRK : soave-Redlich-Kwong EoS
SRK2 : two-parameter mixing rule for the SRK EoS
SRK3 : three-parameter mixing rule for the SRK EoS
SRK3M : modified two-parameter mixing rule for the SRK EoS
TSRK : extended SRK

Greek Letters

α : temperature function in an EoS
β_{ji} : binary interaction parameters in an EoS
Δ : deviation
ω : acentric factor
δ_{ij}, δ_{ji} : interaction parameter in the non-quadratic mixing rule [Eq. (10)]

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