Phase Equilibrium in Supercritical CO_2 Mixtures Using a Modified Kwak-Mansoori Mixing Rule

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The mixing rules proposed by Kwak and Mansoori for the Peng-Robinson equation of state have been modified to describe vapor-liquid equilibrium in mixtures that contain supercritical CO_2. Data in the literature for nine binary liquid—vapor systems containing supercritical CO_2 are used for testing the modified models. The systems studied were binary mixtures containing carbon dioxide with lauric acid, palmitic acid, oleic acid, linoleic acid, 1-octanol, 1-decanol, 2-methyl-1-pentanol, α-pinene, and limonene. The modifications studied included the introduction of a nonquadratic mixing rule proposed by one of the authors and a different interaction parameter for the volume constant of the equation of state. Compared to results in the literature, the Kwak-Mansoori combining rules and the proposed empirical modifications give lower deviations in correlating the solute concentration in the vapor phase, the most important variable for the design of supercritical extraction processes. Contrary to arguments found in the literature, it is also demonstrated that a severe test for an equation of state and its mixing rules is the correlation of the solute concentration in vapor—liquid mixtures. © 2004 American Institute of Chemical Engineers *AIChE J,* 50: 480–488, 2004

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Introduction

The most common method applied to the correlation and prediction of phase equilibria in mixtures containing a supercritical fluid, such as carbon dioxide, is 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 the VdW type available today, those of Redlich and Kwong (1949), of Soave (1972), of Peng and Robinson (1976), and of Patel and Teja (1982), among others, have proven to combine the simplicity and accuracy required for the prediction and correlation of volumetric and thermodynamic properties of fluids (Trebble and Bishnoi, 1986). Let us consider the Peng-Robinson EoS, described by the following equations

$$P = \frac{RT}{V - b} - \frac{a}{V(V + b) + b(V - b)}$$

$$a = a_c \alpha(Tr_i, \omega_i)$$

$$a_c = 0.457235(R^2 Tc_i^2 / Pc_i)$$

$$\alpha(Tr_i, \omega_i) = [1 + m_i(1 - Tr_i^{0.5})]^2$$

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$$m_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2$$

$$b = 0.77786(RTc_i/Pc_i) \tag{1}$$

For mixtures, the EoS parameters a and b are expressed as functions of the concentration of the different components in the mixture, through the so-called *mixing rules.* Until recently, most of the applications of EoS to mixtures considered the use of the classic van der Waals mixing rules, with the inclusion of an interaction parameter for the force constant a. The Peng-Robinson EoS for a mixture is

$$P = \frac{RT}{V - b_m} - \frac{a_m}{V(V + b_m) + b_m(V - b_m)} \tag{2}$$

The classic van der Waals mixing rules are

$$a_m = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j a_{ij} \quad b_m = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j b_{ij} \tag{3}$$

and the combining rules for a_{ij} and b_{ij}, with interaction parameters for the force and volume constants, are

$$a_{ij} = (a_i a_j)^{0.5}(1 - k_{ij}) \quad b_{ij} = (b_i + b_j)(1 - \beta_{ij})/2 \tag{4}$$

It has been recognized, however, that even with the use of interaction parameters, the classic VdW mixing rules do not give accurate results for complex systems (Shibata and Sandler, 1989). During the last 30 years, efforts have been focused on extending the applicability of cubic EoS to obtain accurate representation of phase equilibria in highly polar mixtures, associated mixtures, and other very complex systems. The different approaches presented in the literature include the use of multiple-interaction parameters in the mixing rules (Kwak and Mansoori, 1986), the introduction of the local-composition concept (Heyen, 1981), the connection between excess Gibbs free energy models and EoS (Huron and Vidal, 1979), and the use of nonquadratic mixing rules (Panagiotopoulos and Reid, 1985).

In this article, the mixing rules proposed by Kwak and Mansoori (1986) have been modified to describe vapor—liquid equilibrium in mixtures that contain supercritical CO_2. Also, comparison between the classic van der Waals combining rules, with one and two parameters (Eqs. 4), and the original Kwak-Mansoori combining rules, with one and two parameters, is done. The Kwak-Mansoori combining rules and their modifications are described in the following sections.

Kwak-Mansoori Mixing Rules

A new concept for the development of mixing rules for cubic EoS that is consistent with the statistical mechanical theory of the van der Waals mixing rules was introduced by Kwak and Mansoori (1986). According to the authors, this concept is based on statistical—mechanical arguments and on the fact that rules are for constants of EoS, and not for any thermodynamic state function, which may appear in an EoS. The mixing rules developed by Mansoori and his group did not receive much attention, although they have more flexibility due to the parameterization introduced into two-constant EoS such as the Peng-Robinson equation. To apply these mixing rules the Peng-Robinson EoS was rewritten by Kwak and Mansoori (1986), as follows

$$P = \frac{RT}{V - b_m} - \frac{a_m + RTd_m - 2\sqrt{a_m d_m RT}}{V(V + b_m) + b_m(V - b_m)} \tag{5}$$

It is important to notice that Eq. 5 contains three temperature-independent parameters (a_m, b_m, and d_m), which is different from what is normally presented in the literature. The three EoS constants are expressed using the classic van der Waals mixing rules, as follows

$$a_m = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j a_{ij} \quad b_m = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j b_{ij} \quad d_m = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j d_{ij} \tag{6}$$

with the combining rules of Kwak and Mansoori

$$a_{ij} = (a_i a_j)^{0.5}(1 - k_{ij}) \quad a_i = a_c(1 + m_i)^2$$

$$b_{ij} = \left(\frac{b_i^{1/3} + b_j^{1/3}}{2}\right)^3 (1 - \beta_{ij})$$

$$d_{ij} = \left(\frac{d_i^{1/3} + d_j^{1/3}}{2}\right)(1 - \gamma_{ij}) \quad d_i = a_c m_i^2/RTc_i \tag{7}$$

In these equations, a_c, m_i, and b_i are constants for the classic VdW mixing rule in Eq. 1.

Modified Kwak-Mansoori Mixing Rule

When the mixing rules just described are applied to describe vapor—liquid equilibrium in mixtures containing a supercritical fluid, three interaction parameter must be determined from experimental phase-equilibrium data. This article considers some modifications in order to reduce the deviations between calculated values and experimental data for the solute concentration in the gas phase. Here, we will describe the application of a new general quadratic combining rule and the introduction of an interaction parameter into the volume constant of the EoS that have been proposed by one of the authors (Valderrama et al., 2000). One modification consists of changing the combining rule for b_{12} only, giving origin to the "modified-1 Kwak-Mansoori mixing rule" (KM1). For a binary mixture, these rules are

$$a_{12} = (a_1 a_2)^{0.5}(1 - k_{12})$$

$$b_{12} = \left[\frac{b_1 + b_2(1 - \beta_2)}{2}\right]$$

$$d_{12} = \left(\frac{d_1^{1/3} + d_2^{1/3}}{2}\right)^3 (1 - \gamma_{12}) \tag{8}$$

Table 1. Phase Equilibrium Correlation Results Presented in the Literature for Several CO_2 Solvent(1) + Liquid Solute(2) Systems

System: CO_2+	T (K)	P (MPa)	$\lvert\Delta P\rvert$ (%)	$\lvert\Delta y_1\rvert$ (%)	$\lvert\Delta y_2\rvert$ (%)	EoS	Mixing Rules
Lauric acid (Yau et al., 1992)	423	1–5	3.0	<0.1	68.4	SRK	VdW
Palmitic acid (Yau et al., 1992)	423	1–5	1.2	<0.1	87.2	SRK	VdW
Oleic acid (Zou et al., 1990)	313	7–28	—	0.5	60.5	RK	VdW + P&R
Linoleic acid (Zou et al., 1990)	313	6–27	—	0.3	42.8	RK	VdW
1-Octanol (Weng et al., 1994)	453–483	6–19	6.6	—	23.5	PR	VdW
1-Decanol (Weng et al., 1994)	348–453	7–19	5.2	—	154.1	PT	VdW
2-*m*-1-Pentanol (Weng et al., 1994)	348–453	6–12	3.3	—	102.3	PT	VdW
α-Pinene (Pavlíek and Richter, 1993)	313	3–8	<0.1	0.1	51.2	SRK	VdW-KM
Limonene (Gamse and Marr, 2000)	304	4–6	4.7	0.3	142.6	PR	VdW

Note: In the table, P&R represent the Panagiotopoulos and Reid mixing rules.

A second modification considers the introduction of a concentration-dependent interaction parameter into the combining rule for force constant a_{12}, giving origin to the "modified-2 Kwak-Mansoori mixing rule" (KM2), maintaining the combining rule for d_{12}. For a binary mixture, these rules are

$$a_{12} = (a_1 a_2)^{0.5}(1 - k_{12}) \quad k_{12} = \delta_1 x_1 + \delta_2 x_2$$

$$b_{12} = [b_1 + b_2(1 - \beta_2)]/2 \quad d_{12} = (d_1 + d_2)/2 \qquad (9)$$

One should notice that by making these changes, the theoretical basis of KM mixing rules is somewhat lost and the rules becomes more of the empirical type. However, the main characteristic of the KM proposal, that is, the new parameterization of the EoS, which includes only temperature-independent constants, remains the same in the modifications proposed in this article.

The general equation for the fugacity coefficient in terms of the variables P, T, and V is found in the literature (Prausnitz et al., 1986)

$$RT\ln(\phi_i) = \int_V^\infty \left[\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n_j} - \frac{RT}{V}\right]dV - RT\ln Z \qquad (10)$$

Introducing the modified PR equation into this equation, the fugacity coefficient of a component i in a mixture is

$$\ln\phi_i = \frac{B_i^*}{b_m}(Z-1) - \ln(Z-B) + Q\frac{A}{2\sqrt{2}B}\ln\left[\frac{Z + B(1+\sqrt{2})}{Z + B(1-\sqrt{2})}\right]$$

$$Q = \left(\frac{B_i^*}{b_m} - \frac{H+G}{c} - 2\right)$$

$$H = [1 - (RT/(a_m d_m)^{0.5})d_m](A_i^* - a_m)$$

$$G = [RT - (RT/(a_m d_m)^{0.5})a_m](D_i^* - d_m)$$

$$A = \frac{cP}{R^2T^2} \quad B = \frac{b_m P}{RT}$$

$$c = a_m + d_m RT - 2\sqrt{a_m d_m RT} \qquad (11)$$

The terms A_i^*, B_i^*, and D_i^* are determined from the defined mixing rules as follows:

$$A_i^* = \left(\frac{\partial n a_m}{\partial n_i}\right)_{T,V,n_j} \quad B_i^* = \left(\frac{\partial n b_m}{\partial n_i}\right)_{T,V,n_j} \quad D_i^* = \left(\frac{\partial n d_m}{\partial n_i}\right)_{T,V,n_j} \qquad (12)$$

The different algebraic expressions for A_i^*, B_i^*, and D_i^* are derived from the mixing rules considered in this study.

Interaction parameters, such as k_{12}, δ_1, δ_2, β_{12}, β_2, and γ_{12}, in the KM, KM1, and KM2 combining rules (Eqs. 7, 8, and 9), are usually calculated by regression analysis of experimental phase-equilibrium data, although some authors have attempted to obtain binary interaction parameters from pure-component property data (Graboski and Daubert, 1979; Coutinho et al., 1984). None of these proposals, however, has proven to be of general applicability, and at present there is no accurate predictive way for evaluating the interaction parameters. Thus, data reduction is necessary to evaluate such parameters using nonlinear optimization routines.

The nonlinear regression program developed for this study uses the maximum-neighborhood method of Marquardt, which is an optimum interpolation between the method of local lin-

Table 2. Properties of the Fluids Involved in This Study

Substance	Formulas	M	T_b (K)	T_c (K)	P_c (MPa)	ω
Lauric acid	$C_{12}H_{24}O_2$	200.32	571.85	743.00	1.94	0.8800
Palmitic acid	$C_{16}H_{32}O_2$	256.43	624.15	776.00	1.51	1.0611
Oleic acid	$C_{18}H_{34}O_2$	282.46	633.00	781.00	1.39	1.1872
Linoleic acid	$C_{18}H_{32}O_2$	280.45	628.00	775.00	1.41	1.1762
1-Octanol	$C_8H_{18}O$	130.23	468.35	652.50	2.86	0.5941
1-Decanol	$C_{10}H_{22}O$	158.28	504.07	684.40	2.37	0.6612
2-*m*-1-Pentanol	$C_6H_{14}O$	102.18	421.15	582.00	3.40	0.7262
α-Pinene	$C_{10}H_{16}$	136.24	429.29	632.00	2.76	0.2862
Limonene	$C_{10}H_{16}$	136.24	449.65	660.00	2.75	0.3123
Carbon dioxide	CO_2	44.01	192.52	304.20	7.37	0.2250

Table 3. Details on the Experimental Data Used in This Study

System: CO_2	T (K)	Pressure Range (MPa)	x_2 Range	y_2 Range	Reference
Lauric acid	423	1–5	0.740–0.9471	0.0001–0.0004	Yau et al. (1992)
	473	1–5	0.786–0.9582	0.0018–0.0049	
Palmitic acid	423	1–5	0.736–0.942	0.0001–0.0002	Yau et al. (1992)
	473	1–5	0.780–0.950	0.0002–0.0011	
Oleic acid	313	7–28	0.188–0.338	0.0045–0.0142	Zou et al. (1990)
	333	7–29	0.196–0.350	0.0044–0.0125	
Linoleic acid	313	6–26	0.180–0.280	0.0045–0.0138	Zou et al. (1990)
	333	6–27	0.190–0.320	0.0035–0.0120	
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	
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	
	453	6–19	0.340–0.780	0.0087–0.0231	
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	
α-Pinene	313	3–8	0.093–0.700	0.0024–0.0057	Pavlícek et al. (1993)
	323	4–10	0.050–0.640	0.0027–0.0160	
Limonene	313	6–18	0.112–0.418	0.0011–0.0031	Iwai et al. (1996)
	323	4–9	0.166–0.713	0.0018–0.0078	

Note: In the table the values of pressure and temperature have been rounded to the closest integer. Also, the symbols x_2 and y_2 are the liquid and vapor mole fraction of the solute.

earization and the method of the steepest descent (Marquardt, 1963). The method requires the values of the derivatives of the objective function with respect to the parameters of the proposed model. These values are needed to guide the search to the optimum values of the parameters. In our program these values are numerically calculated, avoiding the complex derivation of the models used, keeping the accuracy required by the optimization algorithm. The optimization subroutine of the program was adapted from Reilly (1972), in which the method is applied to find the optimum parameters of a rate-equation model. Our program looks for all acceptable solutions in a given range to choose as final solution that which gives the lowest deviation for the solute concentration in the gas phase, while maintaining low deviations for the pressure. The method developed for the calculation of the interaction parameters consumes more computer time than other programs available, but guarantees that an absolute optimum parameter will be found, which gives the lowest deviation for the solute concentration in the gas phase. In this way, our method represents an important improvement to what is normally described in the literature as optimization procedures.

Modeling Mixtures Containing Supercritical CO_2

The first efforts to model the phase behavior in systems containing a supercritical fluid were done using the virial EoS (Ewald et al., 1953), but these attempts were not successful. The best results have been obtained using cubic EoS such as SRK and PR (Kurnik et al., 1981). Table 1 shows selected phase-equilibrium results from the literature for several binary vapor—liquid mixtures containing supercritical carbon dioxide. For a set of N experimental points, the deviations $|\Delta P|$ (%), $|\Delta y_1|$ (%), and $|\Delta y_2|$ (%) indicated in the table are defined as follows

$$|\Delta P|(\%) = (100/N)\Sigma|(P^{\mathrm{cal}} - P^{\mathrm{exp}})/P^{\mathrm{exp}}|_i$$

$$|\Delta y_1|(\%) = (100/N)\Sigma|(y_1^{\mathrm{cal}} - y_1^{\mathrm{exp}})/y_1^{\mathrm{exp}}|_i$$

$$|\Delta y_2|(\%) = (100/N)\Sigma|(y_2^{\mathrm{cal}} - y_2^{\mathrm{exp}})/y_2^{\mathrm{exp}}|_i \tag{13}$$

The numbers presented in Table 1 indicate that the concentration of the solute in the gas phase not been well predicted and this should be improved. We believe that the concentration of the solute in the gas phase is the most important variable for the modeling and design of supercritical fluid extraction, since it determines the maximum amount of solute that can be extracted by the supercritical solvent. As seen in the Table 1, errors of over 100% are found in some cases. Thus, the proposed modifications must be able to reduce the errors in correlating the solute concentration in the gas phase while maintaining relatively low deviations for the pressure. This suggested an objective function that includes both the pressure deviations and the deviations in the gas-phase solute concentration. However, it has been found that including the gas-phase solute concentration in the objective function makes no improvement in the results, and the pressure deviations increase. Besides this, it has been demonstrated that the optimum value of the interaction parameters and the minimum overall deviations depend on three main factors: (1) the objective function chosen for the optimization routine; (2) the search interval defined for the interaction parameters; and (3) the initial value of the interaction parameters used to start the iterative procedure (Valderrama and Arce, 1999).

The basic idea in the regression analysis usually employed to determine the interaction parameters is to apply the EoS to the calculation of a particular property and then minimize the differences between predicted and experimental values of that property, according to a specified objective function. The value of the interaction parameters, which minimize the objective function, correspond to the optimum values of the interaction parameters. The objective function

Table 4. Deviations in Pressure- and Gas-Phase Concentration for $CO_2(1)$ + Liquid(2) Systems Using the Peng-Robinson EoS and Different Combining Rules

System: CO_2+	T (K)	P (MPa)	Mix Rule	NP	k_{12}	β_{12}	$\lvert\Delta P\rvert$ (%)	$\lvert\Delta y_1\rvert$ (%)	$\lvert\Delta y_2\rvert$ (%)
Lauric acid	423	1–5	PRa	1	0.0180		4.0	<0.1	279.1
			PRab	2	0.0669	0.0218	7.2	<0.1	227.6
			KMa	1	0.0118		26.0	<0.1	72.3
			KMab	2	0.0392	0.0312	27.9	<0.1	66.5
	473	1–5	PRa	1	0.0113		4.3	0.2	70.3
			PRab	2	0.1057	0.0363	7.3	0.2	61.6
			KMa	1	−0.0008		20.6	0.1	41.1
			KMab	2	−0.0641	−0.0561	19.5	0.2	40.9
Palmitic acid	423	1–5	PRa	1	0.0161		1.4	<0.1	28.8
			PRab	2	−0.0496	−0.0216	2.0	<0.1	22.8
			KMa	1	0.0884		36.3	<0.1	74.2
			KMab	2	−0.1646	−0.1744	24.7	<0.1	63.3
	473	1–5	PRa	1	0.0233		2.0	<0.1	125.2
			PRab	2	0.08437	0.01799	3.7	<0.1	111.6
			KMa	1	0.0127		24.0	<0.1	35.4
			KMab	2	−0.0644	−0.0664	21.8	<0.1	23.9
Oleic acid	313	7–28	PRa	1	0.0728		8.3	0.4	52.4
			PRab	2	0.0615	−0.0289	6.0	0.2	32.1
			KMa	1	−0.312		35.2	0.9	99.9
			KMab	2	−0.3832	−0.4499	4.0	0.9	98.2
			PRa	1	0.0771		13.0	0.4	55.6
	333	7–29	PRab	2	0.0904	0.0353	9.0	0.5	75.4
			KMa	1	−0.3255		31.3	0.8	99.9
			KMab	2	−0.3850	−0.3752	8.8	0.8	98.8
Linoleic acid	313	6–26	PRa	1	0.0702		13.2	0.2	34.1
			PRab	2	0.0879	0.0479	7.6	0.6	71.4
			KMa	1	−0.3130		23.0	0.9	99.9
			KMab	2	−0.3611	−0.3327	6.8	0.9	99.2
	313	6–26	PRa	1	0.0744		24.2	0.2	58.1
			PRab	2	−0.2148	0.1059	29.0	0.5	66.6
			KMa	1	−0.3217		24.0	0.8	100.1
			KMab	2	−0.3699	−0.2988	11.6	0.8	99.4
1-Octanol	403	6–19	PRa	1	0.0915		2.6	0.1	10.8
			PRab	2	0.0784	−0.0227	0.3	0.2	22.4
			KMa	1	−0.0423		18.6	0.7	44.3
			KMab	2	−0.1021	−0.2273	0.2	0.2	21.8
	453	6–19	PRa	1	0.0782		1.1	0.4	14.6
			PRab	2	0.0791	0.0010	1.2	0.4	14.5
			KMa	1	−0.0593		16.8	1.0	26.2
			KMab	2	−0.1185	−0.2087	0.8	0.4	15.4
1-Decanol	348	7–19	PRa	1	0.0901		6.9	0.1	19.4
			PRab	2	0.0901	0.0	6.9	0.1	19.5
			KMa	1	−0.0980		39.6	0.6	82.8
			KMab	2	−0.1267	−0.2854	2.6	0.2	46.1
	403	6–19	PRa	1	0.0452		6.5	0.2	37.7
			PRab	2	0.0444	−0.0004	6.5	0.2	37.6
			KMa	1	−0.1287		36.0	0.2	47.6
			KMab	2	−0.1794	−0.3013	2.8	0.3	58.6
2-*m*-1-Pentanol	348	6–12	PRa	1	0.0652		10.0	0.1	8.1
			PRab	2	−0.1179	−0.2173	2.2	0.1	23.4
			KMa	1	−0.0902		29.7	0.3	43.2
			KMab	2	−0.1227	−0.2317	0.6	0.1	26.1
	403	6–15	PRa	1	0.0911		3.6	0.3	9.3
			PRab	2	0.0911	−0.0011	3.5	0.3	9.2
			KMa	1	−0.0651		16.6	1.0	28.8
			KMab	2	−0.1171	−0.1904	0.4	0.2	10.8
α-Pinene	313	3–8	PRa	1	0.1135		3.1	<0.1	20.1
			PRab	2	0.0649	−0.0532	7.1	<0.1	12.0
			KMa	1	0.0496		23.1	0.3	79.2
			KMab	2	0.0005	−0.2658	5.1	<0.1	10.8
	328	5–9	PRa	1	0.1442		24.7	3.3	350.0
			PRab	2	0.0997	−0.0295	0.2	0.2	33.9
			KMa	1	0.0555		23.0	0.3	49.4
			KMab	2	0.0228	−0.2142	0.6	0.2	29.3
Limonene	313	6–8	PRa	1	0.0954		1.5	<0.1	13.2
			PRab	2	0.0212	−0.0770	13.6	<0.1	14.8
			KMa	1	0.0205		15.4	0.4	160.1
			KMab	2	0.0101	−0.2086	0.7	<0.1	9.6
	323	4–9	PRa	1	0.1001		8.2	0.3	56.7
			PRab	2	0.0965	−0.0026	7.9	0.2	40.5
			KMa	1	0.0270		31.3	0.2	55.4
			KMab	2	0.0028	−0.2630	2.0	0.1	33.2

Table 5. Deviations in the Pressure and in the Gas Phase Concentration for $CO_2(1)$ + Liquid(2) Systems Using the PR EoS and KM Mixing Rule

System: CO_2+	T (K)	P (MPa)	Mixing Rule	p_1	p_2	p_3	$\|\Delta P\|$ (%)	$\|\Delta y_1\|$ (%)	$\|\Delta y_2\|$ (%)
Lauric acid	423	1–5	KM	0.2868	−0.0284	0.2515	27.1	<0.1	34.2
			KM1	−0.1004	0.3358	−0.3085	23.2	<0.1	33.5
			KM2	−0.3903	0.5987	0.9722	5.0	<0.1	23.5
	473	1–5	KM	0.0042	−0.4532	0.5006	1.2	0.2	85.5
			KM1	0.2868	−0.0284	0.2515	47.4	<0.1	32.4
			KM2	−0.6917	−0.0031	0.7219	1.8	<0.1	13.1
	423	1–5	KM	−0.1728	−0.4867	0.3359	1.1	<0.1	25.2
			KM1	−0.2719	−0.0067	0.2301	1.0	<0.1	25.3
			KM2	−0.9989	−0.3455	0.5631	1.4	<0.1	66.9
	473	1–5	KM	−0.1288	−0.2214	0.1066	15.3	0.02	40.9
			KM1	−0.1271	0.2500	−0.018	17.6	<0.1	16.6
			KM2	−0.9977	−0.3150	0.6656	1.0	<0.1	23.9
Oleic acid	313	7–28	KM	0.1136	−0.5554	0.6235	5.6	0.2	25.1
			KM1	−0.0356	−0.0238	0.4522	4.9	0.2	29.3
			KM2	−0.3562	0.3526	−0.4563	12.4	0.3	26.2
	333	7–29	KM	0.0152	−0.4409	0.4976	9.0	0.6	77.2
			KM1	−0.0613	0.0560	0.4080	8.8	0.6	83.1
			KM2	−0.1256	0.8526	−0.2356	23.6	0.5	68.6
Linoleic acid	313	6–26	KM	−0.2185	−0.3558	0.1935	6.5	0.8	95.6
			KM1	−0.1646	0.2808	0.3198	9.0	0.6	71.4
			KM2	−0.4526	−0.8326	−0.1859	46.2	0.5	36.3
	333	6–27	KM	−0.8867	−0.0878	−0.4885	26.2	0.4	59.9
			KM1	−0.1885	0.4253	0.2916	37.6	0.5	78.9
			KM2	−0.2895	−0.3514	−0.1256	45.2	0.4	34.2
1-Octanol	403	6–19	KM	0.3210	−0.2123	0.6543	10.0	0.1	9.1
			KM1	0.2992	−0.0251	0.6489	5.3	0.1	11.5
			KM2	−0.3945	−0.4820	−0.0093	0.3	0.1	11.2
	453	6–19	KM	−0.3814	−0.1366	−0.4819	0.8	0.4	12.8
			KM1	−0.3291	0.08168	−0.3853	1.0	0.4	12.8
			KM2	−0.4169	−0.4386	0.0810	0.8	0.4	12.8
1-Decanol	348	7–19	KM	−0.3076	−0.2407	−0.3567	2.5	0.3	22.6
			KM1	−0.1330	0.0215	−0.0090	6.5	0.1	18.9
			KM2	−0.5216	−0.8388	−0.1462	3.6	0.4	24.7
	403	6–19	KM	0.0609	−0.2957	0.4114	19.0	<0.1	11.4
			KM1	−0.5186	−0.3464	0.1957	1.2	0.1	12.3
			KM2	−0.5186	−0.3564	0.1957	1.2	0.1	12.3
2-*m*-1-Pentanol	348	6–12	KM	−0.0947	−0.1333	0.0021	13.2	0.1	12.2
			KM1	−0.2461	0.0038	−0.2516	8.2	0.1	7.6
			KM2	0.4563	0.0236	0.8523	4.6	0.3	16.2
	403	6–15	KM	0.1164	−0.1661	0.3290	15.1	0.4	12.2
			KM1	−0.3086	0.0026	−0.3391	0.4	0.4	11.4
			KM2	0.4562	0.0456	−0.5263	5.6	0.5	11.3
α-Pinene	313	3–8	KM	0.2439	−0.5747	0.8460	18.4	<0.1	6.1
			KM1	0.2591	−0.3550	0.9290	19.2	<0.1	7.4
			KM2	−0.0428	−0.1301	0.1671	7.8	<0.1	10.7
	328	5–9	KM	0.0033	−0.1236	−0.0679	12.0	0.1	19.6
			KM1	0.276	−0.1305	0.7401	14.7	0.1	15.3
			KM2	−0.0091	0.2085	0.2952	1.0	0.1	11.0
Limonene	313	6–8	KM	−0.1830	−0.2241	−0.5080	5.7	<0.1	19.6
			KM1	−0.0178	0.0974	−0.1110	2.6	<0.1	10.9
			KM2	−0.1181	−0.2111	0.0001	0.6	<0.1	8.7
	323	4–9	KM	−0.2521	−0.1928	−0.7525	9.1	0.1	23.6
			KM1	−0.0160	0.1100	−0.0951	15.3	0.1	28.4
			KM2	−0.1138	−0.1604	0.0410	8.7	0.1	22.6

For KM, $p_1 = k_{12}$, $p_2 = \beta_{12}$, $p_3 = \gamma_{12}$; for KM1, $p_1 = k_{12}$, $p_2 = \beta_2$, $p_3 = \gamma_{12}$; and for KM2, $p_1 = \delta_1$, $p_2 = \delta_2$, and $p_3 = \beta_2$.

is arbitrarily but conveniently defined and several criteria have been presented in the literature. The most popular of these objective functions is the minimization of the bubble-pressure prediction that has been used in this work. The objective function used is

$$W = \sum_{i=1}^{N} \left|(P_i^{\mathrm{cal}} - P_i^{\mathrm{exp}})\right| / P_i^{\mathrm{exp}} \tag{14}$$

In calculating this equation, W is the objective function, P_i^{exp} is the experimental pressure, and P_i^{cal} is the pressure by a given model. The sum is over the N experimental data of the data set.

Applications

Nine systems containing supercritical carbon dioxide have been considered for study. The systems studied were binary mixtures containing carbon dioxide with lauric acid, palmitic acid, oleic acid, linoleic acid, 1-octanol, 1-decanol, 2-methyl-1-pentanol, α-pinene, and limonene. The necessary pure-component data are presented in Table 2. The molecular weight M, the normal boiling temperature T_b, the critical temperature T_c, the critical pressure P_c, and the acentric factor ω are presented in the table. All data were taken from Daubert et al. (1996). Details of the experimental data for the nine binary systems are shown in Table 3. In this table, for each of the temperature, T, the range of pressure, P, in MPa, the range of the liquid-phase solute concentration, x_2, and the range of the gas-phase solute concentration, y_2, are given. Also the source of the data is given for each mixture.

Results and Discussion

Table 4 presents the results found with the Peng-Robinson EoS. Classic VdW combining rules with one interaction parameter, k_{12}, and with two interaction parameters, k_{12} and β_{12} (PRa and PRab), are used. The results are compared with those obtained using Kwak-Mansoori combining rules with one interaction parameter, k_{12}, and with two interaction parameters, k_{12} and β_{12}, KMa, and KMab.

The results presented in Table 4 show that for the solvent concentration in the gas phase (y_1), the deviations are all lower than 1%. Also, for the eighteen isotherms, the lowest absolute deviations occur in four cases for PRa, in six cases for PRab, and in eight cases for KMab. However, average absolute deviations for the solute concentration in the gas phase are high: 77.7% for PRa, 50.5% for PRab, 71.4% for KMa, and 44.8% for KMab. It can be concluded that none of these original combining rules can correlate the solute concentration in the gas phase with acceptable accuracy.

The calculated interaction parameters and the deviations in pressure and gas-phase concentration, using the modified Kwak-Mansoori combining rules are shown in Table 5. In that table, the symbols p_1, p_2, and p_3 represent the parameters k_{12}, β_{12}, and γ_{12} for the mixing rules KM, k_{12}, β_2, and γ_{12} for the mixing rules KM1, and the parameters δ_1, δ_2, and β_2 for the mixing rule KM2. Also the symbols ΔP (%), Δy_1 (%), and Δy_2 (%) are the absolute average deviations for the pressure, for the solvent concentration in the gas phase, and for the solute concentration in the gas phase, respectively.

The deviations shown in Table 5 indicate that any of the combining rules studied give relatively high deviations for the solute concentration in the gas phase, although deviations are lower than those found in the literature (Table 1). Average deviations for the pressure are 11.0% for KM, 12.4% for KM1, and 9.5% for KM2. Average deviations for the solute concentration in the gas phase are 32.9% for KM, 28.2% for KM1, and 24.1% for KM2. Figure 1 shows the results using the modified mixing rules for the system $CO_2(1)$ + 1-decanol(2) at 348 K. For this system, the KM1 model gave the best results.

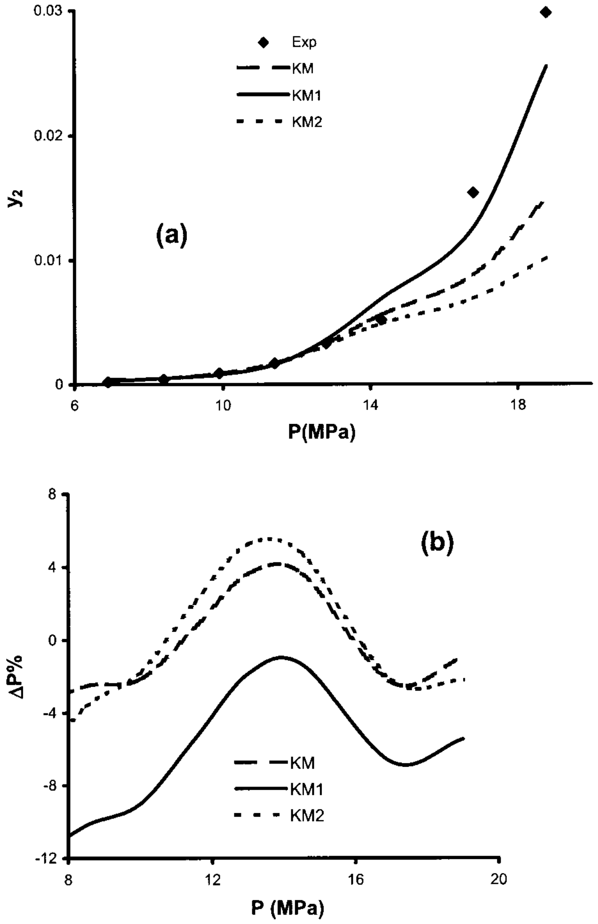

Figure 1. Correlation of equilibrium data for the CO_2(1) + 1-decanol(2) system at 348 K: (a) solute gas concentration vs. experimental pressure, and (b) percent deviation for the pressure.

Despite these relatively high deviations, the errors between calculated and experimental data for the solute concentration in the gas phase are lowered considerably using the proposed mixing rules. Maximum deviations of the order of 130% (limonene in Table 1) are found to be of the order of 73% for oleic acid in Table 5. Average deviations for the solute concentration of the order of 67% in Table 1 are found to be of the order of 23% in Table 5. However, the deviations in the pressure-correlation increase from an average of 4% in Table 1 to 15% in Table 5. This is an expected consequence if the solute concentration in the gas phase is the objective variable to be correlated. As is known, a single cubic EoS cannot give reliable predictions for all volumetric, thermodynamic and phase-equilibrium properties, for all type of fluids and mixtures (Abbot, 1973; Valderrama, 2003).

Table 6 summarizes the deviations found using the different combining rules for the classic mixing rules in the Peng-Robinson EoS. This table clearly shows the improvements achieved with the proposed models. It is also observed that the inclusion of more parameters does not necessarily give lower deviations in the solute concentration in the gas phase. This indicates that the models, as a whole, are not accurate enough and more fundamental modifications are needed.

As stated earlier, it is important to notice that, as a result, the parameterization of Kwak and Mansoori gives an EoS that contains temperature-independent constants (a_m, b_m, and d_m), which is different from what is normally presented in the literature. Also, since the correct temperature dependence of these parameters in any EOS has not yet been found, and modeling of complex systems requires the introduction of interaction parameters, the empirical approach presented here sees reasonable and thermodynamically sound.

Table 6. Summary of Maximum, Minimum, and Average Absolute Deviations in the Correlation of the Pressure and of the Solute Concentration in the Gas Phase Using the Peng-Robinson EoS and Different Combining Rules

	Deviation for the Solute Concentration in the Gas Phase, $\lvert \Delta y_2 \rvert$ (%)							
	Literature	PRa	PRab	KMa	KMab	KM	KM1	KM2
Maximum	137.6	279.1	227.6	160.1	99.4	95.6	83.1	68.6
Minimum	23.0	8.1	9.2	26.2	9.6	6.1	7.4	8.7
Average	67.5	69.1	49.8	68.9	47.3	32.9	28.2	24.1
	Deviations for the Pressure, $\lvert \Delta P \rvert$ (%)							
Maximum	8.5	24.7	29.0	39.6	27.9	27.1	47.4	46.2
Minimum	<0.1	1.1	0.2	15.4	0.2	0.8	1.0	0.3
Average	4.0	7.7	6.7	26.1	7.8	11.0	12.4	9.5

It should be noticed here that a common practice in several applications of EoS to mixtures containing a supercritical fluid found in the literature has been to compare the calculated and experimental solvent concentrations in the gas phase and not the concentration of the solute in the gas phase, as should be done to accurately test the capability of an EoS. Not only that, but in most cases the reported accuracy of the models used for the solute concentration is given as absolute error. Because the concentration of the solute is in the range 0.0001 to 0.11 in mole fraction (Table 3), an absolute error of 0.0001, which is relatively small, could mean a percent error of from 1 to 100% for the solute concentration. For the solvent concentration, however, the percent error in this example is always below 0.1%. The high percent deviations in the solute concentration are not usually reported and discussed in articles related to phase-equilibrium modeling in mixtures containing a supercritical component. Not reporting these high deviations is at least a misleading way of analyzing the accuracy of a proposed model (Valderrama, 2003).

Another point for discussion is related to a conclusion by Benmekki and Mansoori (1987), who have indicated that a serious test for checking the accuracy of an EoS and its mixing rules is the application to the correlation of the gas-solid equilibrium. We have found that this is not accurate enough. In gas-solid equilibrium studies, the EoS and the mixing rule affect the gas-phase fugacity coefficient only. In vapor-liquid equilibrium, this effect occurs in both phases, this being the main reason for the inaccuracies of several models applied in the literature and shown in Table 1. Therefore, this study shows that a more rigid check of the accuracy of the EoS and the mixing rules used is the accurate correlation of the solute concentration in the compressed-gas phase.

Conclusions

Based on the results obtained in this study, the following conclusions are obtained:

(1) The concentration of the solute in the gas phase is correlated with high deviations using the original Peng-Robinson EoS and the Kwak-Mansoori mixing rules with one or two interaction parameters (PRa, PRab, KMa, KMab).

(2) The concentration of the solute in the gas phase can be correlated with higher accuracy using the modified Kwak-Mansoori combining rules (KM1 or KM2);

(3) The concentration of the solvent in the gas phase can be predicted with deviations below 1% with any of the combining rules.

(4) The numerical method developed for the calculation of the optimum parameters in this work proved to be efficient to determine the absolute optimum value for the interaction parameters.

(5) By diminishing the deviations in the solute concentration in the gas phase the deviations in the pressure correlation increase. This is an expected consequence due to the incapacity of a single cubic EoS to give reliable predictions for all volumetric, thermodynamic, and phase-equilibrium properties.

(6) Interaction parameters are needed, but the inclusion of more parameters does not necessarily give lower deviations in the solute concentration in the gas phase.

(7) The parameterization of the PR equation proposed by Kwak and Mansoori, which gives an EOS that includes temperature-independent constants only, allows a more satisfactory correlation of the solute concentration in the gas phase than an EOS, which uses a temperature-dependent force constant.

(8) A severe test for analyzing the accuracy of the EoS and the mixing rules is to calculate the percent deviation of the liquid solute concentration in the compressed-gas phase.

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Notation

a_c = force constant in the EoS of component i
a_i, a_j, b_i, b_j, d_i, d_j = EoS parameters for pure components
a, b, d = EoS parameters for mixtures
a_m, b_m, d_m = EOs parameters for mixtures
a_{ij}, b_{ij}, d_{ij} = EoS interaction constants between components i and j
A_i^*, B_i^*, D_i^* = variables of the derivative for Eq. 11
c = variable for Eq. 11
k_{ij} = binary interaction parameters for the force constant in an EoS
m_i = parameter in the $\alpha(Tr_i, \omega_i)$ function of Soave (1971) in Eq. 1
M = molecular weight
P = pressure
R = ideal-gas constant
T = temperature
T_b = normal boiling temperature
Tr_i = reduce temperature of component i
V = volume
Tc_i = critical temperature of component i
Pc_i = critical pressure of component i
x_i, x_j = mole fraction of components i and j
x, y = liquid- and vapor-phase mole fractions

Greek letters

$\alpha(Tr, \omega)$ = temperature function in an EoS
β_{ij}, β_j, γ_{ij} = interaction parameters for the volume constants in an EoS
δ_i, δ_j = interaction parameters for the force constant in the EoS
Δ = deviation
ω = acentric factor

Abbreviations

EoS = equation of state
KM = Kwak and Mansoori mixing rule
KM1 = Kwak and Mansoori mixing rule, modification 1
KM2 = Kwak and Mansoori mixing rule, modification 2
PT = Patel and Teja EoS
PR = Peng-Robinson EoS
PRa = Peng-Robinson EoS with parameter for a_{ij}
PRab = Peng-Robinson EoS with parameter for a_{ij} and b_{ij}
KMa = KM with parameter for a_{ij}
KMab = KM with parameter for a_{ij} and b_{ij}
P&R = Panagiotopoulos and Reid mixing rule
RK = Redlich-Kwong EoS
SRK = Soave-Redlich-Kwong EoS
VdW = Van der Waals EoS
VdW − KM = Van der Waals mixing rule for KM combination rule
W&S = Wong and Sandler combination rule
WS = Wong and Sandler mixing rule
N = number of data
NP = number of parameters

Greek letters

$\alpha(Tr, \omega)$ = temperature function in an EoS
β_{ij}, β_j, γ_{ij} = interaction parameters for the volume constants in an EoS
δ_i, δ_j = interaction parameters for the force constant in the EoS
Δ = deviation
ω = acentric factor

Superscripts and subscripts

exp = experimental
calc = calculated

Interaction parameters in Table 5

EOS	p_1	p_2	p_3
KM	k_{12}	β_{12}	γ_{12}
KM1	k_{12}	β_2	γ_{12}
KM2	δ_1	δ_2	β_2

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