



Parameters estimation and VLE calculation in asymmetric binary mixtures containing carbon dioxide + *n*-alkanols

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ABSTRACT

In the present work, the estimation of the parameters for asymmetric binary mixtures of carbon dioxide + *n*-alkanols has been developed. The binary interaction parameter k_{12} of the second virial coefficient and non-random two liquid model parameters τ_{12} and τ_{21} were obtained using Peng–Robinson equation of state coupled with the Wong–Sandler mixing rules. In all cases, Levenberg–Marquardt minimization algorithm was used for the parameters optimization employing an objective function based on the calculation of the distribution coefficients for each component. Vapor–liquid equilibrium for binary asymmetric mixtures (CO₂ + *n*-alkanol, from methanol to 1-decanol) was calculated using the obtained values of the mentioned parameters. The agreement between calculated and experimental values was satisfactory.

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1. Introduction

In the last decade, supercritical fluids (SCF) have intensively been proved as environmentally benign media for chemical and related processes. Many processes and products have been developed applying the inherent physical and chemical properties of SCF [1]. The use of SCF represents an attractive option to implement diverse chemical processes in a sustainable manner. The CO₂ is commonly used in processes involving SCF since it is not toxic, not explosive, chemically inert, economic, not corrosive, easily recyclable and available in a high purity. The main disadvantage of the SCF processes is the relatively high cost of the required equipment. However, the quality of the products widely overcomes that of the products obtained by conventional extraction using solvents. This fact may offset the investment in high-pressure equipment [2–4].

Supercritical carbon dioxide, as other supercritical fluids, offers the possibility of reducing the reactor size in a great extent, as well as the acceleration of many chemical processes [1]. The SCF have features of both gases and liquids. Compared to liquid solvents, SCF have a major dissolving capability, higher diffusion coefficient, and

lower viscosity and surface tension than a liquid solvent leading to more favorable mass transfer [5].

The information on the high-pressure behavior of fluids under supercritical conditions has been valuable during the design of new separation processes in various fields like food, pharmaceutical and fine chemical industries [6]. The information of high-pressure phase equilibrium of mixtures containing CO₂ and alcohols is particularly relevant and has been actively studied for various purposes. For instance, the phase equilibrium behavior of low-molecular weight alcohols, such as methanol and ethanol, in CO₂ is essential for the effective evaluation of cosolvents for CO₂-based supercritical processes [7]. Additionally, high-pressure VLE measurements of CO₂ + alkanols systems are of great interest due to their role during the supercritical extraction of thermally labile compounds, dehydration of alcohols, and extraction of natural products using near critical solvents [8]. Finally, CO₂ + alcohol systems have a high potential as supercritical fluid/cosolvent pairs for separation of different metabolites. Therefore, the knowledge of vapor–liquid equilibrium in these systems is needed in order to evaluate the employed models for describing the extraction of biomaterials with supercritical fluid/cosolvent pairs [9].

The evaluation of supercritical extraction processes has its major difficulty in the modeling of VLE. This is related to the high complexity and asymmetry of the mixtures treated [10]. Thus, VLE calculation requires of improved versions of the EOS. Among the many cubic EOS of van der Waals type currently available, the

Abbreviations: EOS, equation of state; NRTL, non-random two liquid; OF, objective function; PR, Peng–Robinson; VLE, vapor–liquid equilibrium.

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equation proposed by Peng and Robinson [11] is widely used due to its simplicity and flexibility [12]. The application of this cubic EOS to systems containing highly non-ideal components requires an appropriate mixing rule for the attractive-term and covolume, which generally are based on excess Gibbs free energy [13,14]. Other models have also been successful as the zero-pressure model [15,16] and the infinite-pressure model [17]. Their capabilities and limitations for asymmetric systems have been discussed in some works [18,19].

VLE at high pressures can be calculated using the available values at low pressures of the activity model parameters. But sometimes, in the case of highly asymmetric mixtures as those containing CO₂, these values are not available. In such case, it is more convenient to calculate the parameters of the activity coefficient models from VLE data using an adequate minimization algorithm and an appropriate objective function. This procedure should have a moderate computing time requirement and a well accuracy in the phase equilibrium prediction [13].

In this work, an objective function based on the calculation of the distribution coefficient has been used to represent both the phase vapor and the pressure behavior in the case of isothermal asymmetric binary mixtures of carbon dioxide and *n*-alkanols at high pressures (CO₂ + *n*-alkanols, from methanol to 1-decanol). The experimental data were correctly correlated with the Peng–Robinson EOS using the Wong–Sandler mixing rules. The binary interaction parameter k_{12} of the second virial coefficient and the non-random two liquid (NRTL) model parameters τ_{12} and τ_{21} were calculated for the VLE of binary asymmetric mixtures at high pressures. For this, a Levenberg–Marquardt minimization algorithm was used.

2. Equation of state and mixing rules

The Peng–Robinson EOS [11] has the following form:

$$P = \frac{RT}{v-b} - \frac{a}{v(v+b) + b(v-b)} \quad (1)$$

where P is the absolute pressure, T is the absolute temperature, R is the ideal gas constant, a and b are the energy and size parameters, respectively. These parameter are calculated from the following correlations:

$$a = 0.457235 \frac{R^2 T_c^2}{P_c} \alpha(T_r) \quad (2)$$

$$b = 0.077796 \frac{RT_c}{P_c} \quad (3)$$

where subscripts c and r denote critical and reduced conditions, respectively. The α function is calculated from:

$$\alpha(T_r) = \left[1 + \kappa \left(1 - \sqrt{T_r} \right) \right]^2 \quad (4)$$

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (5)$$

where ω is the acentric factor. For extending Peng–Robinson EOS to mixtures the Wong–Sandler [17] mixing rules can be used. The a_m and b_m parameters are calculated from:

$$a_m = b_m \left[\sum_i z_i \frac{a_i}{b_i} + \frac{A_\infty^E}{\sigma} \right] \quad (6)$$

with

$$b_m = \frac{\sum_i \sum_j z_i z_j \left(b - \frac{a}{RT} \right)_{ij}}{1 - \sum_i z_i \frac{a_i}{b_i RT} - \frac{A_\infty^E}{\sigma RT}} \quad (7)$$

$$\sigma = \frac{1}{\sqrt{2}} \ln(\sqrt{2} - 1) \quad (8)$$

and

$$\left(b - \frac{a}{RT} \right)_{ij} = \frac{\left(b - \frac{a}{RT} \right)_i + \left(b - \frac{a}{RT} \right)_j}{2} (1 - k_{ij}) \quad (9)$$

where k_{ij} is a binary interaction parameter of the second virial coefficient, z is the molar fraction and A_∞^E is the excess Helmholtz free energy at infinite pressure, which is calculated from NRTL model for binary mixtures [20]:

$$\frac{A_\infty^E}{RT} = \sum_i z_i \left(\frac{\sum_j z_j \tau_{ji} g_{ji}}{\sum_k z_k g_{ki}} \right) \quad (10)$$

Table 1

Experimental conditions for the asymmetric binary mixtures treated.

Carbon dioxide +	np	T (K)	Pressure range (bar)	Reference
Methanol	8	298.15	7.89–59.52	[21]
	11	291.15	5.6–43.3	[22]
	16	303.18	8.9–63.2	
	16	308.15	13.2–70.1	
	17	313.14	13.2–77.2	
Ethanol	8	298.17	11.6–58.2	[22]
	11	303.12	11.6–64.8	
	6	314.50	5.7–81.1	[9]
	9	325.20	62.74–93.49	
	8	337.20	62.19–108.45	
1-Propanol	8	315.00	26.4–71.7	[23]
	10	326.60	34.8–88.8	
	10	337.20	33.0–89.8	
	10	313.40	5.18–81.79	[24]
	9	333.40	6.8–108.22	
1-Butanol	7	293.15	6.30–54.6	[25]
	14	303.15	5.20–67.4	
	8	314.80	46.33–79.84	[9]
	9	325.30	52.26–98.73	
	11	337.20	61.78–117.76	
1-Pentanol	7	333.08	70.9–119.31	[26]
	4	343.69	121.8–135.9	
	4	374.93	145.12–169.22	
	12	426.86	35.63–186.37	
	1-Hexanol	4	431.82	83.63–135.55
7		432.45	22.68–201.28	
1-Heptanol		8	374.63	40.38–145.72
	6	431.54	68.3–168.06	
	8	298.15	6.80–60.9	[28]
	10	316.15	15.6–114.5	
	1-Octanol	12	308.15	15.1–77.4
9		318.19	21.7–97.8	
16		328.15	28.9–151.1	
1-Nonanol	15	328.18	28.6–156	[22]
	10	318.13	25.2–104.4	
	9	308.14	22.3–79.1	
1-Decanol	9	308.14	22.3–77.5	[22]
	9	318.14	21.8–104.7	
	13	328.16	28.9–151.7	

Table 2
Optimal parameters obtained from optimization and deviations between calculated and experimental values.

Parameters	CO ₂ + methanol					CO ₂ + ethanol				
	291.15 K	298.15 K	303.18 K	308.15 K	313.14 K	298.17 K	303.12 K	314.50 K	325.20 K	337.20 K
τ_{12}	1.3345	0.5013	3.2387	2.7720	1.5843	1.3143	0.1705	1.9314	1.1963	1.0835
τ_{21}	-0.3352	0.1187	-0.4343	-0.4156	-0.1363	-0.6677	0.4247	-0.0701	0.2243	0.2871
κ_{12}	0.2205	0.3972	0.1771	0.2144	0.2992	0.4298	0.4504	0.3772	0.4084	0.4071
ΔP	1.1878	1.1723	2.3629	2.2206	0.9024	1.5124	1.6339	1.7598	0.1633	0.3257
Δy	0.0037	0.0016	0.0022	0.0028	0.0025	0.0069	0.0064	0.0010	0.0023	0.0031
Parameters	CO ₂ + 1-propanol					CO ₂ + 1-butanol				
	315.00 K	326.60 K	337.20 K	313.40 K	333.40 K	293.15 K	303.15 K	314.80 K	325.30 K	337.20 K
τ_{12}	2.2793	0.7280	1.6067	2.5113	1.8870	1.5861	1.0752	1.9332	1.8663	1.8003
τ_{21}	-0.0110	0.5953	0.0402	-0.4762	-0.1471	0.1655	0.4405	-0.0061	-0.0445	-0.0833
κ_{12}	0.4065	0.5048	0.4537	0.4422	0.4388	0.5787	0.5812	0.5273	0.5244	0.5221
ΔP	0.2879	0.7484	1.7443	1.3856	0.9273	0.9014	3.2506	0.0866	0.1412	0.0952
Δy	0.0021	0.0011	0.0020	0.0016	0.0051	0.0073	0.0042	0.0008	0.0012	0.0018
Parameters	CO ₂ + 1-pentanol				CO ₂ + 1-hexanol		CO ₂ + 1-heptanol			
	333.08 K	343.69 K	374.93 K	426.86 K	431.82 K	432.45 K	374.63 K	431.54 K	298.15 K	316.15 K
τ_{12}	2.3425	2.3645	1.5248	2.0271	1.4259	-0.5979	2.3674	3.9066	2.6575	2.5770
τ_{21}	-0.3235	-0.3975	-0.0477	-0.7586	-0.7219	1.8222	-0.8955	-1.0822	-0.1594	-0.3556
κ_{12}	0.5633	0.5612	0.5790	0.5460	0.6310	0.6773	0.6597	0.5106	0.6808	0.6772
ΔP	1.0132	0.1887	0.3246	1.4383	0.1367	2.6389	0.6572	2.0066	0.6078	4.0665
Δy	0.0086	0.0089	0.0121	0.0033	0.0058	0.0332	0.0029	0.0459	0.0062	0.0075
Parameters	CO ₂ + 1-octanol			CO ₂ + 1-nonanol			CO ₂ + 1-decanol			
	308.15 K	318.19 K	328.15 K	308.14 K	318.13 K	328.18 K	308.14 K	318.14 K	328.16 K	
τ_{12}	2.5807	1.7590	2.3629	2.9503	1.9111	2.4344	3.0836	2.2640	2.0742	
τ_{21}	-0.1218	0.0606	-0.2511	-0.1062	-0.0169	-0.2631	-0.0749	-0.1460	-0.1706	
κ_{12}	0.7377	0.7579	0.7325	0.7564	0.7926	0.7704	0.7904	0.8130	0.8218	
ΔP	0.6292	0.5795	0.9807	0.4157	0.7922	0.8844	0.5919	1.0967	1.2016	
Δy	0.0015	0.0015	0.0079	0.0017	0.0040	0.0055	0.0005	0.0019	0.0039	

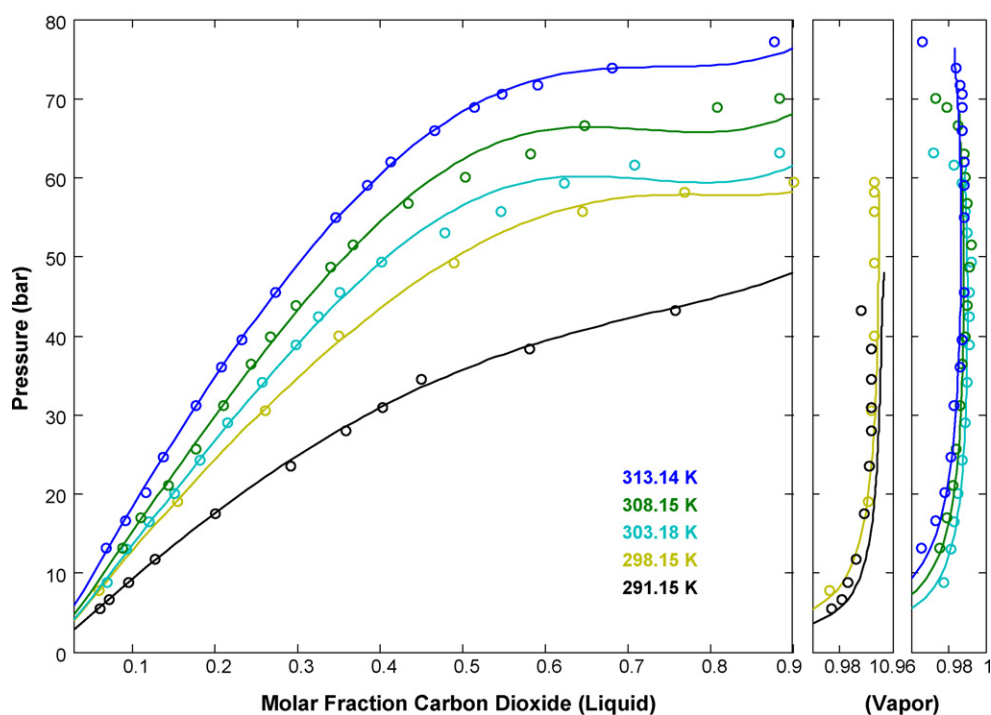


Fig. 1. Experimental and predicted VLE for carbon dioxide + methanol binary system. Experimental data were taken from Ohgaki and Katayama [21] and Chiehming et al. [22]. Prediction performed using the PR EOS coupled with the WS mixing rules.

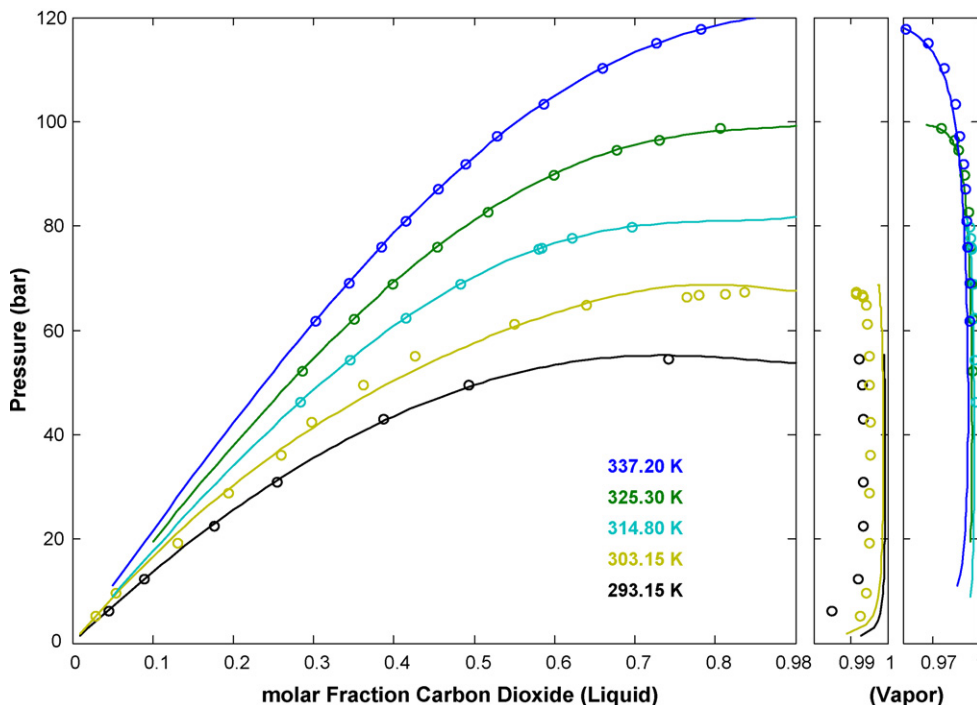


Fig. 2. Experimental and predicted VLE for carbon dioxide + 1-butanol binary system. Experimental data were taken from Secuianu et al. [25] and Jennings et al. [9]. Prediction performed using PR EOS coupled with the WS mixing rules.

$$g_{ij} = \exp(-\alpha_{ij}\tau_{ij}) \tag{11}$$

where α_{12} ($=\alpha_{21}$), τ_{12} and τ_{21} are the three parameters of the NRTL model. A constant value for α_{12} of 0.3 was used in this work. The adjustable parameters of NRTL model, τ_{12} and τ_{21} , and binary interaction parameter k_{12} of the second virial coefficient have been determined using experimental phase equi-

librium data at isothermal conditions for 10 asymmetric binary mixtures.

3. Parameters optimization

Binary interaction parameters for Peng–Robinson EOS and NRTL model have been determined by using Levenberg–Marquardt min-

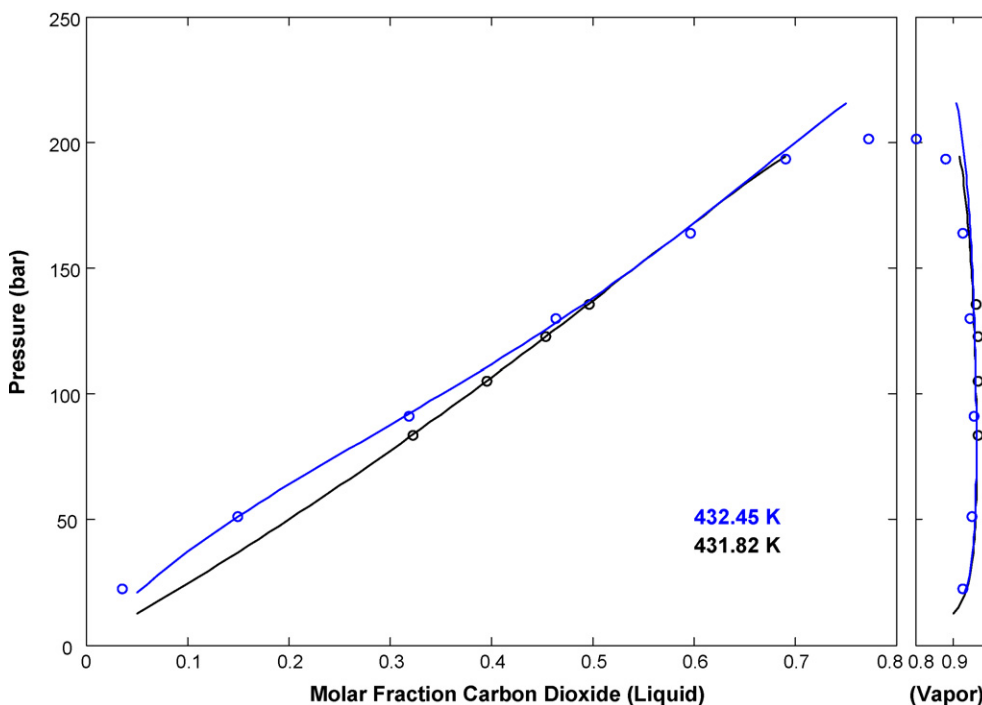


Fig. 3. Experimental and predicted VLE for carbon dioxide + 1-hexanol binary system. Experimental data were taken from Solis et al. [27]. Prediction performed using the PR EOS coupled with the WS mixing rules.

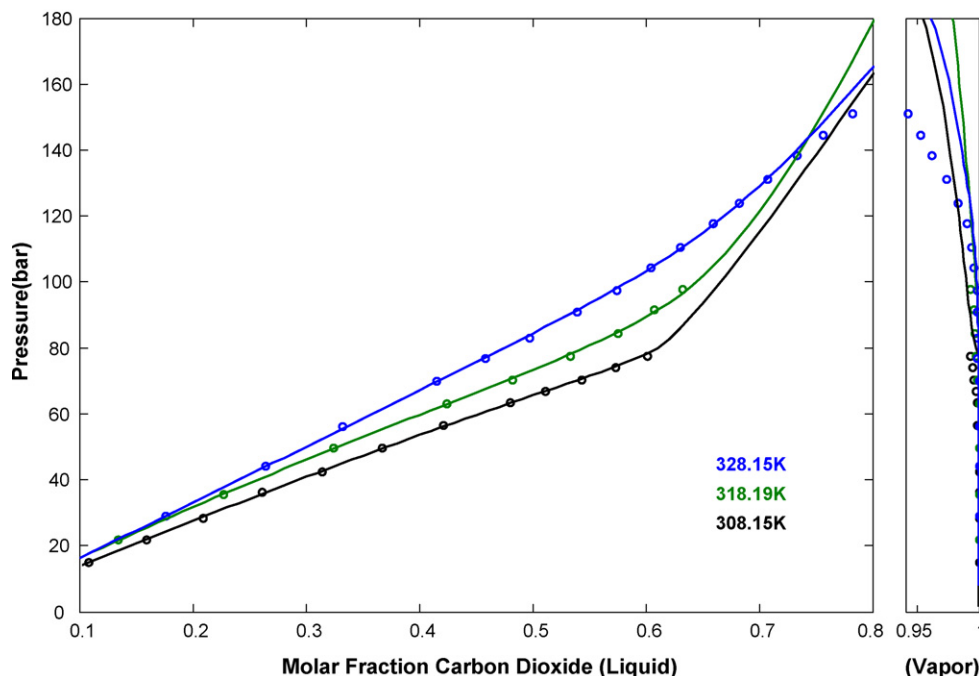


Fig. 4. Experimental and predicted VLE for carbon dioxide + 1-octanol binary system. Experimental data were taken from Chiehming et al. [22]. Prediction performed using the PR EOS coupled with the WS mixing rules.

imization algorithm. The objective function used for all cases is as follows:

$$OF = \sum_{i=1}^{np} \sum_{j=1}^{nc} [y_{i,j}^{exp} - K_{i,j}^{cal} x_{i,j}^{exp}]^2 \quad (12)$$

where np is the number of experimental data points, nc the number of components, y and x are the molar fraction in the vapor and liquid phases, respectively. K is the distribution coefficient between

vapor and liquid phases. The superscripts exp and cal correspond to the experimental and calculated values, respectively. In a previous work [13], it has been found that the objective function represented by Eq. (12) has three principal advantages over the commonly used objective functions based on bubble point pressure and vapor phase composition calculation. Mentioned advantages are: (1) minimum computing time requirement considering that this objective function does not involve additional iterative calculations as the bubble point or isothermal flash for each experimental data point.

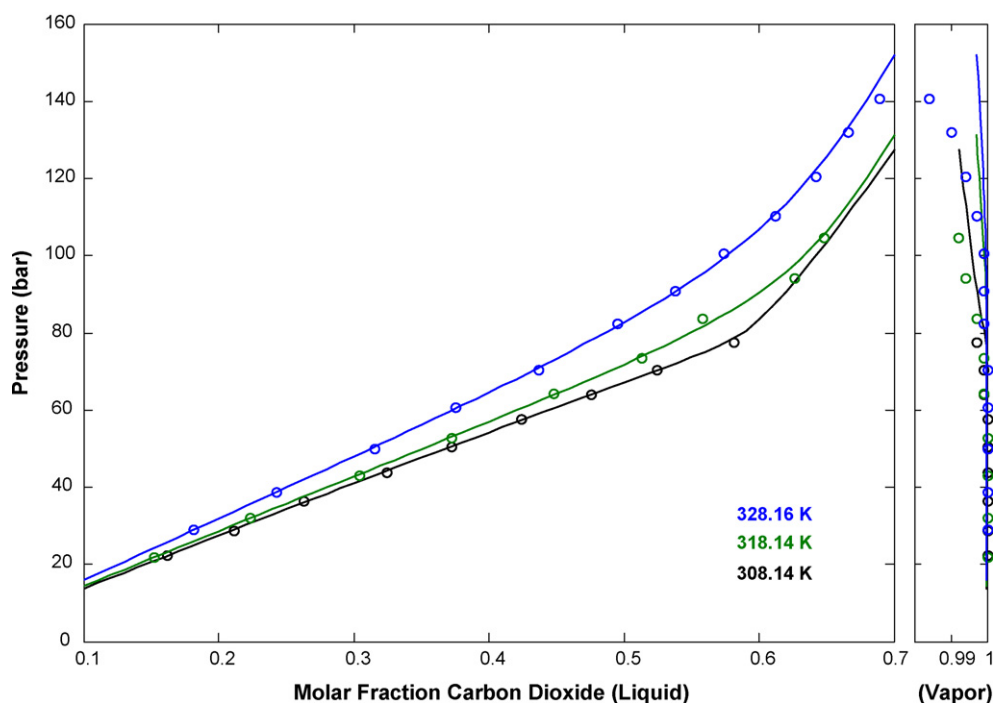


Fig. 5. Experimental and predicted VLE for carbon dioxide + 1-decanol binary system. Experimental data were taken from Chiehming et al. [22]. Prediction performed using the PR EOS coupled with the WS mixing rules.

(2) The optimal second virial coefficient interaction parameter is concordant with the statistical thermodynamic postulates since its value does not violate the quadratic composition dependence of the second virial coefficient. (3) Phase equilibrium calculations using the optimal parameters obtained with this objective function show very good predictions for both vapor phase and pressure. Therefore, all these features make the objective function (12) adequate for parameters optimization from experimental VLE data in highly asymmetric binary mixtures. For this reason, it is used in the present work.

Ten asymmetric binary mixtures containing carbon dioxide and *n*-alkanols (from methanol to 1-decanol) have been treated. The experimental conditions and the literature source of each data set are shown in Table 1, where data for 39 isotherms with 382 experimental points were analyzed.

4. Results and discussion

A total of 39 minimizations runs have been executed. Then, 117 optimal parameters have been obtained for the 10 mixtures involved in the study. These NRTL model parameters (τ_{12} and τ_{21}) and the binary interaction parameter k_{12} of the second virial coefficient of the Peng–Robinson EOS are reported in Table 2. Additionally, deviations between experimental data and calculated values using the Peng–Robinson EOS and the Wong–Sandler mixing rules are also shown in Table 2. These deviations were established through the relative deviations (in percentage) in the bubble point pressure:

$$\Delta P = \sum_{i=1}^{np} \frac{|P_{\text{exp}} - P_{\text{cal}}|}{P_{\text{exp}}} \left(\frac{100}{np} \right) \quad (13)$$

The absolute mean deviation in the molar fraction in the vapor phase was calculated as follows:

$$\Delta y = \sum_{i=1}^{np} |y_{\text{exp}} - y_{\text{cal}}| \frac{1}{np} \quad (14)$$

Graphical results of phase equilibrium calculations using the optimal parameters reported in Table 2 are shown in Figs. 1–5. Experimental and predicted VLE for binary mixture carbon dioxide + methanol is shown in Fig. 1. In mentioned figure, parameters optimization has been developed. For all cases, the agreement between experimental data and calculated values was satisfactory.

Isothermal VLE for carbon dioxide + 1-butanol binary system is shown in Fig. 2. Both liquid and vapor phase predictions were correct for the pressure range analyzed. However, in the mentioned figure, it can be noted that calculations present light deviations near the critical point of the mixture at the five temperatures evaluated. This has been observed for the other treated cases as well. This behavior can be explained by the fact that the experimental data points, in almost all cases, do not include data near the critical point. Therefore the minimizations were developed over the available points.

Fig. 3 shows the experimental and predicted phase equilibrium for the highly asymmetric carbon dioxide + 1-hexanol binary mixture. For the two temperatures analyzed, the vapor phase and liquid phase representations are very accurate related to the experimental points, as can be noted from the deviations reported in Table 2.

Two highly asymmetric binary mixtures are shown in Fig. 4 (carbon dioxide + 1-octanol) and Figure 5 (carbon dioxide + 1-decanol). For these two systems all predictions are correct in the total range of pressure analyzed. However, small deviations in the vapor phase were observed.

5. Conclusions

In the present work, the binary interaction parameter k_{12} of the second virial coefficient and the NRTL model parameters τ_{12} and τ_{21} were optimized for 10 binary mixtures containing carbon dioxide and *n*-alkanols (from methanol to 1-decanol). Phase equilibrium calculations were developed using the Peng–Robinson EOS coupled with the Wong–Sandler mixing rules. Excess Helmholtz free energy at infinite pressure was calculated using NRTL excess Gibbs free energy model. In total, 39 minimizations were carried out for the 10 asymmetric binary mixtures studied.

The capability of the VLE model for representing the experimental data was demonstrated. Then, the use of an adequate mixing rule containing a correction at infinite-pressure results convenient for the satisfactory representation of phase equilibrium of the highly asymmetric binary mixtures evaluated. The optimal values of the binary interaction parameter of the second virial coefficient for all the mixtures studied were found to be in concordance with the statistical thermodynamic postulates considering that such values were in the acceptable range (0–1) and that it increases when the asymmetry of the mixtures also increases.

Here, the capability and efficiency of the objective function denoted by the Eq. (12) for minimizing VLE experimental data at high pressures has been demonstrated. The optimal parameters reported serve as a base to improve phase equilibria predictions in order to model and design chemical processes involving supercritical carbon dioxide and 1-alkanols under non-ideal conditions.

List of symbols

A^E	excess Helmholtz free energy
a, b	equation of state parameters
$(b - a/RT)_{ij}$	cross second virial coefficient
g_{ij}	parameter defined by Eq. (11)
K_{ij}	distribution coefficient
k_{ij}	second virial coefficient interaction parameter
nc	number of components
np	number of experimental data points
P	pressure
R	gas constant
T	temperature
V	volume in molar units
X	liquid molar fraction
Y	vapor molar fraction
Z	molar fraction

Greek letters

Δ	deviation
$\alpha(T_r)$	temperature-dependent alpha function
α_{ij}	NRTL model parameter
K	Peng–Robinson alpha function parameter
τ_{12}, τ_{21}	NRTL model binary interaction parameter
Ω	acentric factor

Subscripts

c	critical point
m	mixture
r	reduced conditions
∞	infinite condition

Superscripts

E	excess property
exp	experimental
cal	calculated

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