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*Ind. Eng. Chem. Res.*, **2005**, 44 (17), 6751-6759 • DOI: 10.1021/ie050075h • Publication Date (Web): 22 July 2005

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# VLE of Carbon Dioxide/Ethanol/Water: Applications to Volume Expansion Evaluation and Water Removal Efficiency

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The Peng–Robinson equation of state (PR-EoS) and the Stryjek and Vera modification of the Peng–Robinson equation of state (PRSV-EoS) were used to predict the vapor–liquid equilibrium of the system carbon dioxide(1)/ethanol(2)/water(3) under various temperatures and pressures. We propose a new algorithm that uses a flash calculation to provide a set of initial values and then solves the highly nonlinear phase equilibrium equations using the Broyden modified Newton–Raphson (BNR) method. With interaction parameters for the constituent binary systems, the ternary vapor–liquid equilibrium prediction shows that, at a given temperature, pressure, and water molar fraction in liquid phase, this algorithm is stable to calculate all other compositions. The calculated results from both the PR-EoS and the PRSV-EoS are in good agreement with the experimental data for the binary and ternary systems. A water removal process using supercritical carbon dioxide was experimentally implemented. The pressure dependence of the volume expansion of the mixture ethanol/water with carbon dioxide was also investigated using a high-pressure view cell. The established phase equilibrium calculation was applied to predict the volume expansion behavior and to evaluate the water removal efficiency. Results show that this ternary phase equilibrium calculation is useful to study the water removal process under high pressure carbon dioxide. It also shows that the volume expansion prediction is good at relatively low ethanol mass fraction in the feeding water/ethanol mixture or at low pressures.

## Introduction

Drug particle formation processes using supercritical fluids (SCF) are becoming convenient and competitive alternatives to some of the conventional processes.<sup>1</sup> One of those SCF-based methods is the supercritical antisolvent (SAS) process that involves the dissolution of the SCF into a solution where the drug was previously dissolved in a solvent and the drug is forced to precipitate due to the expansion of the solution. The choice of the solvent is often the critical stage in the processing of biological macromolecules such as those used in therapeutic applications. Supercritical CO<sub>2</sub> is highly soluble in many organic solvents, but the use of these solvents compromises the biological activity of the therapeutic molecules, namely of proteins. Moreover, successful pharmaceutical formulations are difficult to obtain without involving water in the production process. The low productivity associated with processes where supercritical fluids act as antisolvents is mainly associated with the difficulty of a complete water removal from the initial aqueous solution, which constrains the feed ratio aqueous solution/SCF phase to very small values making the process very time-consuming. However, the use of a cosolvent such as ethanol may improve significantly the miscibility of high-pressure CO<sub>2</sub> in water increasing therefore the process efficiency.<sup>2</sup> Many biological macromolecules are tolerant to moderate concentrations of ethanol, which shows some advantages over other common solvents,

namely low toxicity, FDA approval, and low cost. Moreover, in addition to its use in several SCF-based antisolvent processes (SAS, SEDS) for drug particle formation, the ternary CO<sub>2</sub>/ethanol/water system is also important for supercritical fluid extraction of ethanol from fermentation broths to obtain anhydrous ethanol that finds use as fuel in motors. It is not surprising therefore that this system has attracted many investigators in the past decades.

To carry out the processes mentioned above, we require a complete knowledge of the ternary CO<sub>2</sub>/ethanol/water phase equilibria; in addition, a reliable method to calculate the available phase equilibrium data on this ternary mixture would be very useful. Several equations of state and different mixing rules have been applied to estimate the phase equilibrium behavior of this system. However, as reported, only limited experimental data have been checked, and a truly successful study is yet to be achieved. In early studies, Takishima et al.<sup>3</sup> and Inomata et al.<sup>4</sup> applied with not much success the Patel-Teja EoS to represent the vapor–liquid-phase equilibrium (VLE) of the CO<sub>2</sub>/ethanol/water system. Feng et al.<sup>5</sup> used the PR-EoS and the Vidal mixing rules to investigate the same system but failed to model the results for the ternary system. Nagahama et al.<sup>6</sup> used the PR-EoS and several mixing rules and showed that the agreement between experimental and calculated results was good at low pressures only. Later, De la Ossa et al.<sup>7</sup> used a perturbed-dipolar-hard-sphere EoS to study the binary and ternary phase behaviors and showed that it could successfully represent their experimental data. Dahl et al.<sup>8</sup> used the modified Huron-Vidal mixing rule-2 and the SRK-EoS and achieved good results at low pressures. Lim et al.<sup>9</sup> reported that the Patel-Teja EoS with the Adachie-Sugie

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mixing rules were in good agreement with the experimental data for the binary systems; once more, the ternary calculations did not agree well with their ternary equilibrium composition data. Yao et al.<sup>10</sup> reported that a modified PR-EoS could represent with good accuracy the experimental data at high pressures and 308.2 K. Zhang et al.<sup>11</sup> reported a new study by using SAFT-EoS and showed that this equation predicted well the ternary system comprising 51 experimental points. Yet, in both Yao and Zhang's methods it is not clear how calculations were performed when temperature, pressure, and vapor compositions ( $y_1, y_2$ ) were likely kept equal to the experimental values. Actually this problem was later pointed out by Pfohl et al.<sup>12</sup> in a Letter to the Editor concerning Zhang's paper.

Because of the present unsuccessfully phase equilibrium calculations by means of equations of state on this ternary system, we recently<sup>13</sup> extended the empirical method established by Duarte et al.<sup>14</sup> for the evaluation of the water removal efficiency from ethanol solutions by high-pressure CO<sub>2</sub>. Also, Budich and Br  nner<sup>15</sup> reported an empirical method applied to extraction column calculations. Obviously, these empirical methods are limited in its applications when facing different operating conditions and volumetric properties. Based on the evidence presented above, the aim of this work is to implement a method that accurately models the VLE for the CO<sub>2</sub>/ethanol/water system and then apply that model to the study of the water removal process (low ethanol concentration) and to the volume expansion behavior (high ethanol concentration).

## Equations of State and VLE Calculations

**Equations of State.** In this work, the Peng–Robinson equation of state<sup>16</sup> (PR-EoS) and the Stryjek and Vera modification<sup>17</sup> of the Peng–Robinson equation of state (PRSV-EoS) are adopted to represent the VLE of the ternary and of the binary systems involving carbon dioxide, ethanol, and water, under various temperatures and pressures. Compared to the PR-EoS, the PRSV-EoS considers the attractive term as a function of the temperature and of the acentric factor and requires one additional pure compound parameter ( $\kappa_i$ ). Stryjek and Vera showed that nonpolar, polar nonassociating, and associating compounds were equally well represented by their equation of state.

Peng and Robinson proposed a cubic equation of state of the form

$$P = \frac{RT}{v - b} - \frac{a(T)}{v^2 + 2bv - b^2} \quad (1)$$

where  $T$ ,  $P$ , and  $v$  are the temperature, pressure, and molar volume. Parameters  $a$  and  $b$  are given by

$$a_i = 0.457235 \frac{(RT_{ci})^2}{P_{ci}} \left[ 1 + \kappa_i \left( 1 - \sqrt{\frac{T}{T_{ci}}} \right) \right]^2 \quad (2)$$

$$b_i = 0.077796 \frac{RT_{ci}}{P_{ci}} \quad (3)$$

For the PR-EoS, the  $\kappa_i$  term has the form

$$\kappa_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2 \quad (4)$$

**Table 1. Pure Component Parameters<sup>17</sup>**

compound $i$	$T_{ci}$ (K)	$P_{ci}$ (MPa)	$\omega_i$	$\kappa_{1i}$
carbon dioxide (1)	304.21	7.382	0.225	0.04285
ethanol (2)	513.92	6.148	0.644	−0.03374
water (3)	647.29	22.09	0.344	−0.06635

where  $\omega$  is Pitzer's acentric factor. For the PRSV-EoS,  $\kappa_i$  is given by

$$\kappa_i = \kappa_{0i} + \kappa_{1i} \left( 1 + \sqrt{\frac{T}{T_{ci}}} \right) \left( 0.7 - \frac{T}{T_{ci}} \right) \quad (5)$$

with

$$\kappa_{0i} = 0.378893 + 1.4897153\omega_i - 0.17131848\omega_i^2 + 0.0196554\omega_i^3 \quad (6)$$

For mixtures, we have chosen the Panagiotopoulos–Reid<sup>18</sup> mixing rules

$$a = \sum_i \sum_j x_i x_j (a_i a_j)^{1/2} [1 - k_{ij} + (k_{ij} - k_{ji})x_i] \quad (7)$$

$$b = \sum_i \sum_j x_i x_j \left( \frac{b_i + b_j}{2} \right) \quad (8)$$

Table 1 gives the pure component parameters,  $T_{ci}$ ,  $P_{ci}$ ,  $\omega_i$ , and  $\kappa_{1i}$ .

**Calculation Method.** For a multicomponent system, VLE is obtained equating the fugacities of each component in the vapor phase and in the liquid phase

$$f_i^V(P, T) = f_i^L(P, T) \quad (9)$$

where  $\varphi_i$  is the fugacity coefficient of component  $i$ , that is easily obtained from the equation of state. For each phase

$$\sum_{i=1}^N y_i = 1 \quad (10)$$

$$\sum_{i=1}^N x_i = 1$$

where  $N$  is the number of components.

For the binary systems CO<sub>2</sub>/ethanol, CO<sub>2</sub>/water, and ethanol/water, VLE data were used to correlate the cross interaction parameters  $k_{ij}$  and  $k_{ji}$ . The Simplex optimization method was used to obtain the binary parameters by minimization of the objective function

$$F = \sum_{m=1}^n [(f_{i,m}^L - f_{i,m}^V)^2 + (f_{j,m}^L - f_{j,m}^V)^2] \quad (11)$$

where  $n$  is the number of the experimental data points. The temperature dependence of the interaction parameters was required because different experimental data were used under various temperatures; typically, they are expressed by linear relationships

$$k_{ij} = c_{ij} + d_{ij}T \quad (12)$$

$$k_{ji} = c_{ji} + d_{ji}T \quad (12a)$$

**Table 2. Experimental VLE Data for the Binary and Ternary Systems Involving Water, Ethanol, and Carbon Dioxide**

system	<i>T</i> (K)	<i>P</i> (MPa)	no. of data points	ref
CO <sub>2</sub> /ethanol	314.5	5.550–7.894	6	21
	325.2	6.274–9.349	9	
	337.2	6.219–10.85	8	
CO <sub>2</sub> /water	293.2	7.60–20.27	5	22
	298.2	7.60–20.27	5	
	323.2	4.06–14.1	10	
	333.2	4.06–14.1	10	23
	353.2	4.06–13.1	9	
	307.75–323.75	0.0127	25	
ethanol/water	352.27–369.25	0.1013	13	24
	408.95–424.95	0.6205	11	
CO <sub>2</sub> /ethanol/water	313.31	9.98	7	6
	313.2	8.31,9.21,10.5	6	5
	318.6	8.36,9.11,9.16,10.7	6	
	323.4	8.49,9.11,9.16,10.6	5	
	313.2	7.9,9.1,10.1,12.2,14.2,18.5	22	9
	323.2	9.05,10.1,10.5,11.8	23	
	333.2	10.1,10.5,11.8,14.2,18.5	31	
	343.2	11.3,11.8,14.2,18.5	24	
	289.75	6.058	5	4
	291.75	6.007	4	
	292.75	6.098	6	
	297.95	7.486	6	
	308.15	10.2,13.6,17.0	17	25
	323.15	10.2,13.6,17.0	6	
	333.15	10.2,13.6,17.0	6	
	308.2	10.07,10.08, 10.31	5	3
	383.00	9.905	8	26
	333.15	10.0	14	15

Phase equilibria predictions of the ternary CO<sub>2</sub>/ethanol/water requires only binary parameters that, as it is well-known, are sensitive to the binary parameters, temperature, pressure, and the initial guesses of the compositions. For a fixed temperature, pressure, and mole fraction, calculations can be carried out by using the Newton–Raphson method (NR) or the Broyden modified Newton–Raphson (BNR) method<sup>19</sup> to solve the highly nonlinear equations [eqs 9 and 10] with the initial guesses for  $x_i$  and  $y_i$ . The experimental data are normally the best choice for those initial guesses. Because for this ternary system vapor- and liquid-phase compositions can be quite different (for example,  $x_3$  can be close to 1 and  $x_1$  close to zero, while  $y_1$  is close to 1 and  $y_3$  is close to zero), the iteration for mole fractions or a slight variation of those compositions are too sensitive to achieve a convergent result by using directly either NR or BNR algorithms. Therefore, for the ternary phase equilibria calculations, a careful choice of the initial compositions is crucial. We used the flash calculation to set initial values for  $x_i$  and  $y_i$ . The flash calculation starts with the input of the feed compositions at  $T$  and  $P$  and by solving the Rachford–Rice equation<sup>20</sup> to give the vapor and liquid compositions. This procedure ensures that vapor and liquid phases always coexist under given  $T$  and  $P$  before the highly nonlinear equations are solved and can therefore successfully provide valid initial guesses for  $x_i$  and  $y_i$  by adjusting the feed compositions  $z_i$ . With those valid initial mole fractions, the BNR method can successfully and rapidly (requires less than 7 iterations) be implemented to solve eqs 9 and 10. Moreover, we have also found that the fixed composition affects the final convergence of the program, being more convenient to fix the water liquid mole fraction  $x_3$  due to its insensitivity to the phase separation of this system. We note that the flash calculation can also be used to solve this ternary vapor–liquid-equilibrium problem by adjusting the feed compositions to match the fixed mole fraction (for example,

here we selected  $x_3$ ), but such a procedure cannot ensure that the calculation program be convergent at different conditions.

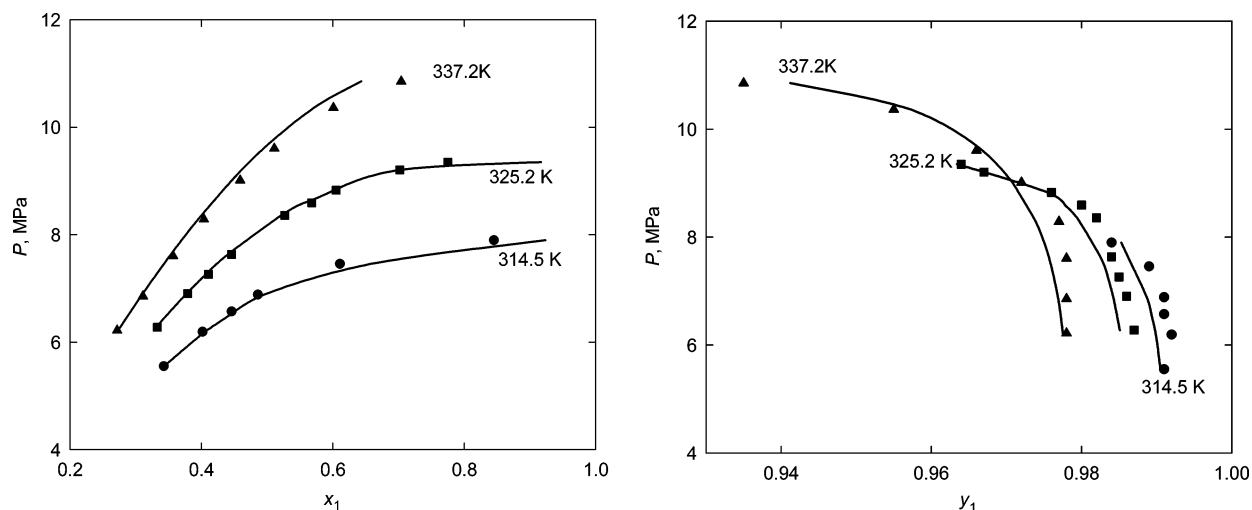
**Data Source.** There is available in the literature abundant VLE data for the binaries CO<sub>2</sub>/ethanol, CO<sub>2</sub>/water, and ethanol/water and also for the ternary CO<sub>2</sub>/ethanol/water. Selected representative binary data and almost all available ternary data are listed in Table 2.

**Modeling Results for the Binary Systems.** Figures 1–4 compare the experimental with predicted VLE from the PRSV-EoS (with the binary parameters listed in Table 3) for the binaries CO<sub>2</sub>/ethanol, CO<sub>2</sub>/water, and ethanol/water. Table 5 presents the average absolute deviations (AAD) obtained from the PRSV-EoS and from the PR-EoS (with the optimized binary parameters listed in Table 4) for each of the binaries and also for the ternary system.

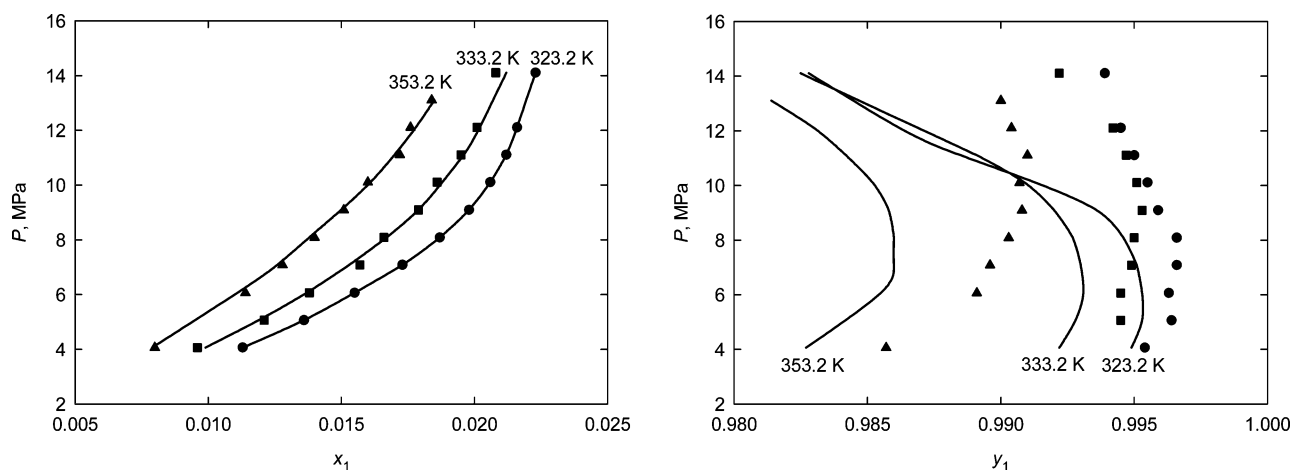
**Modeling Results for the Ternary System.** Using the interaction parameters listed in Tables 3 and 4, Figures 5–9 compare predicted and experimental data at various temperatures and pressures. The overall prediction average absolute deviations (AAD) from the PR-EoS and the PRSV-EoS are presented in Table 5.

## Discussion

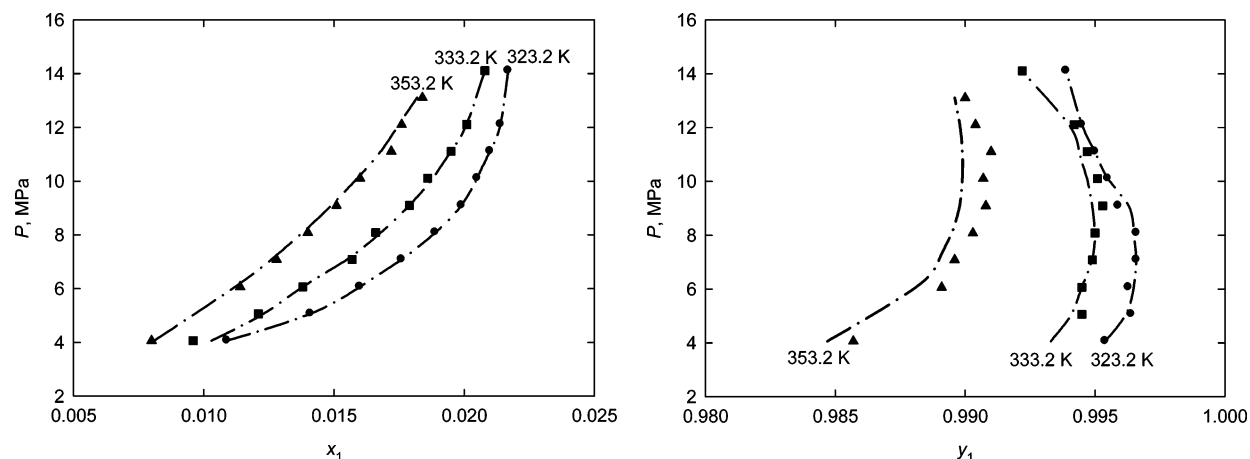
As Table 5 and Figures 1–4 show, the PRSV-EoS can usually correlate accurately the phase behavior of the binaries CO<sub>2</sub>/ethanol, CO<sub>2</sub>/water, and ethanol/water. The correlation results from the PR-EoS are slightly worse than those from the PRSV-EoS, but they are still acceptable though. We tested an alternative objective function [expressed by eq 13] for the correlation of the CO<sub>2</sub>/water binary system that much improves the correlation precision for its vapor phase, as Figure 3 clearly shows. For ethanol/water, a bubble point calculation is performed because of a convergent problem for several of the data points by using the flash method. Therefore, Table 5 presents instead the average absolute deviation in temperature (AADT).



**Figure 1.**  $P$ - $x$ - $y$  diagram of the  $\text{CO}_2$ /ethanol system at different temperatures. Experiment: ● 314.5 K; ■ 325.2 K; ▲ 337.2 K. Correlated with the PRSV-EoS: —.



**Figure 2.**  $P$ - $x$ - $y$  diagram of the  $\text{CO}_2$ /water system at different temperatures. Experiment: ● 323.2 K; ■ 333.2 K; ▲ 353.2 K. Correlated with the PRSV-EoS: —.

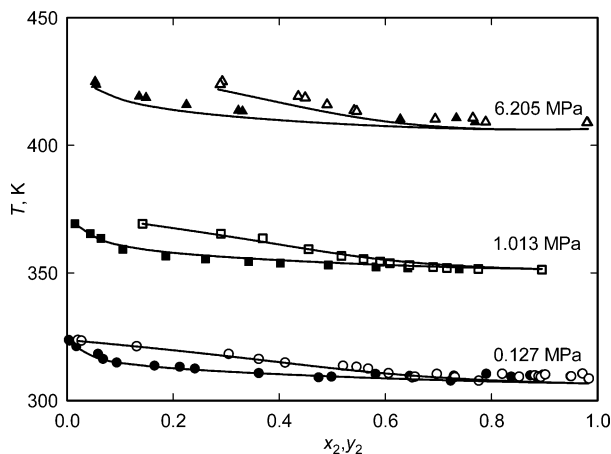


**Figure 3.**  $P$ - $x$ - $y$  diagram of the  $\text{CO}_2$ /water system at different temperatures. Experiment: ● 323.2 K; ■ 333.2 K; ▲ 353.2 K. Correlated with the PRSV-EoS [ $\text{CO}_2$ /water binary parameters from eq 13]: - - -.

As shown in Table 5 and in Figures 6 and 7, both the PRSV-EoS and the PR-EoS are able to predict the ternary VLE data in good agreement with the experimental data. Yet, both equations of state overestimate the ethanol content in the liquid phase near the plait point, as indicated in Figures 5, 8, and 9. Figure 5 shows that the  $\text{CO}_2$ /water binary interaction parameters have an important role on the prediction of the ternary

system. The same figure also reveals that eq 13 improves the correlation results for the  $\text{CO}_2$ /water binary; however, it does not improve the prediction for the ternary system, in particular when the ethanol molar fraction is relatively high. We must point out that both sets of the  $\text{CO}_2$ /water interaction parameters listed in Table 3 (for the PRSV-EoS) and in Table 4 (for the PR-EoS) cannot describe satisfactorily  $y_3$ , the mole fraction





**Figure 4.**  $T$ - $x$ - $y$  diagram of ethanol/water at 0.127, 1.013, and 6.205 MPa. Experiment: solid symbols (liquid phase); open symbols (vapor phase). Correlated with the PRSV-EoS: —.

**Table 3. Optimized Binary Interaction Parameters from the PRSV-EoS**

system	$k_{ij}$		$k_{ji}$	
	$c_{ij}$	$d_{ij} \times 10^4$	$c_{ji}$	$d_{ji} \times 10^4$
CO <sub>2</sub> (1)/ethanol(2)	-0.025121	4.4875	0.0039559	2.7141
CO <sub>2</sub> (1)/water(3)	-0.43903	10.916	0.051035	-1.6038
CO <sub>2</sub> (1)/water(3) <sup>a</sup>	-0.48321	12.015	0.17289	1.0977
ethanol(2)/water(3)	-0.16281	1.1970	-0.28803	5.7827

<sup>a</sup> Binary interaction parameters obtained using the alternative objective function,

$$F = \sum_{j=1}^n [0.6 \times (x_{1j}^{\text{exp}} - x_{1j}^{\text{calc}})^2 + 0.4 \times (y_{1j}^{\text{exp}} - y_{1j}^{\text{calc}})^2] \quad (13)$$

**Table 4. Optimized Binary Interaction Parameters from the PR-EoS**

system	$k_{ij}$		$k_{ji}$	
	$c_{ij}$	$d_{ij} \times 10^4$	$c_{ji}$	$d_{ji} \times 10^4$
CO <sub>2</sub> (1)/ethanol(2)	-0.024788	4.4690	0.0039842	2.7121
CO <sub>2</sub> (1)/water(3)	-0.44626	10.847	0.055491	-1.4790
CO <sub>2</sub> (1)/water(3) <sup>a</sup>	-0.48629	11.860	0.19205	-4.1849
ethanol(2)/water(3)	-0.16629	1.2255	-0.29997	5.6741

<sup>a</sup> Binary interaction parameters from eq 13.

of water in the vapor phase in the ternary system, despite the AADs obtained are small (the relative deviations are large).

To determine the influence of the liquid-phase ethanol content on the vapor phase water composition, important for a water-removal process, Figure 10 compares experimental equilibrium data with model predictions using two different sets [eqs 11 and 13] of CO<sub>2</sub>/water interaction parameters. As Figure 10 shows, the two sets of the CO<sub>2</sub>/water interaction parameters are alternative for different cases: the set of binary parameters obtained from eq 13 is valid only for low ethanol concentrations, while the other set [from eq 11] is preferable at high ethanol concentrations.

## Water Removal

**Experiment.** Figure 11 shows schematically the experimental apparatus used to measure the water removal efficiency from an ethanol aqueous solution with high-pressure CO<sub>2</sub>.

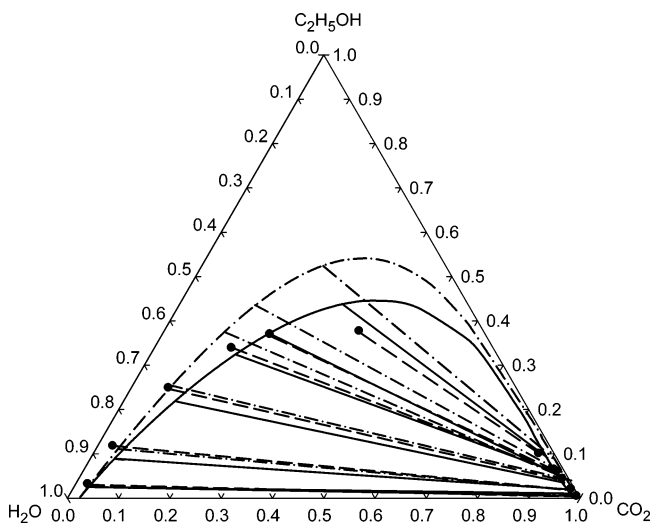
Each experimental run starts by injecting an ethanol/water solution of known composition into a homemade

**Table 5. Average Absolute Deviations (AAD) from PRSV-EoS and PR-EoS for Binary and Ternary Systems**

system	EoS	AAD	no. of data points
CO <sub>2</sub> /ethanol	PRSV	AAD <sub>x1</sub> =0.0198, AAD <sub>y1</sub> =0.0018	23
	PR	AAD <sub>x1</sub> =0.0220, AAD <sub>y1</sub> =0.0021	
CO <sub>2</sub> /water	PRSV	AAD <sub>x1</sub> =0.0002, AAD <sub>y1</sub> =0.0038	39
	PR	AAD <sub>x1</sub> =0.0003, AAD <sub>y1</sub> =0.0044	
CO <sub>2</sub> /water <sup>a</sup>	PRSV	AAD <sub>x1</sub> =0.0001, AAD <sub>y1</sub> =0.0003	39
	PR	AAD <sub>x1</sub> =0.0001, AAD <sub>y1</sub> =0.0002	
ethanol/water	PRSV	AAD <sub>T</sub> =1.55K, AAD <sub>y1</sub> =0.0173	49
	PR	AAD <sub>T</sub> =1.66K, AAD <sub>y1</sub> =0.0270	
CO <sub>2</sub> /ethanol/water	PRSV	AAD <sub>x1</sub> =0.0271, AAD <sub>y1</sub> =0.0152	201
	PR	AAD <sub>x1</sub> =0.0304, AAD <sub>y1</sub> =0.0171	
CO <sub>2</sub> /ethanol/water <sup>a</sup>	PRSV	AAD <sub>y2</sub> =0.0105, AAD <sub>y3</sub> =0.0064	201
	PR	AAD <sub>x1</sub> =0.0304, AAD <sub>y1</sub> =0.0171	
	PRSV	AAD <sub>y2</sub> =0.0115, AAD <sub>y3</sub> =0.0065	
	PR	AAD <sub>x1</sub> =0.0478, AAD <sub>y1</sub> =0.0186	
	PRSV	AAD <sub>y2</sub> =0.0104, AAD <sub>y3</sub> =0.0092	
	PR	AAD <sub>x1</sub> =0.0473, AAD <sub>y1</sub> =0.0194	
	PRSV	AAD <sub>y2</sub> =0.0113, AAD <sub>y3</sub> =0.0091	
	PR	AAD <sub>x1</sub> =0.0473, AAD <sub>y1</sub> =0.0194	

<sup>a</sup> Binary CO<sub>2</sub>/water parameters from eq 13.

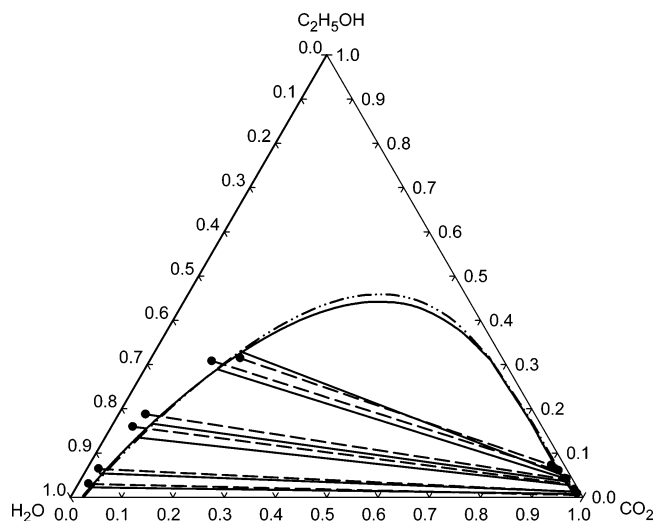
$$\text{AAD} = \text{AAD}_x = \frac{1}{n} \sum_{j=1}^n |x_j^{\text{calc}} - x_j^{\text{exp}}| \quad (x = x_i; y_i; T)$$



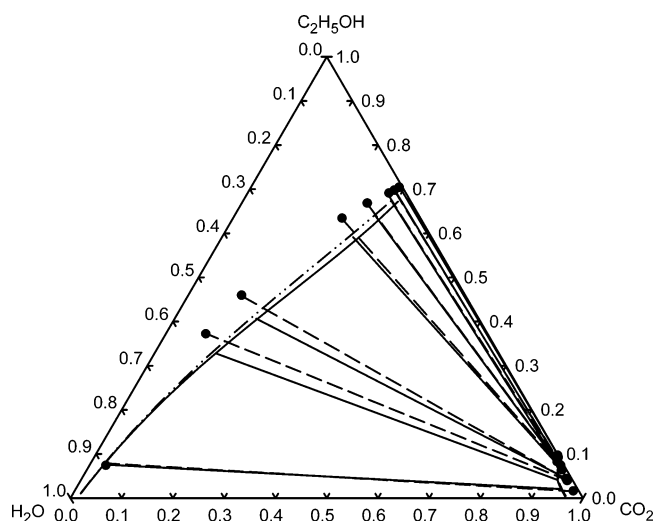
**Figure 5.** VLE of the ternary ethanol/water/CO<sub>2</sub> at 308.2 K and 10.2 MPa. Experiment: ●. Calculated: — PRSV-EoS; - - - PRSV-EoS with CO<sub>2</sub>/water binary parameters from eq 13.

460 cm<sup>3</sup> high-pressure visual cell, placed in a temperature-controlled air bath. The cell is then pressurized with CO<sub>2</sub> (98% pure, supplied by Ar Líquido, Portugal) using a Newport Scientific motor-driven gas compressor (model 46-13421-2). The gas circulates first through a temperature-controlled storage cylinder for temperature equilibration. The working pressure is controlled by a back-pressure regulator (Tescom, model 26-1722-24). When the working pressure is reached, the back pressure opens, and the liquid is extracted by the circulating CO<sub>2</sub>. The CO<sub>2</sub> consumed is totalized in a flow meter (Omega model FLR 1000). The extraction ends when only one phase is observed inside the cell. All the extraction runs were carried out at 10.0 MPa and 313.2 K with CO<sub>2</sub> flow rates from 3 to 7 g min<sup>-1</sup>.

**Calculation Method.** A step-by-step procedure<sup>13</sup> and the PRSV-EoS were used to calculate the relevant quantities in the experimental process described above. The first step was to determine the initial working point at the system's pressure (10.0 MPa) and temperature (313.2 K) from the initial feed of the aqueous ethanol



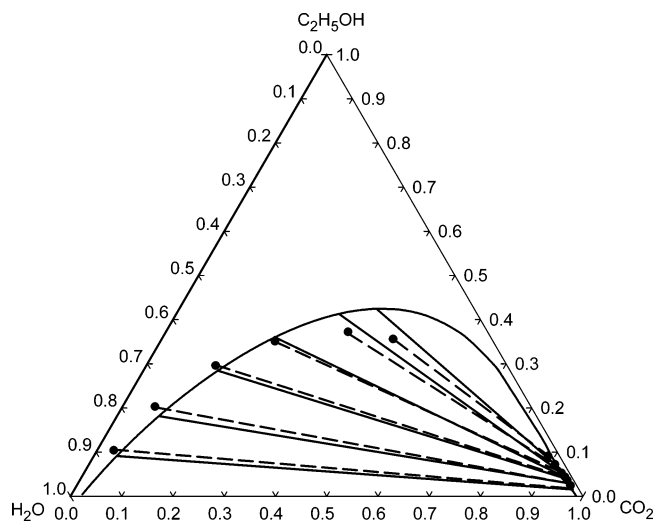
**Figure 6.** VLE of the ternary ethanol/water/CO<sub>2</sub> at 313.2 K and 10.1 MPa. Experiment: ●. Calculated: — PRSV-EoS; - - - PR-EoS.



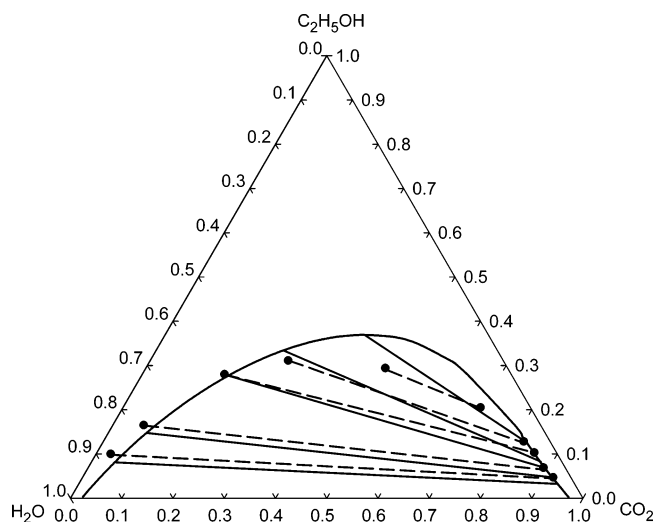
**Figure 7.** VLE of the ternary ethanol/water/CO<sub>2</sub> at 383.0 K and 9.91 MPa. Experiment: ●. Calculated: — PRSV-EoS; - - - PR-EoS.

solution. This step required an initial guess of the number of moles of CO<sub>2</sub> and used then the equation of state and a flash calculation method to obtain a new CO<sub>2</sub> mole number. By iteration, the number of moles of CO<sub>2</sub> corresponding to the measured cell volume under given pressure, temperature, and feed of ethanol and water were calculated, and the first working point ( $z_1, z_2, z_3$ )<sub>0</sub> was determined. The next step was to obtain the next working points, the  $k$ th point ( $z_1, z_2, z_3$ ) <sub>$k$</sub>  with a charge of  $n_{in}$  mol CO<sub>2</sub> (or CO<sub>2</sub>+ethanol) while discharging  $n_{out}$  mol CO<sub>2</sub> + ethanol + water from the vapor phase. Here  $n_{in}$  should be small enough to keep the results steadily unchanged; our calculations showed that 1% or less of the initial CO<sub>2</sub> mole number was a convenient choice (experiment also required that CO<sub>2</sub> flow rates should be small enough, here 3–7 g min<sup>-1</sup> that was small compared to the total CO<sub>2</sub> consumed). Last, we determined  $n_{out}$  until the liquid-phase disappeared (i.e., when the CO<sub>2</sub> vapor phase mole fraction reached 0.9999). This also required an iteration procedure by using the equation of state and a flash calculation method, starting from an initial guess of  $n_{out}$ .

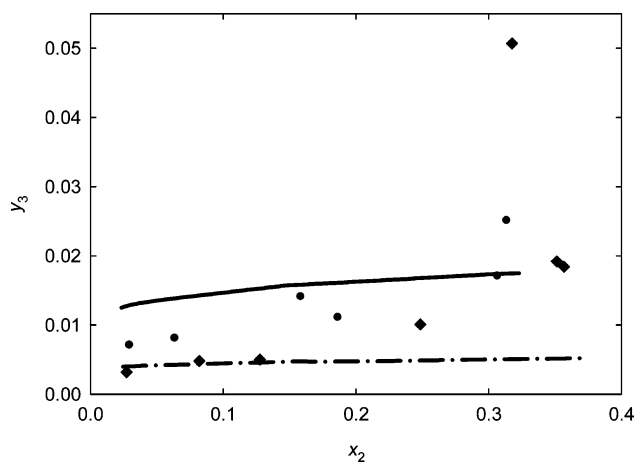
**Results.** Using the calculation method described above, several extraction pathways were simulated for



**Figure 8.** VLE of ethanol/water/CO<sub>2</sub> at 333.2 K and 11.8 MPa. Experiment: ●. Calculated: — PRSV-EoS.



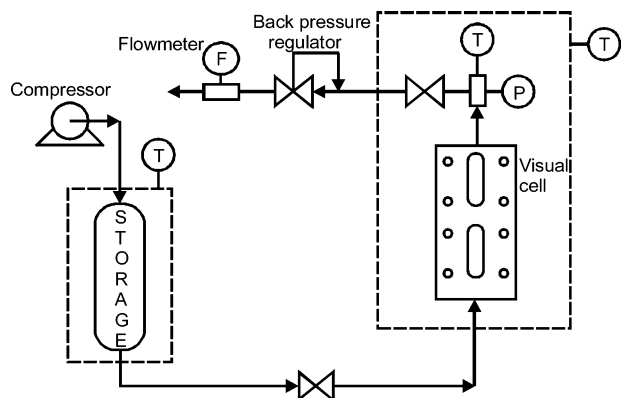
**Figure 9.** VLE of ethanol/water/CO<sub>2</sub> at 343.2 K and 18.5 MPa. Experiment: ●. Calculated: — PRSV-EoS.



**Figure 10.** Effect of the ethanol content in liquid phase ( $x_2$ ) on the water composition in vapor phase ( $y_3$ ). Experiment: ● (10.1 MPa, 313.2 K); ◆ (9.98 MPa, 313.3 K). Calculated with PRSV-EoS at 10.0 MPa and 313.2 K using two different sets of CO<sub>2</sub>/water interaction parameters: — [eq 11]; - - - [eq 13].

different initial mass fractions of ethanol and different ethanol feeds. Table 6 presents the variables that were kept constant in these simulations. Figure 12 shows the simulated results from the PRSV-EoS with the CO<sub>2</sub>/





**Figure 11.** Schematic of the apparatus used to obtain the water removal efficiency from ethanol solutions with high-pressure CO<sub>2</sub>.

**Table 6. Fixed Variables in the Simulation**

pressure	temperature	vessel volume	water content
10.0 MPa	313.2 K	200 cm <sup>3</sup>	0.5 mol

**Table 7. Comparison of Experimental Water Extraction Efficiencies (at 10.0 MPa, 313.2 K) with Those Predicted from the PRSV-EoS**

water/ ethanol (g)	mass fraction of ethanol	CO <sub>2</sub> consumed (mol)			
		expt	pred <sup>a</sup>	pred <sup>b</sup>	empirical <sup>13</sup>
1.3	0.1	18	8	17	16
2.4	0.2	30	12	29	27
5.1	0.5	38	10	38	38
1.8	0.6	11	7	10	9
3.6	0.7	14	7	15	12

<sup>a</sup> CO<sub>2</sub>/water binary parameters from eq 11. <sup>b</sup> CO<sub>2</sub>/water binary parameters from eq 13.

water parameters from eq 13. The same figure indicates that there exists a larger selectivity of the CO<sub>2</sub> for ethanol in the ternary system. It is evident that without ethanol feed the extraction enhancement promoted by the ethanol initial fraction ends rapidly and the system tends to a binary CO<sub>2</sub>/water behavior. It was also observed that the efficiency for complete water removal is little affected by the initial ethanol content.

Table 7 compares the water extraction efficiencies obtained experimentally at 10.0 MPa and 313.2 K with those predicted from the PRSV-EoS. There is a fairly good agreement between the experimental and predicted values using the CO<sub>2</sub>/water parameters from eq

13. Yet the results are unsatisfactory with the set of CO<sub>2</sub>/water parameters obtained from eq 11. This is because the CO<sub>2</sub>/water parameters from eq 13 give a very good description of the water content in the vapor phase at low ethanol concentration of the liquid phase, as Figure 10 shows. Table 7 also shows that the calculated results from an empirical method<sup>13</sup> fit well the data; yet, in most cases, it slightly underestimates the CO<sub>2</sub> consumptions.

## Volume Expansion

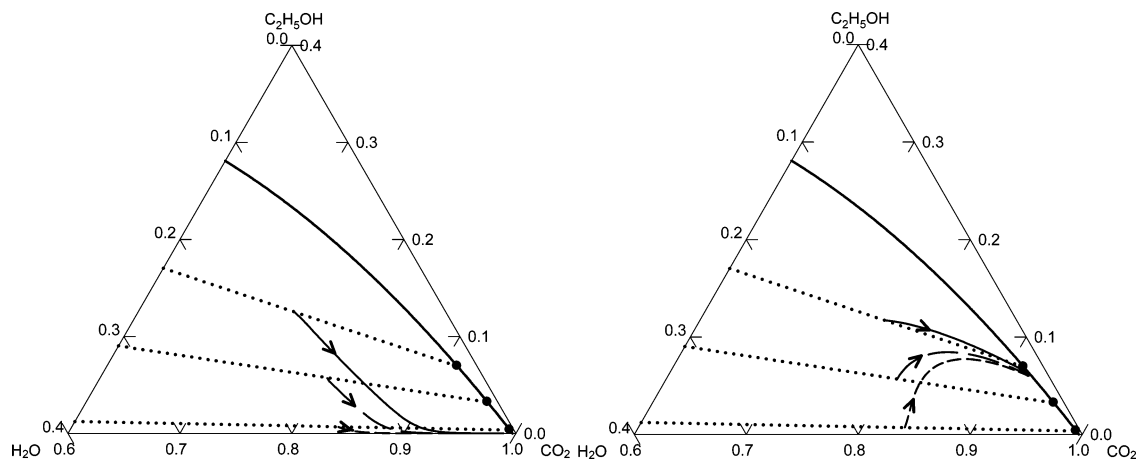
**Experiment.** To measure the ethanol/water volume expansion with CO<sub>2</sub> addition, an important factor to determine the operation conditions in a typical SAS process, we used the same apparatus schematically shown in Figure 11. The cell volumes corresponding to different liquid levels were carefully calibrated with pure water. The height of the meniscus of the liquid levels was measured with a micrometer cathetometer with an accuracy of 0.01 mm.

**Prediction.** An obvious advantage of using equations of state is that volumetric properties are conveniently obtained and therefore give volume expansions. The calculation procedure is simple and requires only the first step, already described above in the water removal calculation. Here, the volume expansion at pressure  $P$  and temperature  $T$  is defined as

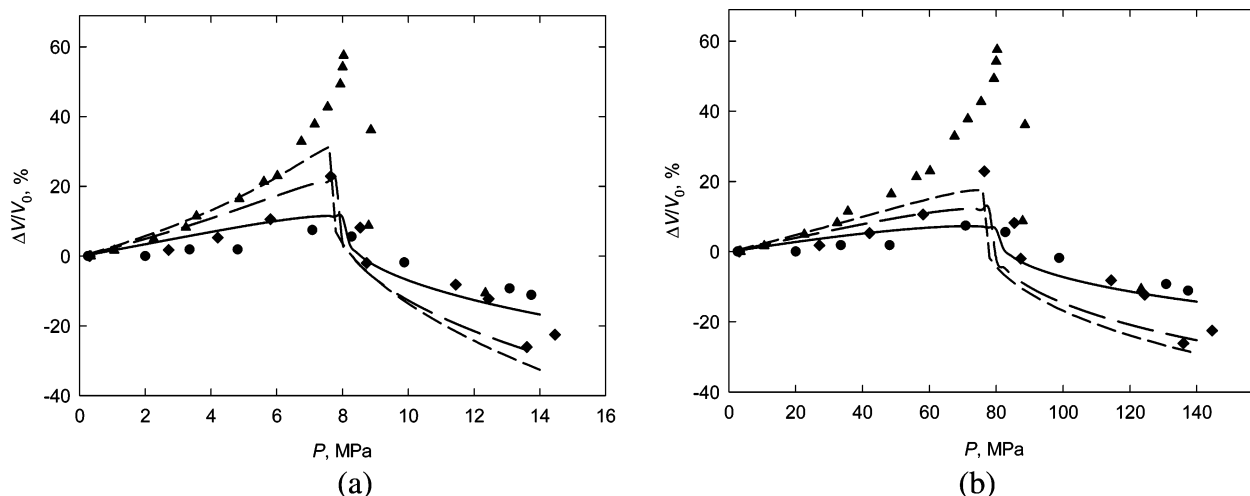
$$\frac{\Delta V}{V_0} = \frac{V(T, P, x_1) - V_0(T, P = 0.1 \text{ MPa}, x_1 = 0)}{V_0(T, P = 0.1 \text{ MPa}, x_1 = 0)} \quad (14)$$

where  $V_0$  is the initial total volume of the CO<sub>2</sub>-free ethanol/water saturated liquid mixture at atmospheric pressure,  $V$  is the total volume of the liquid ternary system CO<sub>2</sub>/ethanol/water at pressure  $P$ , and  $x_1$  is the mole fraction of the antisolvent (CO<sub>2</sub>) in the solution.

Figure 13 shows the volume expansions of CO<sub>2</sub>/ethanol/water at different pressures. The results show that there is a pressure limit (close to 7.8 MPa, the critical pressure of the CO<sub>2</sub>/ethanol binary mixture) up to which the liquid volumes increase and then decrease dramatically. Figure 13 also indicates that the agreement between the predicted and the experimental data is good at low initial mass fraction of ethanol (for example 0.5) or at low pressures (less than that of the mixture's critical pressure). After the critical point, there



**Figure 12.** Enlargement of the CO<sub>2</sub>-rich side of the ternary ethanol/water/CO<sub>2</sub> diagram showing extraction pathways at 10.0 MPa and 313.2 K with different initial ethanol mass fractions (0.7: —, 0.5: - - -, 0.1: ····) without ethanol feed (left) and with an ethanol feed of 0.05 mass fraction (right).



**Figure 13.** Volume expansions of ethanol/water by CO<sub>2</sub> addition at 313.2 K and different pressures. Symbols: experiment. Lines: predicted from PRSV-EoS. Initial ethanol mass fractions: 0.5 (●, —); 0.72 (◆, ---); 0.81 (▲, - · - ·). (a) CO<sub>2</sub>/water binary parameters from eq 11; (b) CO<sub>2</sub>/water binary parameters from eq 13.

is a large deviation between the predicted and the experimental data. When the initial mass fraction of ethanol is high (up to 0.81), the equilibrium mole fractions of ethanol in the liquid are between 0.39 and 0.63, and therefore the CO<sub>2</sub>/water parameters from eq 13 cannot describe the volume expansion even at low pressures as Figure 13(b) shows.

## Conclusions

Considering the potential application of the ternary system carbon dioxide/ethanol/water in different chemical engineering processes, namely in particle formation processes using supercritical fluid techniques and in supercritical fluid extraction processes, the phase equilibrium description of this system was reviewed and re-explored in particular by a mathematical algorithm. In this work, the simple and commonly used Peng–Robinson equation of state (PR-EoS) and the Stryjek and Vera modification of the Peng–Robinson equation of state (PRSV-EoS) were used to predict the ternary vapor–liquid equilibrium under various temperatures and pressures; we established a new algorithm that combined a flash calculation with the Broyden modified Newton–Raphson (BNR) method. This calculation shows the following: (1) The algorithm is stable to calculate all other compositions ( $x_1$ ,  $x_2$ ,  $y_1$ ,  $y_2$ ,  $y_3$ ) at constant temperature, pressure, and water mole fraction in the liquid ( $x_3$ ). Fixing  $x_3$  is preferred due to its insensitivity to the phase separation of this system. (2) The calculated results from both the PR-EoS and the PRSV-EoS are in good agreement with the experimental data for the binary and the ternary systems. For the PRSV-EoS the prediction average absolute deviations (AAD) for 201 experimental points of the ternary system are 2.7%, 1.6%, 1.1%, and 0.64% with respect to, respectively,  $x_1$ ,  $y_1$ ,  $y_2$ , and  $y_3$ . For the PR-EoS they are 3.0%, 1.7%, 1.2%, and 0.65%. (3) CO<sub>2</sub>/water binary interaction parameters have an important role in the prediction of the ternary system. Two sets of parameters were obtained from different objective functions. Both sets cannot fully describe the water mole fraction in the vapor phase of the ternary system. Yet one set is preferable for predicting the liquid compositions of the ternary system except around the plait point.

The water removal data from an aqueous solution by supercritical carbon dioxide were experimentally mea-

sured. Ethanol/water volume expansions at different pressures with high-pressure carbon dioxide were also measured in a view cell. The established phase equilibria calculations were applied to predict the volume expansion behaviors and evaluate the water removal efficiency. The results obtained show the following: (1) The calculation method using the selected equations of state can be efficiently applied to study the water removal process. Our simulation results indicate that without ethanol feed the extraction enhancement promoted by the ethanol initial fraction ends rapidly and the system tends to a binary CO<sub>2</sub>/water behavior. (2) There is a fairly good agreement between the experimental and the predicted CO<sub>2</sub> consumption for complete removal of water with respect to a given ethanol/water mixture. (3) The volume expansion prediction is good only for relatively low initial mass fractions of ethanol (about 0.5) or for pressures less than the mixture's critical point (about 7.8 MPa). After this critical pressure, noticeable differences exist between the predicted results and the experimental data.

## Acknowledgment

For financial support the authors are grateful to FCT, Lisbon (Project POCI/EQU/55911/2004 and post-doc grant BPD/5526/2001), European Union Program FED-ER, and NSFC, China (Project 20406015).

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Received for review January 19, 2005

Revised manuscript received June 7, 2005

Accepted June 23, 2005

IE050075H