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Correlation of Vapor–Liquid Equilibrium for Carbon Dioxide + Ethanol + Water at Temperatures from 35 to 70°C

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ABSTRACT

A simple mathematical model, based on polynomial functions, was used to correlate experimental vapor–liquid equilibrium (VLE) data for the CO_2 + ethanol + water system. The data were collected from the literature for temperatures 35, 40, 50, 60, and 70°C and pressures from 10 MPa to 18.5 MPa. This model is able to reproduce the equilibrium compositions of the two phases within the experimental error given in the group of selected publications.

INTRODUCTION

Supercritical CO_2 extraction from liquid solutions is a promising area, in spite of process difficulties that remain to be solved. It can lead to much lower operating costs than extraction from solids, as it is basically a continuous process that can be totally automated (1). Carbon dioxide can be used as the solvent for food and other human consumption products because of its established nontoxicity.

In the late 1970s and in the 1980s, numerous investigators worked on supercritical fluid extraction of ethanol from fermentation broths to obtain "dry" ethanol, to be used as fuel in motors. Although this has been abandoned as a

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possible application, a wealth of information on the phase equilibria of the CO_2 + ethanol + water system resulted from that work.

This system will continue to be important for several reasons. On one hand, it may be used as a model ternary mixture for the evaluation of mass transfer in countercurrent extraction (2). On the other hand, many fermented and distilled beverages contain valuable substances in minute quantities in hydroalcoholic solutions. Processes are being developed to extract these substances with supercritical carbon dioxide (3–5). Moreover, water and ethanol are two of a short (and ever-diminishing) list of solvents that may be used without restrictions in food and related industries. Hydroalcoholic mixtures are currently used to extract many substances from plants, and supercritical carbon dioxide may play a role in further fractionation of the resulting extracts.

The design of extraction columns to carry out the above-mentioned separations requires a detailed knowledge of the equilibrium compositions of the phases in contact. As CO_2 + ethanol + water will be present in much larger quantities than the other substances, a reliable method to correlate the available phase equilibrium data on this ternary mixture would be very useful.

Several equations of state (EOS) and different mixing rules have been applied to estimate the phase equilibrium behavior of the complex CO_2 + ethanol + water system (6–14). However, even in the cases where good quantitative agreement is obtained for the binary mixtures, it has been impossible to reproduce the experimental VLE results for the ternary CO_2 + ethanol + water mixture for the whole composition range.

Lim et al. (8) reported that the Patel-Teja EOS with the Adachie-Sugie mixing rule gives good agreement between experimental data and calculated values for the binary systems CO_2 + ethanol, CO_2 + water, and ethanol + water, but this model failed in correlating the ternary equilibrium compositions.

Yao et al. (9) report that the geometric mean combination rule for parameter b in a modified Peng-Robinson equation (PRM) allowed the reproduction of experimental results at 35°C up to higher $x_{\text{ethanol}} : x_{\text{water}}$ ratios than all other equations so far used by other authors. However, the parameters of the equation necessary for the equilibrium calculations are not reported in the available literature and no reliable comparison could be made.

Brunner and his co workers developed computational thermodynamic methods for correlating phase equilibria, using several van der Waals-type EOS and many variations of the mixing rules (15). These models qualitatively correlate binary and multicomponent phase equilibria by adjusting the interaction parameters to measured data. However, they cannot correlate the distribution coefficients and the separation factors of complex mixtures with sufficient accuracy for design purposes (16).

Bünz (10, 17) has successfully correlated the binary systems CO_2 + ethanol, CO_2 + water, and ethanol + water, using the Peng-Robinson EOS with the Adachie-Sugie and the Panagiotopoulos-Reid-Wong-Sandler mixing rules. Nevertheless, using the interaction parameters determined for each of the binary systems, the prediction of the phase behavior of the ternary system is not satisfactory. Although the slopes of the calculated tie lines are nearly consistent with the experimental ones, the estimated values of concentrations are far from the experimental concentration values. Bünz, using the phase equilibrium program (15), also performed an exhaustive work on the prediction of the ternary VLE using different EOS and several mixing rules. Significant deviations (Δx) of EOS-predicted equilibrium compositions from experimental data, at high pressures ($p > 10$ MPa), and for equilibrium compositions with $x_{\text{ethanol}} > 0.25$ are reported here. At 50°C and 10 MPa, for $x_{\text{ethanol}} = 0.37$ the deviation is $\Delta x = 0.1$ (10).

In this work, a particularly simple, yet powerful, procedure was applied to the available VLE data on hydroalcoholic + CO_2 mixtures (6–10, 18–20). The aim of the work was to achieve a simple method to interpolate and extrapolate data on liquid–fluid equilibrium compositions, within the experimental error, at given temperature and pressure conditions.

Selected Literature Data and Correlation Model

Three (liquid–liquid–gas) phases coexist at equilibrium for CO_2 + ethanol + water, under some conditions of temperature, pressure, and composition (13, 21). Higher-order critical phenomena in the CO_2 + ethanol + water system were reported by Shvarts and Efremova (22). At 47.4°C and 9.3 MPa, critical phenomena involving all three phases simultaneously were observed. However, for the conditions usually found in supercritical carbon dioxide extraction—temperatures higher than 35°C and pressures above 10 MPa—only one or two phase regions were observed (23).

A bibliography on VLE data covering a temperature range from 35 to 70°C and pressures from 10 to 18.5 MPa was compiled, because these intervals of pressure and temperature are those of potential interest for supercritical extraction applications. The data used in the correlation and the corresponding literature references (6–10, 18–20) are included in Table 1. Most of these data correspond to a type of ternary diagram that is called Type One, in the usual nomenclature for liquid–liquid equilibria (24). This means that there is total miscibility in the binary CO_2 + ethanol, and the ternary exhibits a plait point. The VLE curve is therefore continuous. The only exception in the selected data is at 70°C and the lower pressure, where the ternary diagram is Type Two, in the same nomenclature, and the VLE curve has two branches.

The aim of this work was to develop a simple algorithm to calculate the liquid–fluid equilibrium compositions for CO_2 + ethanol + water, by interpolation or extrapolation from experimental data, at 35, 40, 50, 60, and 70°C. The

TABLE 1
Bibliography of Experimental VLE Data of CO_2 + Ethanol + Water System

References:	T (°C)	p (MPa)
Gilbert and Paulaitis 1986 (18)	35	10.2; 13.6; 17.0
Takishima et al. 1986 (6)	35	10.1; 10.3
Nagahama et al. 1988 (7)	40	10.1
Inomata et al. 1990 (19)	35	10.2
Horizoe et al. 1993 (20)	40	10.1
Lim et al. 1994 (8)	40	10.1; 14.2; 18.5
	50	10.1; 10.5; 11.8
	60	11.8; 14.2; 18.5
	70	11.8; 14.2; 18.5
Yao et al. 1994 (9)	35	9.85
	40	9.81
	50	9.81
Bünz 1995 (10)	35	17

construction of the correlation algorithm starts with the conversion of the equilibrium compositions (in mole fraction), at each temperature and pressure, into rectangular coordinates X'_{CO2} and X'_{C2H5OH}, using Eqs. (1) and (2).

$$X'_{CO2} = (x_{CO2} + 1 - x_{H2O}) \cdot \cos(\pi/3) \quad (1)$$

$$X'_{C2H5OH} = x_{C2H5OH} \cdot \sin(\pi/3) \quad (2)$$

where x denotes the mole fraction composition for each experimental point in either the liquid or gas phase.

A polynomial function of the type

$$X'_{C_2H_5OH} = a_0 + a_1 X'_{CO_2} + a_2 X'^2_{CO_2} \quad (3)$$

is then fitted by a least-squares method.

Equation (3) correlates, in rectangular coordinates, the two branches, gas and liquid of the coexistence curve, with the exception of the data at 70°C and 12 MPa, where, as pointed out above, there is no plait point, and the coexistence curve is discontinuous.

Each experimental tie line corresponds, in the new coordinates, to an equation of the form

$$X'_{C_2H_5OH} = A + mX'_{CO_2} \quad (4)$$

The slopes m of the tie-lines were plotted, at each temperature and pressure, as a function of X'_{CO_2}. It was found that the variation was very nearly linear. Consequently, linear regression of the slopes of the experimental tie lines versus liquid equilibrium composition (X'_{CO_2}) was performed, and the following equation used to interpolate a new tie line for any given liquid equilibrium composition

$$m = b_0 + b_1 X'_{CO_2} \tag{5}$$

Coefficients for Eqs. (3) and (5) are reported in Tables 2 and 3, respectively. In Table 2, the standard deviation of the fit that measures the amount of error in the prediction of $X'_{C_2H_5OH}$ for an individual X'_{CO_2}, was also included. As was pointed out above, at 70°C and 12 MPa there are two sets of parameters in Table 2, one describing the liquid branch of the equilibrium curve and the other describing the gaseous branch.

A standard calculation with the above-described algorithm might proceed as follows

1. Take initial ethanol concentration in ethanol/water mixture and convert to rectangular coordinates—Eq. (1)—to give X'_{0,C_2H_5OH}
2. Calculate the slope (and intercept) of the operating line that joins the initial feed concentration ($0, x_{0,C_2H_5OH'}\ 1 - x_{0,C_2H_5OH}$) to the pure supercritical CO_2 point (1, 0, 0).

TABLE 2
Coefficients of Quadratic Equations Fitted to Experimental VLE Data (Eq. 3), in Rectangular Coordinates

T (°C)	p (MPa)	$a_0/10^{-2}$	a_1	a_2	$\lvert\Delta X'_{C_2H_5OH}\rvert$ [a]
35	10	−1.912	1.406	−1.396	0.007
	14	−1.020	1.326	−1.326	0.008
	17	−0.779	1.310	−1.312	0.007
40	10	−1.836	1.319	−1.304	0.007
	14	−2.247	1.440	−1.431	0.005
	18.5	−2.865	1.376	−1.359	0.004
50	10	−1.832	1.3641	−1.353	0.004
	12	−1.427	1.304	−1.297	0.003
60	12	−1.634	1.348	−1.339	0.003
	14	−1.023	1.274	−1.275	0.006
	18.5	−1.411	1.247	−1.248	0.006
70	12 [b]	−1.472	1.315	−1.223	0.008
	[c]	339.624	−5.054	1.634	0.001
	14	−1.463	1.284	−1.279	0.005
	18.5	−0.200	1.135	−1.149	0.007

[a] The standard error is a measure of the amount of error in the prediction of $X'_{C_2H_5OH}$ for an individual X'_{CO_2}.

[b] Parameters of the polynomial equation fitted to the equilibrium liquid compositions.

[c] Parameters of the polynomial equation fitted to the equilibrium gas compositions.

TABLE 3
Parameters of the Linear Regression of the Slopes of Experimental Tie Lines versus Liquid Composition (Eq. 5), in Rectangular Coordinates

	T				
	35°C	40°C	50°C	60°C	70°C
p (MPa)	$b_0/10^{-2}$ b_1	$b_0/10^{-2}$ b_1	$b_0/10^{-2}$ b_1	$b_0/10^{-2}$ b_1	$b_0/10^{-2}$ b_1
10	1.856	0.148	1.448	—	—
	−1.226	−1.092	−1.194	—	—
12	—	—	0.204	−0.253	1.161
	—	—	−1.036	−1.127	−1.668
14	0.688	0.181	—	0.183	0.126
	−1.101	−1.023	—	−1.067	−1.059
17	0.186	—	—	—	—
	−1.051	—	—	—	—
18.5	—	1.551	—	0.235	0.197
	—	−1.638	—	−0.948	−0.872

3. Determine the intercept of the operating line with the polynomial function—Eq. (3)—to obtain $X'_{CO_2,L}$ and $X'_{C_2H_5OH,L}$. This point is liquid phase concentration of carbon dioxide and ethanol in rectangular coordinates.
4. Calculate the slope of the tie line by inserting $X'_{CO2,L}$ into Eq. (5).
5. Calculate the intercept A by inserting the slope m and known liquid phase concentrations $X'_{CO_2,L}$ and $X'_{C_2H_5OH,L}$ into equation (4).
6. Determine the interception of the tie line,—Eq. (4),—with the polynomial function,—Eq. (3),—to obtain $Y'_{CO_2,V}$ and $Y'_{C_2H_5OH,V}$.
7. Reconvert liquid and vapor roots in rectangular coordinates to ternary compositions.

The algorithm described above is schematically presented in Fig. 1.

RESULTS AND DISCUSSION

In Fig. 2, experimental and calculated data are plotted at 35°C and 17 MPa. The experimental results are from two different sources, Gilbert and Paulaitis (18) and Bünz (10). The tie lines plotted in this figure are calculated by Eq. (5), starting at each experimental liquid equilibrium concentration. The calculated tie lines are virtually coincident with the experimental tie lines.

Selectivities defined by the ratio of the distribution coefficient of ethanol and water ($\alpha = y_{ethanol} : x_{ethanol}) : (y_{water} : x_{water})$ were used to test the predic-

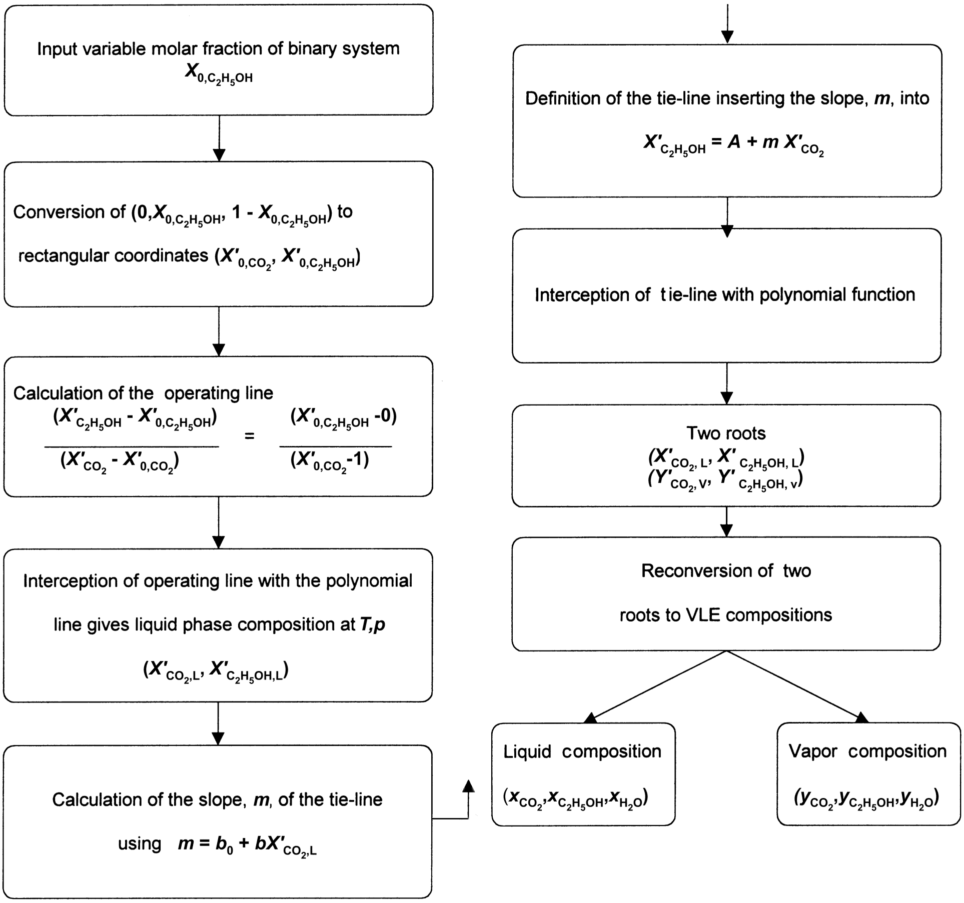


FIG. 1 Block diagram for the algorithm used in the correlation model of VLE data.

tive capability of the method. In fact, deviations between experimental and calculated values expressed in selectivities are usually larger than when only each equilibrium composition is considered.

In Table 4 the selectivities obtained in this work are compared with selectivities calculated from experimental VLE data published in the literature.

Figure 3 compares calculated selectivities from this work with those obtained by de la Ossa et al. (11) and Kuk and Montagna (25), that were not included in the correlation. The reported data from de la Ossa et al. were excluded because of the absence of the CO_2 equilibrium liquid compositions; those of Kuk and Montagna do not include tables with values of experimental

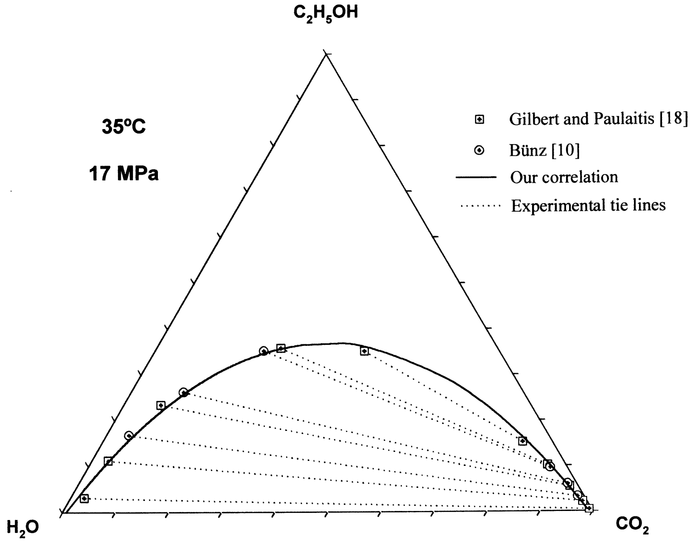


FIG. 2 Ternary diagram of CO_2 + ethanol + water system at 35°C and 17 MPa. Comparison between calculated and experimental vapor–liquid equilibrium data.

vapor–liquid equilibrium compositions. However, the latter authors report selectivity values as a function of ethanol composition in the initial binary mixture (hydroalcoholic feed) that allow a straightforward comparison with the data calculated here. The comparison showed good agreement with selectivities from Kuk and Montagna but deviate significantly from the values determined by de la Ossa et al.

TABLE 4
Comparison of Selectivities α* Determined in Our Work with Values Obtained with Experimental Tie Lines Included in the Correlation

T	p/MPa	$\frac{x_{ethanol}}{x_{ethanol} + x_{water}}$	Our work Selectivity (α)	Other authors
35°C	10	0.27	9	9[6]; 10[18]
		0.39	6	6[18]; 6[9]
	17	0.26	8	9[18]; 9[10]
40°C	10	0.035	36	36[8]; 55[7]
		0.1	36	39[7]; 30[9]

* $\alpha = (y_{ethanol}/x_{ethanol})/(y_{water}/x_{water})$.

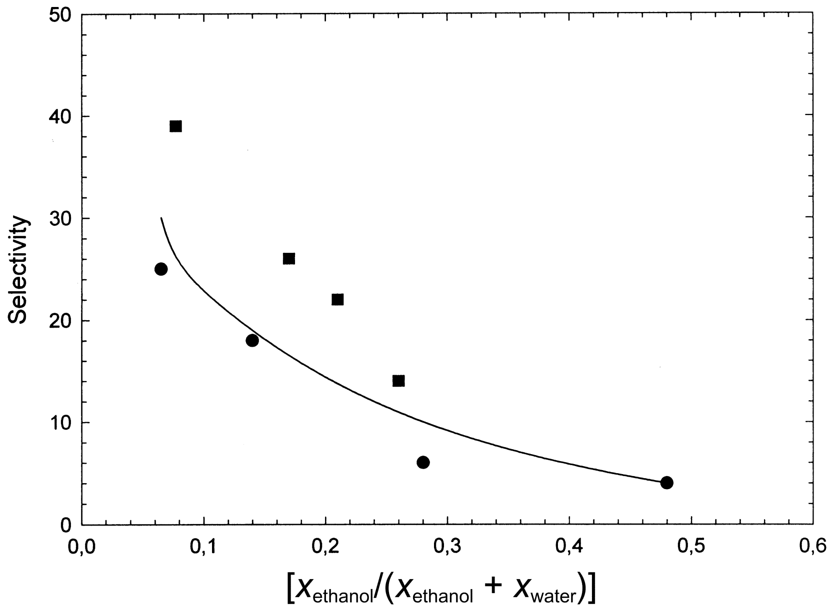


FIG. 3 Comparison of selectivities $\alpha = (y_{ethanol}/x_{ethanol})/(y_{water}/x_{water})$ at different compositions of ethanol in feed, at 40°C and 10 MPa [— this work, ● Kuk and Montagna (25), ■ de la Ossa et al. (11)].

The correlating capability of the model for the phase equilibrium of the CO_2 + ethanol + water system at different conditions of temperature and pressure studied in this work is summarized in Fig. 4. Experimental equilibrium data are compared to those evaluated using the algorithm developed in this work. The polynomial method gave good correlation in the whole range of concentrations for all temperatures and pressures covered. The mean deviation of the predicted equilibrium vapor–liquid compositions is $\Delta x < 0.05$ in the whole concentration range.

The equilibrium curve at 14 MPa and 313 K predicts, in the vicinity of the plait point, ethanol concentrations that seem slightly too high. The absence of experimental tie lines in this concentration range leads to a set of predicted values richer in ethanol than expected, compared to the equilibrium curves obtained for the other pressure conditions.

The capability of this predictive model to estimate phase equilibrium compositions at p,T conditions not reported in literature was tested by comparing the calculated selectivities obtained by extrapolation with experimental selectivities. The procedure to evaluate the errors associated to the extrapolation in pressure at the same temperature and to the extrapolation in temperature at the

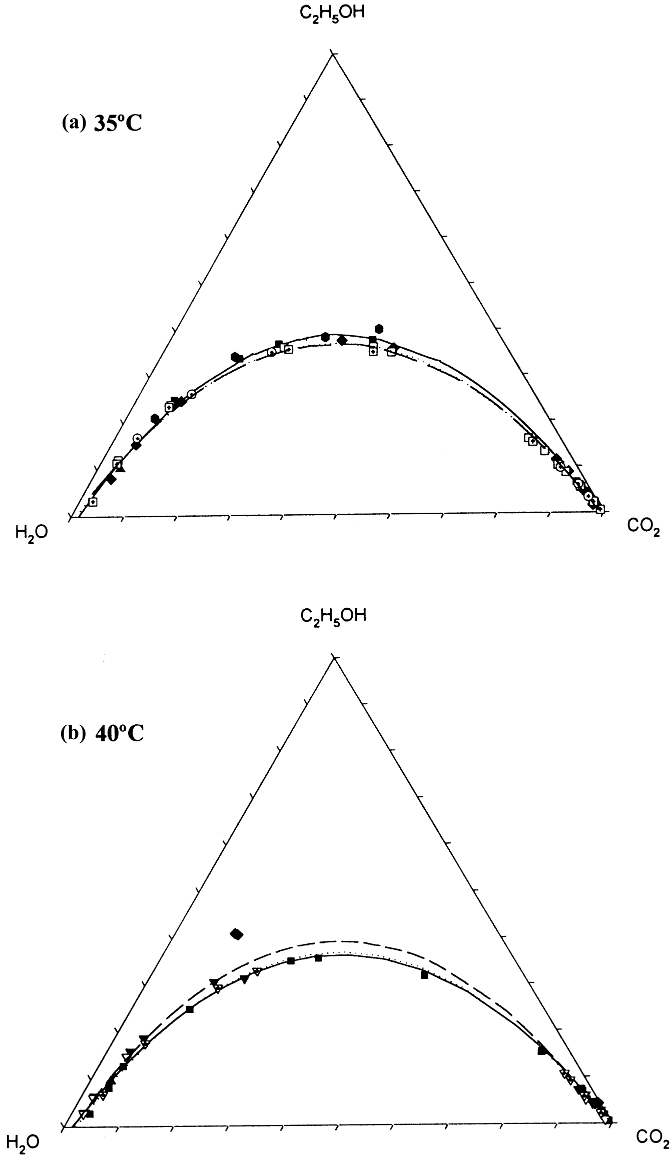
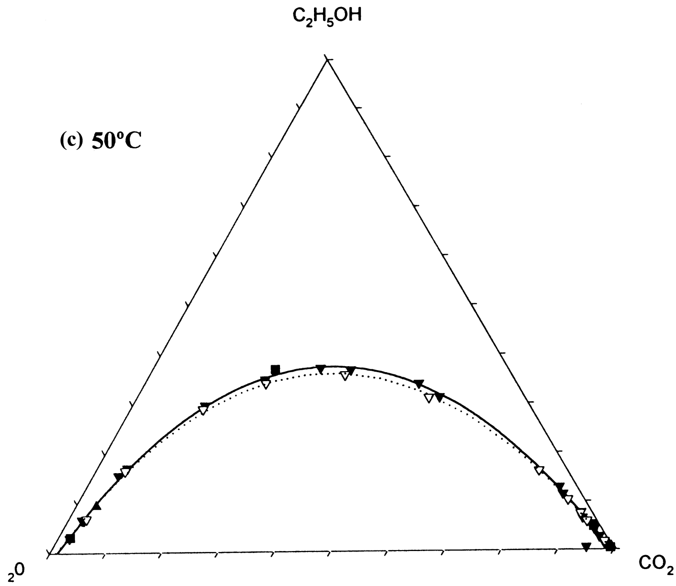


FIG. 4 Ternary diagrams of CO_2 + ethanol + water system at differents temperatures as function of pressure. Comparison between calculated and experimental vapor–liquid equilibrium data. (A) $T = 35°C$, 10 MPa [■ Gilbert and Paulaitis (18), ◆ Takishina et al. (6); ⬢ Inomata et al. (14), ▲ Yao et al. (9), — this work]; 14 MPa [□ Gilbert and Paulaitis (18), ······ this work]; 17 MPa [⊞ Gilbert and Paulaitis (18), ⊕ Bünz (10), – – this work]. (B) $T = 40°C$, 10 MPa [■ Nagahama et al. (7), ◆ Horizoe et al. (20)]; ▼ Lim et al. (8), ▲ Yao et al. (9), — this work]; 14 MPa [▽ Lim et al. (8), – – this work]; 18 MPa [▽ Lim et al. (8), ······ this work].



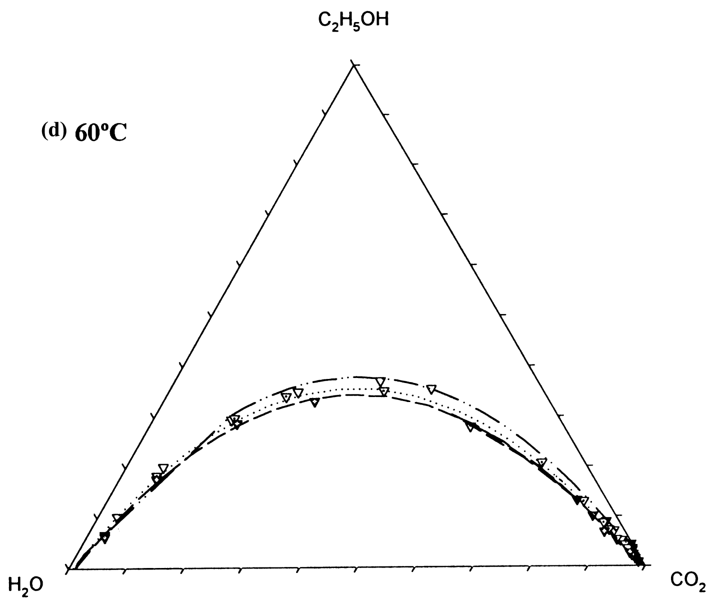


FIG. 4 (Continued) (C) $T = 50°C$, 10 MPa [■ Gilbert and Paulaitis (18), ▼ Lim et al. (8), ▲ Yao et al. (9), — this work]; 12 MPa [▽ Lim et al. (8), ······ this work]. (D) $T = 60°C$, 12 MPa [▽ Lim et al. (8), —·····— this work]; 14 MPa [▽ Lim et al. (8), ······ this work]; 18.5 MPa [▼ Lim et al. (8), - - this work].

(*continued*)

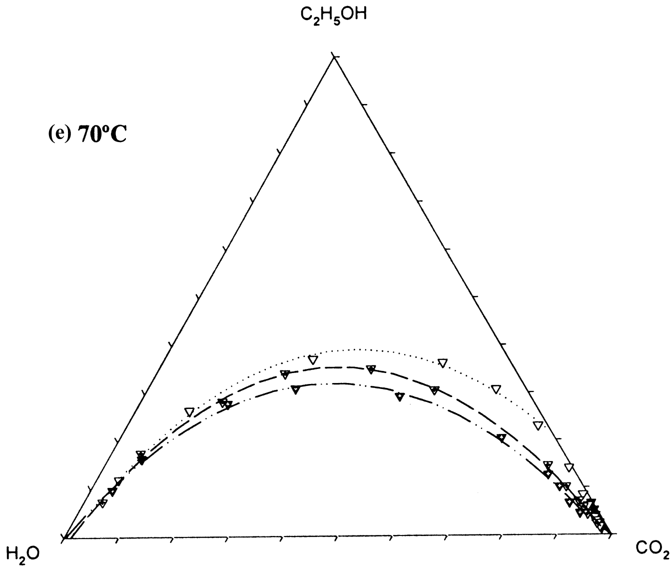


FIG. 4 (Continued) (E) T = 70°C, 11.8 MPa [▽ Lim et al. (8), ····· this work]; 14 MPa [▽ Lim et al. (8), —— this work]; 18.5 MPa [▼ Lim et al. (8), —·— this work].

same pressure consisted of:

- using calculated phase equilibrium compositions at 35°C and 10 MPa and at 35°C and 14 MPa, phase equilibrium compositions were estimated at 35°C and 17 MPa;
- using calculated phase equilibrium compositions at 35°C and 14 MPa and at 60°C and 14 MPa, phase equilibrium compositions were estimated at 70°C and 14 MPa.

In Fig. 5, the calculated selectivities are compared as a function of ethanol composition in the liquid phase. The comparison showed that the deviations of the predicted selectivities from the experimental values are less than 15% for $x_{ethanol} > 0.2$ and increases up to 25% for mixtures poorer in ethanol. These results are of the same magnitude as the deviations between experimental selectivities from other sources (11, 25).

As reviewed in the introduction, models have been developed using several EOS and different mixing rules trying to describe the phase equilibrium behavior of the complex CO_2 + ethanol + water system. As a matter of fact, a rigorous thermodynamic method such as EOS that also could be used for simultaneous computation of calorimetric and volumetric properties along with phase compositions cannot be substituted by an empirical method. However,

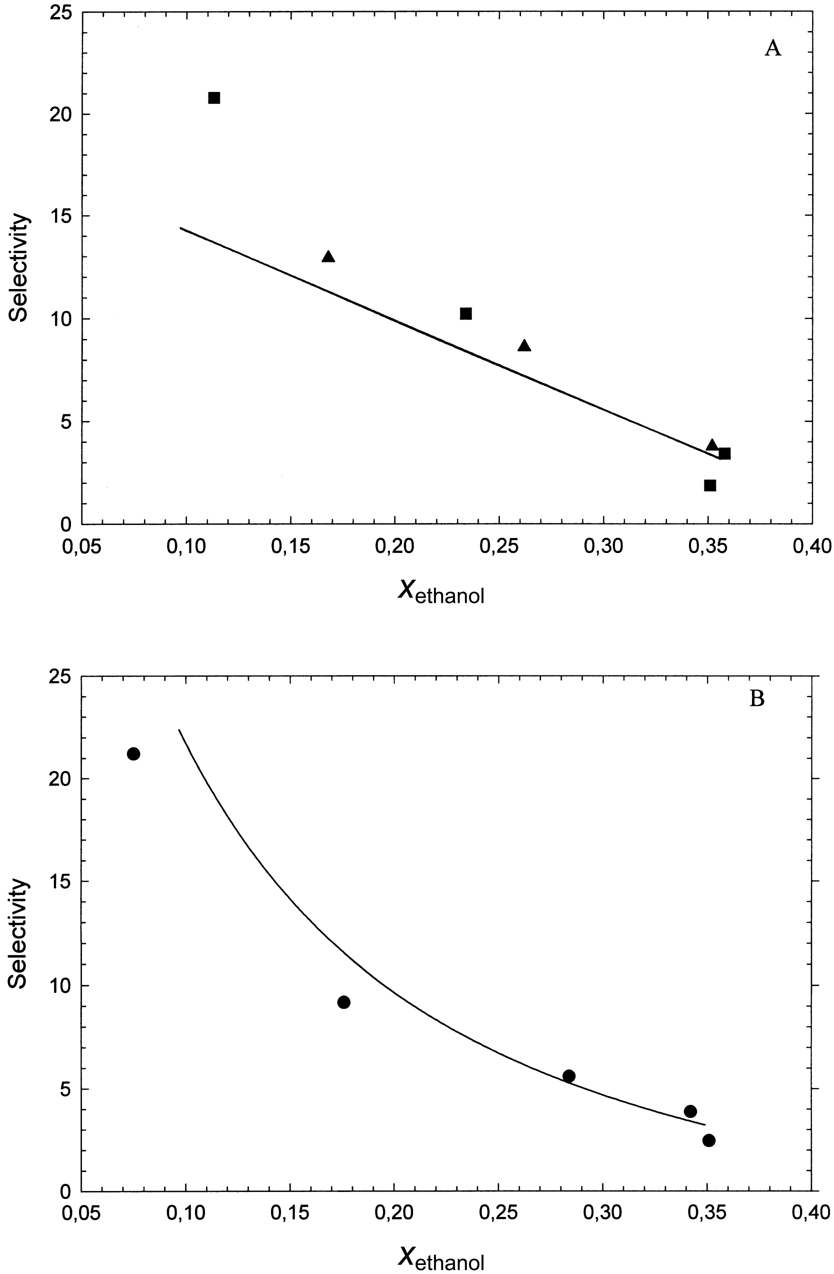


FIG. 5 Comparison of selectivities $\alpha = (y_{ethanol}/x_{ethanol})/(y_{water}/x_{water})$ at different compositions of ethanol in the liquid phase. (A) 35°C and 17 MPa [— this work, ▲ Paulatis et al. (18), ■ Bünz (17)]; (B) 70°C and 14 MPa [— this work, ● Lim et al. (8)].

the need to describe the phase behavior of this ternary mixture for practical applications utilizing supercritical fluids was the specific motivation for developing the current correlation. This simple predictive method is well-suited for phase equilibrium calculations at pressures and temperatures usually chosen in supercritical extraction processes. At the temperature and pressure conditions reported in the literature only discrete tie lines are available; with the present algorithm the vapor–liquid phase compositions can be predicted, over the entire composition range, within the experimental error. Another major advantage of this procedure is the ability to calculate vapor–liquid phase compositions for temperatures and pressures outside the given conditions, as illustrated in Fig. 5.

CONCLUSIONS

Vapor–liquid equilibrium of the CO_2 + ethanol + water system has been correlated. The method described in this work correlates vapor–liquid equilibrium concentrations for temperatures of 35, 40, and 50°C, in a pressure range of 10 MPa $\leq p \leq$ 18.5 MPa, and for temperatures of 60 and 70°C and pressures from 12 to 18.5 MPa. The mean deviation of the predicted equilibrium vapor–liquid compositions is $\Delta x < 0.05$ in the entire concentration range. Selectivities calculated were favorably compared with data from sources that were not included in the input data for the correlation.

Because good agreement was obtained in the high-pressure vapor–liquid equilibrium for the CO_2 + ethanol + water system with this method, it can be applied for process design and modeling of a supercritical fluid extraction process from hydroalcoholic mixtures.

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