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HIGH PRESSURE PHASE EQUILIBRIUM IN CARBON DIOXIDE+ETHANOL SYSTEM

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Sunt prezentate date de echilibru lichid-vapori (ELV) la 343.2 şi 363.2 K la presiuni între 1 şi 14 MPa şi date critice (presiune-temperatură-compoziţie) pe intervalul de presiune între 9 şi 14 Mpa, pentru sistemul dioxid de carbon + etanol. Metoda experimentală folosită în această lucrare a fost o metodă analitică statică cu luare de probe din faza lichidă folosind un injector "on line" cuplat cu un gaz cromatograf pentru analiză. Datele de ELV măsurate pentru sistemul dioxid de carbon + etanol au fost modelate cu o ecuaţie cubică generală de stare, folosind regulile clasice de amestecare van der Waals.

Un set unic de parametri, ales astfel încât să reprezinte bine maximul în presiunea critică, a fost utilizat predictiv pentru calcularea datelor de echilibru şi a punctelor critice. Rezultatele arată o concordanţă satisfăcătoare între model şi datele experimentale.

Vapor–liquid equilibria (VLE) data at 343.2 and 363.2 K and pressures between 1 and 14 MPa, and critical data (pressure - temperature - composition) at pressures between 9 MPa and 14 MPa for the carbon dioxide + ethanol system are reported. The experimental method used in this work was a static analytical method with liquid phase sampling using a rapid on-line sampler injector coupled to a gas chromatograph for analysis. Measured VLE data for carbon dioxide + ethanol system were modeled with a general cubic equation of state using classical van der Waals mixing rules.

A single set of interaction parameters, representing well the critical pressure maximum was used in this work to calculate the VLE data and critical points. The results show a satisfactory agreement between the model and the experimental data.

Keywords: equation of state, VLE, carbon dioxide, ethanol.

1. Introduction

Supercritical fluid extraction is an important alternative to conventional methods, such as extraction, particle micronization, material processing, chromatography or crystallization/purification.

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High-pressure vapor–liquid equilibrium measurements of carbon dioxide + alcohol systems are of interest due to their importance in the supercritical extraction of thermal labile compounds, dehydration of alcohols using supercritical carbon dioxide, and extraction of natural products using near critical solvents.

The carbon dioxide + ethanol mixture is very important industrially and the system has received much attention [1,2]. The goals of this work were to add new experimental VLE data and critical points measured using a rapid on-line sampler injector (ROLSI) [3], and to represent the global phase behavior of carbon dioxide + ethanol system with a simple cubic EOS model, based on a single set of interaction parameters.

Therefore, in this work we made new VLE measurements using a static-analytical method, in a high-pressure visual cell with variable volume, for carbon dioxide + ethanol. New critical points (pressure - temperature - composition) were also measured in the same visual cell.

In our previous papers [1,2], the global phase behavior of carbon dioxide + ethanol system was modeled with the cubic general equation of state (GEOS) [4-6], coupled with classical van der Waals mixing rules (two parameters conventional mixing rule—2PCMR). This cubic equation is a generalized form with four parameters for all cubic equations of state with two, three and four parameters.

A single set of interaction parameters, representing well the critical pressure maximum (CPM) was used to model the global phase behavior of the carbon dioxide + ethanol system [1]. The same set of parameters is used in this work to represent the new VLE data and critical points.

2. Apparatus and procedure

A detailed description of the experimental apparatus was presented in earlier papers [2,7]. The apparatus is based on a high pressure visual cell with variable volume, to which a rapid on-line sampler injector (ROLSI) was added and coupled with a gas chromatograph (GC). The set-up is shown in fig. 1. The ROLSI is connected by a capillary to the equilibrium cell. A heating resistance is used to heat the expansion chamber of the sampler injector in order to have liquid samples vaporized rapidly. The transferring line between ROLSI and the GC is heated by means of a linear resistor coupled to an Armines /CEP/TEP regulator. The GC (Perichrom 2100) uses a thermal conductivity detector, TCD, and a 30 m long and 0.530 mm diameter column HP-Plot/Q. The GC carrier gas is helium at a flow rate of 30 mL/min. The apparatus was completed with a syringe pump Teledyne ISCO model 500D.

The procedure is similar to that used in our previous work [2,7]. The entire internal loop of the apparatus including the equilibrium cell was rinsed several times with carbon dioxide. Then, the equilibrium cell was evacuated with a vacuum pump. The cell was filled with alcohol, which was degassed by using a vacuum pump and vigorously stirring. The lighter component (in this case CO_2) is introduced with the syringe pump into the equilibrium cell to set the pressure to the desired value. Then the cell was heated to the experimental temperature. To facilitate the approach to an equilibrium state, the mixture in the cell was stirred for a few hours. Then the stirrer was switched off, and the mixture was allowed for about 1 h to completely separate the coexisting phases. Samples of liquid phase are withdrawn by ROLSI and analyzed with GC. Normally at least six samples of the liquid phase were analyzed at the equilibrium temperature and pressure, in order to check the repeatability. The sample sizes being very small, the equilibrium pressure in the cell remains constant.

The calibration of the TCD for CO_2 and ethanol is done by injecting (using gas chromatographic syringes) known amounts of each component. Calibration data are fitted to quadratic polynomials to obtain the mole number of the component versus chromatographic area. The correlation coefficients of the GC calibration curves were 0.999 for carbon dioxide and 0.997 for ethanol.

The critical points were obtained in this work following the procedure of Scheidgen [8]. At a fixed temperature (for example 373 K), the pressure in the cell was increased by introducing CO_2 with the syringe pump. The transition from heterogeneous (two phases) to the homogeneous range is visually observed. Then, by slowly cooling (1-3 K) the pressure in the cell decreases and the inverse transition from homogeneous to heterogeneous range can be observed. The temperature and the pressure of the opalescence point are considered as the critical point coordinates. The composition corresponding to the critical point is obtained by sampling from the homogeneous mixture. The procedure is then repeated by introducing new amounts of CO_2, and slowly cooling.

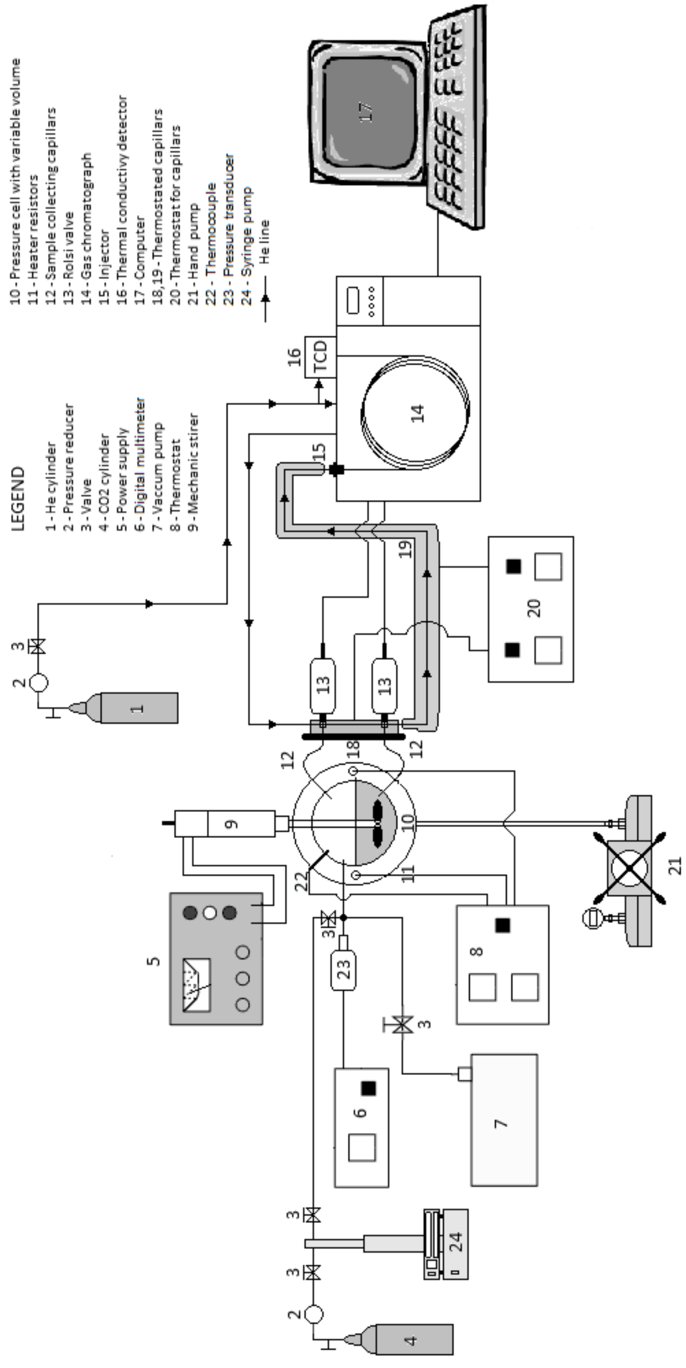

Fig. 1. High pressure phase equilibrium set-up

3. GEOS3C equation of state

List of symbols

a, b, c, d	- parameters in GEOS
AAD	- absolute average deviation
B	- dimensionless parameter in GEOS3C, eq. (5)
C_1, C_2 and C_3	- parameters in GEOS3C temperature function
H	- enthalpy
M	- molar mass
P, P^S	- pressure, saturation pressure
R	- universal gas constant
S	- entropy
T	- temperature
V, V^L, V^V	- molar volume, liquid volume, vapor volume
Y	- thermodynamic function (general notation)
Z	- compresibility factor

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α_c	- Riedel's criterium (parameter in GEOS)
β	- reduced temperature function in GEOS
Ω_a, Ω_b, Ω_c, Ω_d	- parameters of GEOS
ω	- acentric factor

Subscripts

c	- critical property
r	- reduced property

As pointed out previously [4-6], the cubic GEOS equation is a general form for all the cubic equations of state with two, three and four parameters. This is the meaning of the statement “general cubic equation of state” used for GEOS.

$$P = \frac{RT}{V-b} - \frac{a}{(V-d)^2 + c} \tag{1}$$

The four parameters a, b, c, d for a pure component are expressed by:

$$a = a_c\,\beta^2(T_r), \quad a_c = \Omega_a \frac{R^2T_c^2}{P_c}, \quad b = \Omega_b \frac{RT_c}{P_c} \tag{2a}$$

$$c = \Omega_c \frac{R^2T_c^2}{P_c^2}, \quad d = \Omega_d \frac{RT_c}{P_c} \tag{2b}$$

The temperature function used is:

$$\beta(T_r) = T_r^{-m} \tag{3}$$

with the reduced temperature $T_r = T / T_c$.

The expressions of the parameters Ω_a, Ω_b, Ω_c, Ω_d are:

$$\Omega_a = (1-B)^3 \qquad \Omega_b = Z_c - B \qquad \Omega_c = (1-B)^2(B-0.25) \qquad \Omega_d = Z_c - 0.5(1-B) \tag{4}$$

$$B = \frac{1+C_1}{\alpha_c + C_1} \qquad \alpha_C \text{ - Riedel's criterion} \tag{5}$$

As observed, the *a*, *b*, *c*, *d* coefficients of the cubic GEOS equation are finally function of critical data (T_c P_c and V_c), *m* and α_c parameters.

In this work, the coefficients *a*, *b*, *c*, *d* were obtained for mixtures using the classical van der Waals mixing rules:

$$a = \sum_i \sum_j x_i x_j a_{ij} \qquad b = \sum_i \sum_j x_i x_j b_{ij}$$

$$c = \sum_i \sum_j x_i x_j c_{ij}\,; \qquad d = \sum_i x_i d_i \tag{6}$$

$$a_{ij} = (a_i a_j)^{1/2}(1-k_{ij})\,; \qquad b_{ij} = \frac{b_i + b_j}{2}(1-l_{ij})$$

$$c_{ij} = \pm(|c_i||c_j|)^{1/2} \qquad \text{(with ``+'' for } c_i, c_j > 0 \text{ and ``}-\text{'' for } c_i \text{ or } c_j < 0\text{).} \tag{7}$$

Generally, negative values are common for the *c* parameter of pure components.

The GEOS parameters *m* and α_c of each component were estimated by constraining the EOS to reproduce the experimental vapor pressure and liquid volume on the saturation curve between the triple point and the critical point. The values of critical data and GEOS parameters of the pure components are given in Table 1.

The binary interaction parameters, k_{12} and l_{12}, ($k_{12} = 0.06$, $l_{12} = -0.01$) were estimated in our previous paper [1], to represent well the critical pressure maximum and to decrease the temperature of the UCEP (upper critical end point) at lower temperature (~270 K). The carbon dioxide + ethanol system is a Type I phase behavior, according to the classification of van Konynenburg and Scott [9], but the EOS model can predict a type II behavior with an UCEP. In this case the temperature of UCEP must be decreased at low temperature values. The region of the Type I (II) phase behavior can be obtained by tracing the tricritical and double critical end point boundary curves in the k_{12}–l_{12} global phase diagram of Polishuk et al. [10]. These types of phase behavior are located on the left side of the tricritical boundary. The values of the interaction binary parameters (k_{12} and l_{12}) fulfilling these requirements are $k_{12} = 0.06$, $l_{12} = -0.01$.

The calculations were made using the software package PHEQ, developed in our laboratory [11].

4. Results and discussion

The equilibrium compositions for the carbon dioxide + ethanol binary system were measured at 343.2 and 363.2 K and pressures between 1 and 14 MPa and the results are shown in Figs. 2 and 3. GEOS predictive calculations with the single set of parameters (k_{12} = 0.06, l_{12} = −0.01) were done for the new experimental data of this work.

Table 1

Critical data [12] and GEOS parameters for carbon dioxide and ethanol [13]

Component	T_c /K	P_c /MPa	V_c /(cm^3/mol)	α_c	m
CO_2	304.1	73.8	93.9	7.0517	0.3146
C_2H_5OH	513.9	61.4	167.1	9.3121	0.6146

Fig. 2 and 3 show a comparison of our experimental data (symbols) at T = 343 K, and T = 363 K with the prediction results by GEOS equation (line). It can be seen, that both sets of data are satisfactorily represented by the curve obtained with the GEOS equation. Taking into account the semipredictive approach used in our previous work [1], the single set of interaction parameters leads to satisfactory prediction of VLE for the carbon dioxide + ethanol system.

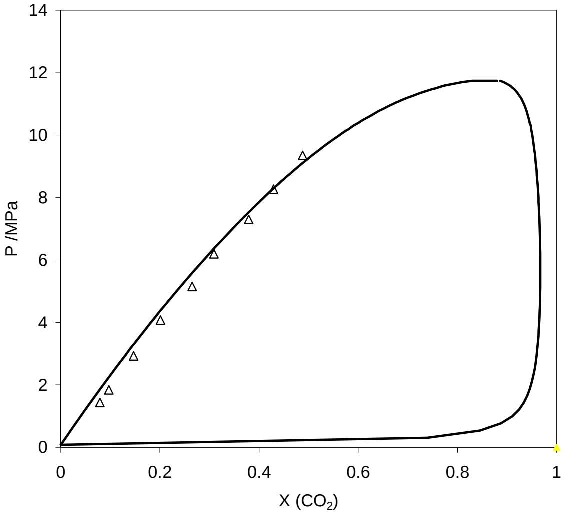

Fig. 2. Phase equilibrium data for the carbon dioxide (1) + ethanol (2) system at T = 343.2 K; △ experimental data; — GEOS/2PCMR prediction

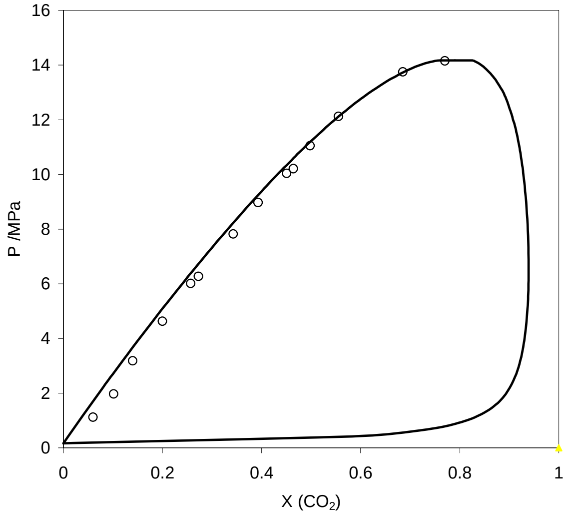

Fig. 3. Phase equilibrium data for the carbon dioxide (1) + ethanol (2) system at $T = 363.2$ K; ○ experimental data; — GEOS/2PCMR prediction

The critical properties (P_c, T_c, X_{1c}) for the carbon dioxide + ethanol binary system, measured in this work at pressures between 9 MPa and 14 MPa, are shown in Figs. 4 and 5. The compositions of critical points were obtained as those for VLE by gas chromatographic analysis.

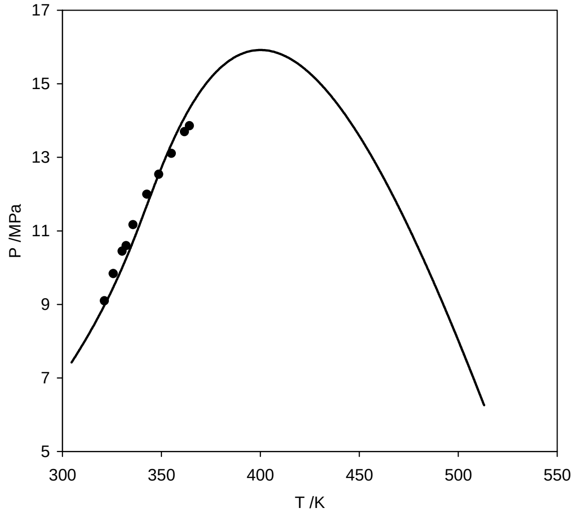

Fig. 4. P-T fluid phase diagram of carbon dioxide + ethanol system. ●, critical points measured in this work; — GEOS/2PCMR prediction

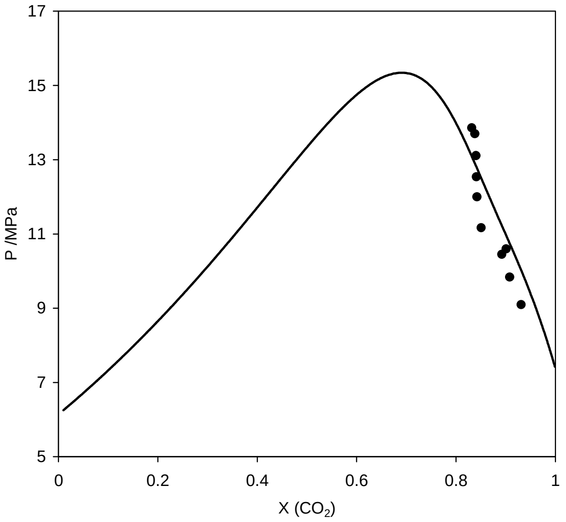

Fig. 5. P-X fluid phase diagram for carbon dioxide + ethanol system. ●, critical points measured in this work; — GEOS/2PCMR prediction

In these figures we have illustrated also the prediction with GEOS/2PCMR for $k_{12} = 0.06$ and $l_{12} = -0.01$. As can be seen in the Figs. 2-3, the liquid phase data are well represented by the predicted curves, with GEOS equation. This fact leads to a reasonable prediction of the vapor phase curve, which is also shown in the figures. It can be observed that the critical pressure maximum is a little overestimated.

5. Conclusions

In this work we report new measured VLE data with a static-analytical method using a rapid on-line sampler injector coupled to a GC for analysis, in a high-pressure visual cell with variable volume, for carbon dioxide + ethanol at 343.2 and 363.2 K and pressures between 1 and 14 MPa. New critical points (pressure - temperature - composition) were measured in the same visual cell at pressures between 9 MPa and 14 MPa.

Measured VLE and critical data for carbon dioxide + ethanol system were modeled with a general cubic equation of state (GEOS) using classical van der Waals mixing rules.

A single set of interaction parameters, representing well the critical pressure maximum was used in this work to represent the new VLE data and critical points. The predictions show a satisfactory agreement between the model and the experimental data.

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