U.P.B. Sci. Bull., Series B, Vol. 77, Iss. 1, 2015 ISSN 1454-2331

VALIDATION OF A NEW APPARATUS FOR DETERMINING HIGH-PRESSURES PHASE EQUILIBRIUM OF MIXTURES

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The experimental setup of a new apparatus for measuring high-pressure phase behavior using the static method is described. The new experimental setup was validated measuring vapor–liquid equilibria (VLE) data for the carbon dioxide + 1-undecanol system at 333.15 K and at pressures up to 150.20 bar. The experimental results are discussed and compared with available literature data. Measured VLE data and literature data for carbon dioxide + 1-undecanol system were modeled with cubic equations of state (EoS) using classical van der Waals (two-parameter conventional mixing rule, 2PCMR) mixing rules.

Keywords: experimental methods, vapor–liquid equilibria, carbon dioxide, 1-undecanol, equation of state

1. Introduction

An important role in cost-effective design and operation of chemical and biochemical plants plays the accurate knowledge of phase behavior and of thermophysical properties of fluids [1-3]. While the thermodynamic properties determine the feasibility of a given process, the transport properties have a major impact on sizing of the equipment [1]. Accurate and reliable thermodynamic and transport property data, over a wide range of mixtures and conditions, are required due to the diversity of products and applications [1-3].

In the Thermodynamic Research Laboratory of Politehnica University of Bucharest were conducted in the last years a series of experimental and theoretical investigations of the phase equilibria for binary mixtures of carbon dioxide and alcohols [4-6]. A new equipment for measuring high-pressure phase behavior of systems containing carbon dioxide has been commissioned. The method used is static-analytical with phases sampling. In this study we present the validation

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results for the carbon dioxide + 1-undecanol system. The high-pressure measurements were conducted at 333.15 K, as experimental data are available in literature at the same temperature. The new experimental data are in good agreement with previous measurements for the system investigated.

The new measurements and available literature data were modeled with cubic equations of state (EoS) coupled with classical van der Waals mixing rules. The equations of state used are the cubic general equation of state, GEOS [7,8], Peng-Robinson, PR [9], and Soave-Redlich-Kwong, SRK [10]. The model results were compared to the new data reported in this work and to available literature VLE data. The results show a good agreement between the models and the experimental data.

2. Experimental section

Materials. Carbon dioxide (mass fraction purity > 0.997) was provided by Linde Gaz Romania, Bucharest, Romania, and 1-undecanol (mass fraction purity > 0.999) was an Aldrich product. The chemicals were used as supplied.

Apparatus and Procedure. The new setup is schematically shown in Fig. 1. The main part of the installation used in this work is a high pressure visual cell (4) with constant volume built by SEPAREX Supercritical Fluid Technology, project 4261 type SC350 [11]. The cell consists in a sapphire tube enclosed by two metallic lids and offers a complete view on the full cell volume. The visual cell is placed on a thermostation (5), it has a protection jacket, and it is equipped with appropriate instrumentation, such as a pressure gauge (6) and a thermocouple (7) for the accurate measurement of pressure and temperature. The temperature of the cell is controlled by a circulatory thermostat model Lauda E 110 (9) connected to the heating jacket. The setup was also completed with a Teledyne ISCO model 500D syringe pump (3).

The apparatus used in this work is based on the static-analytical method with liquid and vapor phase sampling. The procedure is the same as in our previous papers [4-6]. 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 charged with alcohol, and then, it was slightly pressurized with carbon dioxide to the experimental pressure and 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 about 1 h was allowed to pass until the coexisting phases were completely separated. Samples of the liquid and vapor phase were collected by depressurization and expansion into glass traps, by using manually operated valves. The valves were operated in such a way as to keep almost constant the pressure in the visual cell ($\Delta P < 0.5$ bar).

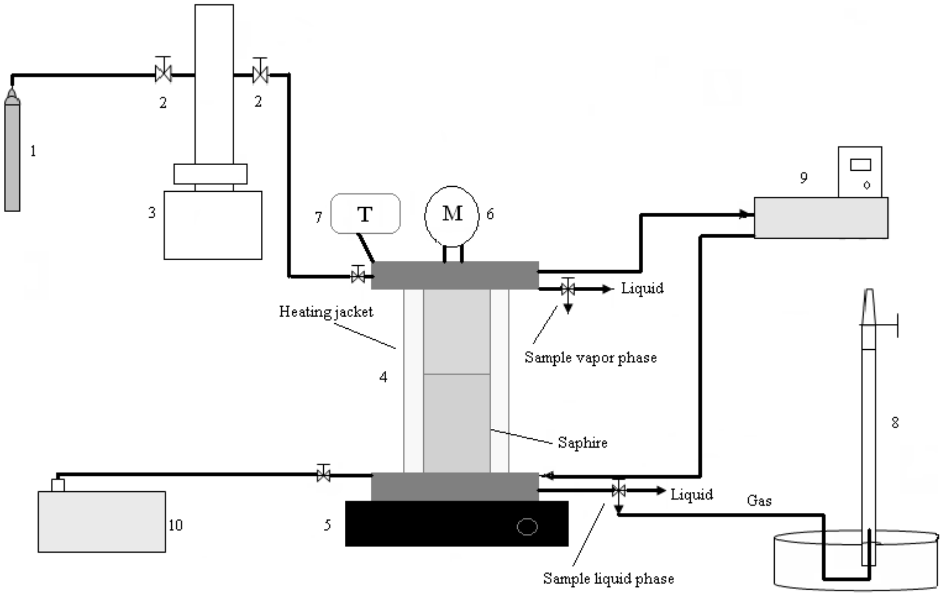

Fig. 1. Schematic diagram of experimental apparatus: 1, carbon dioxide cylinder; 2, valves; 3, syringe pump; 4, visual cell Separex; 5, thermostation with magnetic stirrer; 6, pressure gauge; 7, thermocuple; 8, burette; 9, water bath; 10, vacuum pump

The total amounts of the organic substance in the glass trap were about 0.1 g. The amount of carbon dioxide in the liquid phase was obtained by expansion in a glass bottle of calibrated volume. In a typical experiment, the measured volumes of carbon dioxide were about 15 cm^3 from the liquid phase. The liquid samples of both phases were weighed with a precision balance (A&D Instruments Ltd., type HM-200, Tokyo, Japan) with an accuracy of ± 0.0001 g.

For the liquid phase equilibrium compositions, the relative uncertainty of the mole fraction was calculated using the procedure given by Scheidgen [12]. The average relative uncertainty was < 2%.

The platinum temperature probe connected to a digital indicator was calibrated against the calibration system Digital Precision Thermometer with PT 100 sensor (Romanian Bureau of Legal Metrology-BRML). The uncertainty of platinum probe is estimated to be within ± 0.1 K using a similar procedure as described in previous paper [4].

The pressure gauge connected to the cell was a HEISE® model 3089 digital pressure indicator, for 500 bar and 0.05% accuracy. It was calibrated at 323.15 K with a precision hydraulic dead-weight tester (model 580C, DH-Budenberg SA, Aubervilliers, France). The uncertainty of the pressures is estimated to be within ± 0.015 MPa using a procedure described previously [4], for a pressure range between 0.5 – 20 MPa.

3. Modeling

The modeling of phase behavior of this system was made with the cubic GEOS, PR, and SRK EoS coupled with classical van der Waals mixing rules (2PCMR). The cubic GEOS [7,8] is:

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

with the classical van der Waals mixing rules:

$$a=\sum_i\sum_j x_i x_j a_{ij} \qquad b=\sum_i\sum_j x_i x_j b_{ij} \tag{2}$$

$$c=\sum_i\sum_j x_i x_j c_{ij} \qquad d=\sum_i x_i d_i \tag{3}$$

$$a_{ij}=\left(a_i a_j\right)^{1/2}\left(1-k_{ij}\right) \qquad b_{ij}=\frac{b_i+b_j}{2}\left(1-l_{ij}\right) \qquad c_{ij}=\pm\left(c_i c_j\right)^{1/2} \tag{4}$$

with "+" for c_i, $c_j > 0$ and "–" for c_i, $c_j < 0$. Generally, negative values are common for the c parameter of pure components.
The four parameters *a*, *b*, *c*, *d* for a pure component are expressed by:

$$a=\frac{R^2T_c^2}{P_c}\beta(T_r)\Omega_a \qquad b=\frac{RT_c}{P_c}\Omega_b \tag{5}$$

$$c=\frac{R^2T_c^2}{P_c^2}\Omega_c \qquad d=\frac{RT_c}{P_c}\Omega_d \tag{6}$$

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

$$\Omega_a=(1-B)^3 \qquad \Omega_b=Z_c-B \qquad \Omega_c=(1-B)^2(B-0.25) \tag{7}$$

$$\Omega_d=Z_c-\frac{(1-B)}{2} \qquad B=\frac{1+m}{\alpha_c+m} \tag{8}$$

where P_c, T_c, and Z_c (critical compressibility factor) are the critical data.

The temperature function used is:

$$\beta(T_r) = T_r^{-m} \tag{9}$$

The cubic GEOS parameters m and α_c 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 critical dat, acentric factor, and cubic GEOS parameters of the pure components are given in Table 1.

Table 1

Critical data, acentric factor, and GEOS parameters for carbon dioxide + 1-undecanol

Component	***T*c/K**	***P*c/MPa**	***V*c/cm^3·mol^{-1}**	***ω***	***α*$_c$**	***m***
CO_2	304.21	7.383	0.0939	0.22362	7.0517	0.3146
1-undecanol	521.24	2.147	0.7150	0.62474	8.8368	0.7953

The SRK [10] and PR [9] EoSs respectively are:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)} \tag{10}$$

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)+b(V-b)} \tag{11}$$

As pointed out previously [13], the relations (7) and (8) are general forms for all the cubic equations of state with two, three, and four parameters. The parameters of the SRK EoS can be obtained from the eqs. (7) and (8) by setting [13] the following restrictions: $\Omega_c = -(\Omega_b/2)^2$ and $\Omega_d = -\Omega_b/2$. It follows

$$\Omega_c = (1-B)^2(B-0.25) = -\frac{(Z_c-B)^2}{4} \tag{12}$$

$$\Omega_d = Z_c - 0.5(1-B) = -\frac{(Z_c-B)}{2} \tag{13}$$

It results: $Z_c(SRK) = 1/3$, and the relation for B (SRK)

$$B = 0.25 - \frac{1}{36}\left(\frac{1-3B}{1-B}\right)^2 \tag{14}$$

Solving iteratively this equation gives $B(SRK) = 0.2467$, and correspondingly $\Omega_a(SRK) = (1-B)^3 = 0.42748$ and $\Omega_b(SRK) = Z_c - B = 0.08664$.

For PR EoS we set the restrictions [13]: $\Omega_c = -2(\Omega_b)^2$ and $\Omega_d = -\Omega_b$. It results

$$B = 0.25 - \frac{1}{8}\left(\frac{1-3B}{1-B}\right)^2 \tag{15}$$

$$Z_c = \frac{1+B}{4} \tag{16}$$

giving $B(PR) = 0.2296$ and $Z_c(PR) = 0.3074$.

The calculations were made using the software package PHEQ, developed in our laboratory [14].

4. Results and Discussion

New high-pressures vapor-liquid equilibrium (VLE) data for the carbon dioxide + 1-undecanol binary system were measured at 333.15 K and pressures between 11.27 and 150.20 bar. The values are typically averages of two or three measurements. The new VLE measurements are given in Table 2.

Table 2

Mole Fractions of Component 1 in the Liquid Phase, X_1, and Mole Fractions of Component 1 in the Vapor Phase, Y_1, at Various Pressure, P, for the Binary System Carbon Dioxide (1) + 1-Undecanol (2) at 333.15 K

P/MPa	X_1	Y_1
1.127	0.1116	0.9988
1.834	0.1631	0.9990
3.510	0.2614	0.9991
5.006	0.3515	0.9994
6.533	0.4263	0.9996
8.763	0.5386	0.9995
12.749	0.6324	0.9972
15.020	0.6796	0.9953

Fig. 2 shows the comparison of our data at 333.15 K with the existing literature data at the same temperature. As can be seen, the new data are in good agreement with the measurements of Pöhler [15] at 333.2 K.

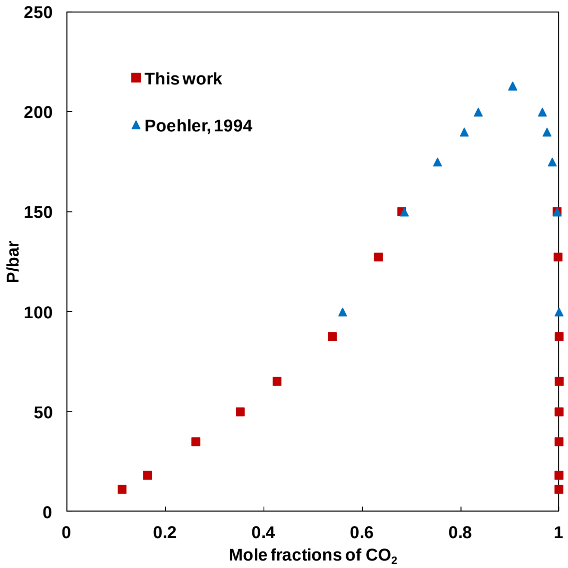

Fig. 2. Comparison of measured and literature VLE data for carbon dioxide + 1-undecanol at 333.15 K: (■), this work; (▲), Pöhler [15]

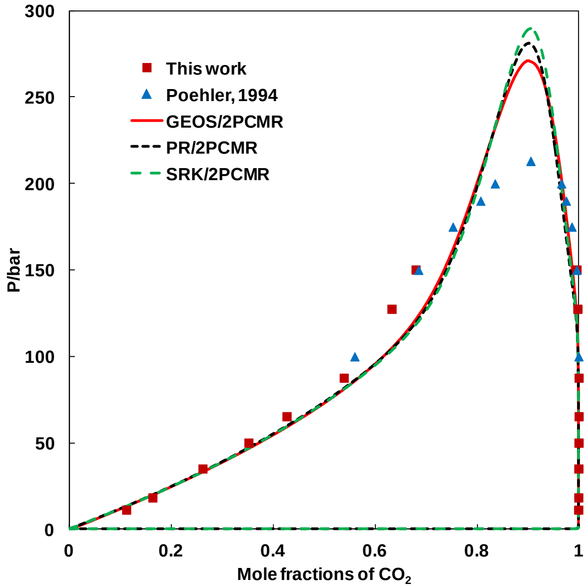

Fig. 3. Comparison of experimental data for the carbon dioxide + 1-undecanol system and correlations by GEOS, PR, and SRK

Measured data for the carbon dioxide + 1-undecanol system were correlated with the GEOS, PR, and SRK EOS coupled with classical van der Waals mixing rules. As the experimental data used in the binary interaction parameters optimization are those reported in the present paper together with those of Pöhler, the average absolute deviations in bubble point pressure (AADP, %) is high and similar for all models (~12.0%), while the average absolute deviations in vapor phase compositions (AADY, %) is very small (~0.2%). The AADP (%) and AADY (%) are calculated by the equations:

$$AADP(\%) = \frac{1}{N_{\exp}} \sum_{i=1}^{N_{\exp}} \left| \frac{P_i^{\exp} - P_i^{calc}}{P_i^{\exp}} \right| \cdot 100 \tag{17}$$

$$AADY(\%) = \frac{1}{N_{\exp}} \sum_{i=1}^{N_{\exp}} \left| Y_i^{\exp} - Y_i^{calc} \right| \cdot 100 \tag{18}$$

Although the calculated errors in pressure are rather high, the correlations by GEOS, PR, and SRK are in good agreement with the new experimental data presented in this work and less accurate for the data measured by Pöhler [15], which are measured at very high pressures up to the critical point of the mixture (Fig. 3).

The critical maximum pressure seems overestimated by all three models compared with the data reported by Pöhler [15]. It can be remarked that Scheidgen [12] reports the critical point at 254.64 bar for this temperature. The smallest deviations is obtained with GEOS, about 50 bar compared with the critical point reported by Pöhler [15] and less than 10 bar compared with that of Scheidgen [12], while the highest error for the critical pressure is given by SRK, about 80 bar.

5. Conclusions

New VLE experimental data for the binary system carbon dioxide + 1-undecanol were measured at 333.15 and pressures up to 150.20 bar, with a high-pressure static apparatus. Measured and literature VLE data for carbon dioxide + 1-undecanol system were well modeled with cubic equations of state (GEOS, PR, and SRK) using classical van der Waals (two-parameters conventional mixing rule, 2PCMR) mixing rules.

Acknowledgements

This work has been funded by the Sectoral Operational Programme Human Resources Development 2007−2013 of the Romanian Ministry of Labour, Family and Social Protection through the Financial Agreement POSDRU/107/1.5/S/76903.

The authors also acknowledge the financial support received from the Romanian Executive Unit for Financing Higher Education, Research, Development, and Innovation.

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