



Phase equilibria of carbon dioxide + 1-nonanol system at high pressures

Catinca Secuianu*, Viorel Feroiu, Dan Geană

Department of Applied Physical Chemistry and Electrochemistry, "Politehnica" University of Bucharest, 1-7 Gh. Polizu Street, 011061 Bucharest, Romania

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ABSTRACT

Vapor–liquid–equilibria (VLE) and vapor–liquid–liquid equilibria (VLLE) data for the carbon dioxide + 1-nonanol system were measured at 303.15, 308.15, 313.15, 333.15, and 353.15 K. Phase behavior measurements were made in a high-pressure visual cell with variable volume, based on the static-analytic method. The pressure range under investigation was between 1.15 and 103.3 bar. The Soave–Redlich–Kwong (SRK) equation of state (EOS) coupled with both classical van der Waals and a Gibbs excess energy (G^E) mixing rules was used in semi-predictive approaches, in order to represent the complex phase behavior (critical curve, liquid–liquid–vapor (LLV) line, isothermal VLE, LLE, and VLLE) of the system. The topology of phase behavior is correctly predicted.

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1. Introduction

The knowledge of the high-pressure phase behavior of carbon dioxide mixtures is an important problem in modern industry. The phase equilibrium properties of the related mixtures are essentially needed in the development of supercritical fluid techniques for a wide variety of processes, such as SCF extraction, reaction, fractionation, nanoparticle formation, separation of non-volatile mixtures, supercritical fluid chromatography, hydrothermal crystal growing, hydrothermal destruction of hazardous waste, polymer processing, etc., as well as in the simulation of petroleum reservoirs, enhanced oil recovery, carbon capture and storage, the transportation and storage of natural gas, refrigeration and heat-pump cycles, and the study of geological processes [1].

High-pressure vapor–liquid equilibrium measurements of carbon dioxide + alcohol systems are of interest due to their importance in different chemical processes, such as the supercritical extraction of thermal labile compounds, dehydration of alcohols using supercritical carbon dioxide, and extraction of natural products using near critical solvents [2,3].

Among the carbon dioxide + alcohols systems, the carbon dioxide + 1-nonanol system has not been widely studied. Lam et al. [4] have reported the upper critical endpoint (UCEP) of the three phase liquid–liquid–vapor (LLV) curve and the quadruple point (Q-point) solid–liquid–liquid–vapor (SLLV) for this system, Scheidgen [5] has measured the critical curve between 299.88 and 378.78 K, and several isotherms between 303 K and 393 K, but at pressures higher

than 100 bar, Chang et al. [6] have determined vapor–liquid equilibria (VLE) at 308.14, 318.13, and 328.18 K, Pfohl et al. [7] have measured liquid–liquid equilibria (LLE) at 303.15 K and between 113 and 340 bar, and Artal et al. [8] has reported solubilities at 323.15 K.

The first objective of this paper was to add new experimental data. Therefore, in this paper we present new vapor–liquid (VLE), liquid–liquid (LL), and vapor–liquid–liquid equilibria (VLLE) data for the carbon dioxide + 1-nonanol system at 303.15, 308.15, 313.15, 333.15 and 353.15 K up to 103.3 bar, the pressure–temperature up to the upper critical endpoint (UCEP) for the three phase curve and phase compositions of the two liquid phases as a function of temperature along the liquid–liquid–vapor (LLV) line. The binary system studied in the present work is a part of an extensive study on mixtures containing carbon dioxide + alcohols [9–19].

The second goal of this work was to represent the global phase behavior of this system with a simple model, using semi-predictive procedures. The advances in developing thermodynamic models with different complexities are listed in several reviews [20–23]. However, equations of state (EOSs) models are the most common approach for the correlation and prediction of phase equilibria and properties of the mixtures. Cubic and generalized van der Waals equations of state were actively studied, since van der Waals proposed his famous equation in 1873 [22]. Although the cubic EOSs have their known limitations [24–27], they are frequently used for practical applications. Cubic EOSs offer the best balance between accuracy, simplicity, reliability and speed of computation [22]. Therefore, cubic equations of state remain important and easy tools to calculate the phase behavior in many systems [20], even for complex mixtures like petroleum fluids, as recently was shown [28–30].

* Corresponding author. Tel.: +40 21 4023988; fax: +40 21 3154193.

E-mail addresses: tina@catedra.chfiz.pub.ro, c.secuianu@imperial.ac.uk (C. Secuianu).

Accurate modeling of asymmetric, highly non-ideal systems consisting of carbon dioxide and alcohols, using equations of state models can be a very difficult and challenging task [19,24,27]. However it was shown that simple EOS models [19,21,24,27] can be used to predict qualitatively and quantitatively the phase behavior of these complex mixtures.

The Soave–Redlich–Kwong (SRK) [31] cubic equation of state coupled with both classical van der Waals (two parameters conventional mixing rules, 2PCMR) and a G^E -EOS mixing rule were used to model the carbon dioxide + 1-nonanol system. The Huron–Vidal (HV) mixing rules [32] coupled with the reduced UNIQUAC excess Gibbs energy model [33,34] were chosen. Using semi-predictive approaches, the models were used to represent the complex phase behavior (critical curve, LLV line, isothermal VLE, LLE, and VLLE) of the system. The topology of phase behavior is qualitatively correct described in both cases. The calculations results were compared to the new data reported in this work, and to all available literature data. The results show a satisfactory agreement between the models and the experimental data.

2. Experimental

2.1. Materials

Carbon dioxide (mass fraction purity >0.997) was provided by Linde Gaz Romania, Bucharest, Romania, and 1-nonanol (mass fraction purity >0.980) was a Fluka product. The chemicals were used as supplied.

2.2. Apparatus and procedure

A detailed description of the experimental apparatus was presented in our previous publications [10,11]. 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 [9–19]. 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; 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. The average stirring time is about 2 h. 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 phases 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 the pressure in the visual cell almost constant. The total amounts of the organic substance in the glass trap were about 0.05 and 0.2 g for the vapor and liquid phases, respectively. The amount of carbon dioxide in each phase was obtained by expansion in a glass bottle of calibrated volume. In a typical experiment, the measured volumes of carbon dioxide were about 100 cm³ from the vapor phase and 50 cm³ 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.

3. Modeling

The phase behavior (critical curve, LLV line, isothermal VLE, LLE, and VLLE) of the carbon dioxide + 1-nonanol binary system was modeled using the Soave–Redlich–Kwong (SRK) equation of state (EOS) [31] coupled with classical van der Waals mixing rules and with Huron–Vidal (HV)-residual UNIQUAC mixing rules [33,34].

This G^E -EOS model was chosen based on previous results with mixtures containing hydrogen bonding compounds (Tables 2 and 4, in [34]).

The Soave–Redlich–Kwong equation of state is [31]:

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

The Huron and Vidal mixing rules [32] for the SRK EOS are given by:

$$b = \sum_i x_i b_i \quad (2)$$

$$\frac{a}{bRT} = \sum_i x_i \left(\frac{a_i}{b_i RT} - \frac{\ln \gamma_i(P \rightarrow \infty)}{\ln 2} \right) \quad (3)$$

where $\gamma_i(P \rightarrow \infty)$ is the activity coefficient of the component in the mixture at infinite pressure.

The HV mixing rule is based on a reduced UNIQUAC model suitable for infinite pressure conditions [33,34]. The model is reduced to its residual part only:

$$\ln \gamma_i(P \rightarrow \infty) = q_i \left[1 - \ln \left(\sum_j \theta_j \tau_{ji} \right) - \sum_j \frac{\theta_j \tau_{ij}}{\sum_k \theta_k \tau_{kj}} \right] \quad (4)$$

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \quad (5)$$

$$\tau_{ij} = \exp \left(-\frac{u_{ij}}{T} \right) \quad (6)$$

The interaction parameters are considered temperature dependent [33,34]:

$$u_{ij} = u_{ij}^0 + u_{ij}^1 \frac{1}{T} \quad (7)$$

The calculations were made using the software package PHEQ, developed in our laboratory [35]. The critical curves were calculated using the method proposed by Heidemann and Khalil [36], with numerical derivatives given by Stockfleth and Dohrn [37].

4. Results and discussion

Vapor–liquid and vapor–liquid–liquid equilibria data for the carbon dioxide + 1-nonanol system were measured in this work at 303.15, 308.15, 313.15, 333.15 and 353.15 K and pressures between 11.5 and 103.3 bar. The results are given in Tables 1 and 2 and plotted in Fig. 1. For the VLE and VLLE measurements, the uncertainty of the mole fractions is typically ± 0.001 and always <0.003. As usually

Table 1

Mole fractions of component 1 in the liquid phases, X_{L1} , X_{L2} , and mole fractions of component 1 in the vapor phase, Y_1 at various pressures, P , and at 303.15 K for the binary system carbon dioxide (1) + 1-nonanol (2).

P (bar)	X_{L1}	X_{L2}	Y_1
13.0	0.1071		0.9984
21.4	0.1764		0.9989
31.7	0.2671		0.9993
46.6	0.3936		0.9991
53.5	0.4494		0.9989
60.7	0.5032		0.9986
66.2	0.5570		0.9982
70.8	0.6447	0.9916	0.9980
76.3	0.6517	0.9913	
81.7	0.6540	0.9907	
85.6	0.6583	0.9896	

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