

Phase compositions and saturated densities for the binary systems of carbon dioxide with ethanol and dichloromethane

I. Tsivintzelis, D. Missopolinou, K. Kalogiannis, C. Panayiotou*

Department of Chemical Engineering, Aristotle University of Thessaloniki, GR-54124 Thessaloniki 54006, Greece

Received 20 March 2004; accepted 4 June 2004

Abstract

The compositions and densities of the liquid and vapor phases of two binary systems at equilibrium were measured on a new experimental apparatus over a range of temperatures and pressures. The studied systems are: CO₂–ethanol at 313.2 and 328.2 K; CO₂–dichloromethane at 308.2, 318.2 and 328.2 K and for pressures ranging from ambient up to ca. 9 MPa. Some of our measurements are critically compared with corresponding literature values. These measurements are ideally suited for testing equation-of-state models. The recently developed quasi-chemical hydrogen-bonding (QCHB) model was used for correlating the experimental data. A satisfactory agreement was obtained between experimental and calculated phase compositions and saturated densities.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Vapor–liquid equilibria; High pressure; Statistical thermodynamics

1. Introduction

Experimental data on phase compositions and saturated densities of mixtures over an extended range of temperature and pressure are of primordial importance for a rational design and for appropriate operation of separation units in the chemical industry. This is especially true for a multitude of processes which reside upon a number of advantages of supercritical fluids over the conventional solvents. Such processes include the supercritical anti-solvent (SAS) process for the production of nanoparticles, the polymer impregnation, the production of polymeric membranes and of porous polymeric materials and the supercritical fluid extraction. It is essential to stress that in many cases it is crucial to have information on the densities of the supercritical systems involved. Simultaneous measurements of phase compositions as well as densities of the phases at equilibrium are also useful for testing thermodynamic models, especially, equation-of-state models.

The most common supercritical solvent is carbon dioxide, which is often used in combination with various cosolvents or modifiers. The system of carbon dioxide and ethanol is

of particular interest in biomaterials processing [1], while the system of carbon dioxide with dichloromethane is of wide interest in many polymer and pharmaceutical processes [2,3].

Many researchers [4–7] have measured with analytical methods the compositions of the phases at equilibrium, but relatively few experimental data are available in the open literature on saturated densities of mixtures as the above-mentioned mixtures with carbon dioxide. The system of carbon dioxide with ethanol has attracted particular interest. Tanaka and Kato [8] used an analytical method for measuring phase compositions and saturated densities for this system. Chang et al. [9,10] used a new technique for measuring saturated densities and mole fractions for various binary systems including the system CO₂ + ethanol.

On the other hand, bubble and dew points of binary mixtures can be determined by a synthetic method with a variable volume cell. Gonzalez et al. [11] have used this technique for measuring the solubility of CO₂ in dichloromethane.

In this work we first describe a new recirculation type (analytical method) apparatus, equipped with two U-tube vibration densitometers for the measurement of saturated densities and a gas chromatograph for the determination of phase compositions. This apparatus was used for obtaining high pressure vapor–liquid equilibrium data for the system CO₂

* Corresponding author. Tel.: +30-2310-996223;
fax: +30-2310-996223.
E-mail address: cpanayio@auth.gr (C. Panayiotou).

+ ethanol at 313.2 and 328.2 K, and for the system CO₂ + dichloromethane at 308.2, 318.2, and 328.2 K. The validity of the measurements was confirmed by critical comparison with previously published data in the literature.

The new experimental data are subsequently treated with the recently developed quasi-chemical hydrogen-bonding (QCHB) model [12–14]. This is an equation-of-state model applicable to non-polar systems as well as to highly non-ideal systems with strong specific interactions – including intramolecular and cooperative hydrogen bonding – to liquids as well as to vapors, including supercritical systems. The performance and the limitations of the model are discussed.

2. Experimental

2.1. Description of the apparatus

A schematic diagram of the new apparatus is shown in Fig. 1. As already mentioned, this is a recirculation-type apparatus (analytical method) equipped with two densitometers, for the measurement of saturated densities and with a gas chromatograph for the determination of the phase compositions.

The main parts of the apparatus are: an equilibrium cell (A), two vibrating densitometers (B and C), two Milton Roy pumps (E and F) for the recirculation of the two phases, a gas chromatograph (D), two sampling valves (G, H), three Pt-100 thermocouple probes (TI) and a pressure transducer (PI). The apparatus was placed in a constant-temperature air bath, whose temperature was controlled with a PID temperature regulator.

The high-pressure equilibrium cell was made of stainless steel and its capacity is 202.1 cm³. It is equipped with two sapphire windows, which allow for the visual observation of the two phases. The pressure transducer was cali-

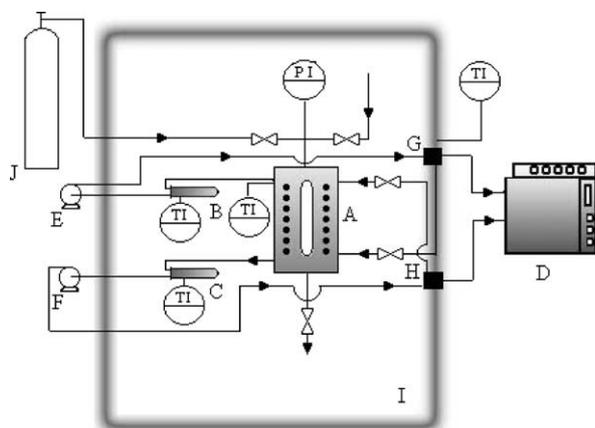


Fig. 1. Schematic diagram of the experimental apparatus: (A) equilibrium cell; (B and C) vibrating densitometers; (D) gas chromatograph; (E and F), pumps; (G and H) sampling valves; (I) air bath; (J) CO₂ tank.

brated against a Metronex dead-weight tester, model MTU 600. The accuracy in pressure is ± 0.01 MPa. The thermometers were Pt-100 and calibrated against NPL, UK, class 1. The accuracy in temperature measurements is ± 0.01 K. Two high-pressure Anton Paar vibrating tube densitometers, models DMA-512, were used for the measurement of densities.

For the determination of the phase compositions a Carlo Erba gas chromatograph, model GC-6000-Vega, was used. It was equipped with a thermal conductivity detector (TCD) and a column packed with Poropak-Q 80/100. Helium was used as a carrier gas at a flow rate of 22 mL min⁻¹. The column and the detector temperatures were 150 and 170 °C, respectively. The gas chromatograph was connected to the recirculation lines through two Rheodyne sampling valves. The volume of the vapor sampling valve (Rheodyne 7000) was 20 μ L and the volume of the liquid sampling valve (Rheodyne 7413) was 1 μ L.

2.2. Experimental procedure

The calibration of the thermal conductivity detector for ethanol and dichloromethane was achieved by injecting known amounts of pure compounds through calibrated syringes and sampling valves. The obtained data were correlated with a linear equation. The calibration for CO₂ was made through the sampling valves. The CO₂ mass (moles), at various pressures, was calculated with the corresponding IUPAC equation of state [15]. The obtained data were correlated with a quadratic polynomial equation.

As already mentioned, the saturated densities were determined by two Anton Paar vibrating densitometers. The vibration period of each U-tube densitometer is represented by the following equation:

$$\rho = K(\tau^2 - B) \quad (1)$$

where τ is the vibration period, ρ is the density of the fluid which fills the tube, while K and B are instrument constants. The instrument constant, K , depends, both, on temperature and pressure. It is determined from the measurement of the oscillation periods of two fluids, 1 and 2, of known densities by the following equation:

$$K(T, P) = \frac{\rho_1 - \rho_2}{\tau_1^2 - \tau_2^2} \quad (2)$$

where ρ_1 and ρ_2 are the known densities of the two fluids, and τ_1 and τ_2 are the corresponding vibration periods. When $K(T, P)$ is known, the density, ρ , of an unknown fluid is obtained from the following equation:

$$\rho(T, P) = \rho_1(T, P) - (\tau_1^2 - \tau^2)K(T, P) \quad (3)$$

In this work the densitometers were calibrated with water and nitrogen at each temperature of interest and for the entire range of pressures.

Prior to running any experiments, the whole apparatus was cleaned with a sufficient number of rinses with liq-

uid and supercritical CO₂ and thoroughly evacuated. The well-degassed organic solvent was introduced through an on-off valve. Subsequently, liquid CO₂ was pumped into the equilibrium cell with a Milton Roy dual piston reciprocating pump. After the system had reached the set temperature, the recirculation began. Typically and far below the critical point, the system was reaching equilibrium in about 2 h. At higher pressures, the recirculation was maintained for a maximum of 4 h. For pressures near the critical point, the recirculation rate was kept low and, in some cases, the system was left overnight in order to reach equilibrium.

Once been at equilibrium, the system was left standing for half an hour and the vibration periods in both densitometers were recorded. Afterwards, samples from both phases were injected into the gas chromatograph. Each sample was analyzed, at least four times, and the average of individual results is reported as the equilibrium composition. The repeatability of vapor and liquid mole fraction values was within ± 0.0005 . When the sampling was completed, the vibration periods were again recorded in order to ensure that the equilibrium was maintained. During measurements, the fluctuation in temperature of the equilibrium cell and (inside the cells of) the densitometers was, in all cases, lower than 0.02 K.

2.3. Materials

Ethanol (>99.9% purity) was obtained from J.T. Baker Inc. Dichloromethane (>99.9% purity) was obtained from Fluka Chemie. CO₂ was obtained from Air Liquide Méditerranée (>99.98% purity). All materials were used as received and without any further purification.

3. Experimental results

The apparatus described in the previous section was used in order to obtain simultaneous data for the composition and densities of the vapor and liquid phases at equilibrium for the binary systems: CO₂ + ethanol at 313.2 and 328.2 K, and CO₂ + dichloromethane at 308.2, 318.2, and 328.2 K. The measurements were isothermal and the compositions and densities were measured by varying the pressure of the system. The experimental results are summarized in Tables 1–4.

In the vast majority of cases and at a given temperature and pressure, we report, both, compositions and densities of the phases at equilibrium. At some pressures we do not report the densities or the compositions. All the missing densities have large uncertainty because the vibration period of the densitometer was not constant (it was largely fluctuating around some value). Thus, near the critical point it was very difficult to measure precisely the density. In compensation for the missing densities we report some additional density data in Tables 2 and 4 at other pressures. We added these data because density data are more rare than corresponding phase compositions in the literature.

Table 1
Phase compositions for the system CO₂ (1)–ethanol (2)

<i>P</i> (MPa)	<i>y</i> ₁	<i>x</i> ₁	<i>P</i> (MPa)	<i>y</i> ₁	<i>x</i> ₁
<i>T</i> = 313.2 K					
1.60	0.9881	0.0875	6.59	0.9893	0.4519
2.12	0.9903	0.1162	7.26	0.9841	0.5733
3.27	0.9916	0.1834	7.51	0.9795	0.6615
3.81	0.9931	0.2139	7.66	0.9779	0.7200
5.21	0.9915	0.3176	7.82	0.9755	0.8437
<i>T</i> = 328.2 K					
1.65	0.9726	0.0778	5.82	0.9803	0.2825
2.10	0.9769	0.0950	6.80	0.9797	0.3453
2.78	0.9805	0.1245	8.26	0.9700	0.4742
3.50	0.9821	0.1623	8.91	0.9662	0.5410
4.37	0.9822	0.2075	9.24	0.9624	0.5922
5.02	0.9821	0.2384	9.42	0.9549	0.6351

Table 2
Saturated densities for the system CO₂–ethanol

<i>P</i> (MPa)	ρ^v (g cm ⁻³)	ρ^l (g cm ⁻³)	<i>P</i> (MPa)	ρ^v (g cm ⁻³)	ρ^l (g cm ⁻³)
<i>T</i> = 313.2 K					
0.62	0.0109	0.7768	4.89	0.1112	0.8101
0.82	0.0142	0.7784	5.21	0.1214	0.8115
1.60	0.0285	0.7851	5.60	0.1352	0.8138
2.12	0.0395	0.7892	6.59	0.1811	0.8192
2.76	0.0532	0.7939	6.99	0.2052	0.8190
3.27	0.0651	0.7967	7.26	0.2266	0.8150
3.54	0.0729	0.8003	7.51	0.2511	0.8049
3.81	0.0796	0.8035	7.66	0.2675	0.7890
4.64	0.1028	0.8082	7.82	0.2970	0.7394
<i>T</i> = 328.2 K					
1.65	0.0301	0.7642	5.02	0.1028	0.7852
2.10	0.0368	0.7673	5.82	0.1264	0.7886
2.78	0.0501	0.7741	6.80	0.1608	0.7917
3.50	0.0654	0.7778	7.61	0.1948	0.7928
3.74	0.0710	0.7791	8.26	0.2298	0.7915
4.37	0.0863	0.7792	8.91	0.2779	0.7844

In order to test the reliability of the new apparatus, the phase composition data for the system CO₂ + ethanol at 313.2 K were compared with corresponding data previously reported by Chang et al. [9,10], Jennings et al. [1], Joung et al. [7] and Suzuki et al. [6]. These results are summarized in Fig. 2. As observed in this figure, our measurements and the literature data are in good agreement.

Saturated density data for mixtures are rare in the literature, so our measurements were compared only with those reported by Chang et al. [9,10]. These results are summarized in Fig. 3. As observed, the measured and literature data are in good agreement for pressures up to 7.0 MPa.

4. Correlation with the QCHB model

4.1. The QCHB formalism

The QCHB model is particularly suited for treating our experimental data since it is a model applicable to the liquid

Table 3
Phase compositions for the system CO₂ (1)–dichloromethane (2)

<i>P</i> (MPa)	<i>y</i> ₁	<i>x</i> ₁	<i>P</i> (MPa)	<i>y</i> ₁	<i>x</i> ₁
<i>T</i> = 308.2 K					
1.92	0.9249	0.1802	5.93	0.9686	0.7763
2.41	0.9396	0.2352	6.41	0.9714	0.8533
3.13	0.9517	0.3269	6.72	0.9741	0.8942
3.86	0.9593	0.4281	7.16	0.9795	0.9413
4.52	0.9627	0.5342	7.29	0.9817	0.9551
5.08	0.9650	0.6286	7.48	0.9851	0.9718
<i>T</i> = 318.2 K					
1.49	0.8725	0.1151	5.84	0.9480	0.5978
2.04	0.9051	0.1640	6.41	0.9489	0.6791
2.85	0.9299	0.2411	7.03	0.9530	0.7887
3.61	0.9410	0.3203	7.74	0.9547	0.8716
4.43	0.9442	0.4124	8.17	0.9554	0.9137
5.06	0.9468	0.4926	8.32	0.9522	0.9327
<i>T</i> = 328.2 K					
2.05	0.8691	0.1391	6.54	0.9339	0.5804
3.10	0.9084	0.2245	7.00	0.9363	0.6355
3.70	0.9210	0.2793	7.63	0.9342	0.7088
4.58	0.9280	0.3588	7.95	0.9323	0.7481
5.31	0.9308	0.4332	8.55	0.9302	0.8223
5.76	0.9318	0.4874	8.85	0.9259	0.8556

as well as to the vapor and to supercritical state and, in addition, it can handle hydrogen bonding. In what follows, we will first summarize the essential formalism. Details may be found elsewhere [12–14]. We will adhere to the most recent formalism and adopt Staverman's equation for the combinatorial term [13].

According to QCHB model, each fluid of type *i* in our system is characterized by three Lattice-Fluid scaling con-

Table 4
Saturated densities for the system CO₂–dichloromethane

<i>P</i> (MPa)	ρ^v (g cm ⁻³)	ρ^l (g cm ⁻³)	<i>P</i> (MPa)	ρ^v (g cm ⁻³)	ρ^l (g cm ⁻³)
<i>T</i> = 308.2 K					
1.92	0.0391	1.2353	5.93	0.1683	0.9198
2.41	0.0450	1.2151	6.41	0.1985	–
3.13	0.0674	1.1768	6.72	0.2221	–
3.86	0.0876	1.1315	7.16	0.2689	–
4.52	0.1086	1.0809	7.29	0.2866	–
5.08	0.1291	1.0261	7.48	0.3311	–
<i>T</i> = 318.2 K					
1.49	0.0298	1.2411	5.06	0.1257	1.0728
2.04	0.0411	1.2237	5.84	0.1499	1.0078
2.85	0.0587	1.1939	6.41	0.1763	0.9511
3.61	0.0775	1.1600	7.03	0.2118	0.8757
4.43	0.1000	1.1158	7.74	0.2727	0.7613
<i>T</i> = 328.2 K					
2.05	0.0402	1.2101	6.54	0.1674	0.9911
3.10	0.0625	1.1766	7.00	0.1879	0.9504
3.70	0.0767	1.1534	7.63	0.2239	–
4.58	0.0997	1.1143	7.95	0.2468	–
5.31	0.1218	1.0753	8.49	0.2966	–
5.76	0.1370	1.0489	8.55	0.2987	–
6.14	0.1506	1.0222	8.85	0.3558	–
6.49	0.1642	0.9964	–	–	–

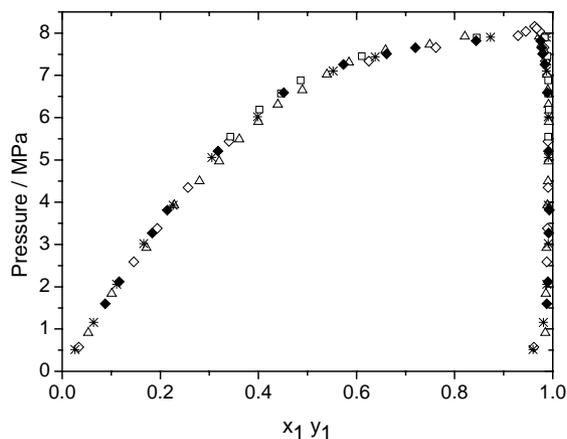


Fig. 2. Comparison of experimental vapor–liquid equilibrium data for the CO₂ (1)–ethanol (2) system: (◆) this work (313.2 K); (□) Jennings et al. (314.5 K) [1]; (*) Suzuki et al. (313.4 K) [6]; (◇) Joung et al. (313.4 K) [7]; (△) Chang et al. (313.15 K) [9].

stants and one geometric or surface-to-volume-ratio factor. The three scaling constants are: the mean interaction energy per segment, ε_i^* , the hard-core volume per segment, v_i^* , and the hard-core density, $\rho_i^* = 1/v_{sp,i}^*$. One equivalent set of scaling constants is the temperature T_i^* , the pressure, P_i^* , and the number of segments per molecule, r_i . The molecules are arranged on a quasi-lattice of N_r sites, N_0 of which are empty, and of coordination number z , assumed to be equal to 10 in this work. Each molecule has $q_i = s_i r_i$ external intermolecular constants, where s_i is its geometric factor. These constants for the fluids of interest in this work were obtained from Ref. [13] and are reported in Table 5. Similar scaling constants, indicated without subscript, are defined for the mixture through the following combining and mixing rules.

The average segmental interaction energy for a binary mixture is given by

$$\varepsilon^* = P^* v^* = RT^* = \theta_1^2 \varepsilon_1^* + \theta_2^2 \varepsilon_2^* + 2\theta_1 \theta_2 \varepsilon_{12}^* \quad (4)$$

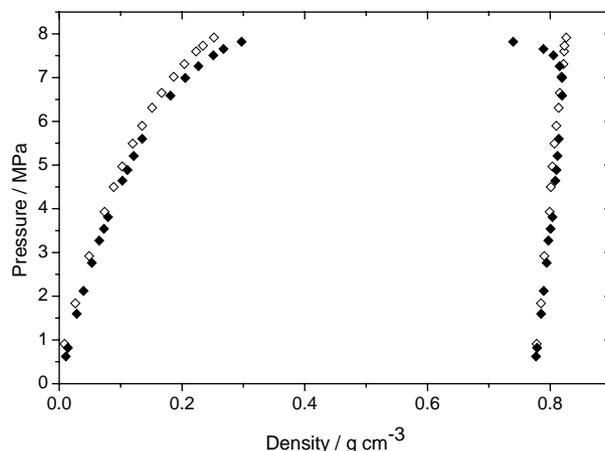


Fig. 3. Comparison of experimental saturated density data for the system CO₂–ethanol: (◆) this work (313.2 K); (◇) Chang et al. (313.15 K) [9].

Table 5
Scaling parameters for pure fluids [13]

Fluid	$\varepsilon^* = RT^*$ (J mol ⁻¹)	$v^* = \varepsilon^* P^{*-1}$ (cm ³ mol ⁻¹)	$v_{sp}^* = \rho^{*-1}$ (cm ³ g ⁻¹)	$s = q/r$
CO ₂	3040	5.970	0.707	0.909
Ethanol	4347	10.608	1.128	0.903
Dichloromethane	4835	8.700	0.685	0.881

where a Berthelot-type combining rule is adopted for the cross term:

$$\varepsilon_{12}^* = (1 - k_{12})\sqrt{\varepsilon_1^* \varepsilon_2^*} \quad (5)$$

The average segmental volume is given by

$$v^* = \phi_1^2 v_1^* + 2\phi_1 \phi_2 v_{12}^* + \phi_2^2 v_2^* \quad (6)$$

where

$$v_{12}^* = (1 - \lambda_{12})\frac{1}{2}(v_1^{*1/3} + v_2^{*1/3})^3$$

The adjustable parameters k_{12} and λ_{12} are determined by fitting the experimental data through a Simplex least-squares minimization procedure.

The site fractions ϕ_i and the surface fractions θ_i in the above equations are defined as following:

$$\phi_i = \frac{r_i N_i}{rN} = \frac{x_i r_i}{r}, \quad i = 1, 2 \quad (7)$$

and

$$\theta_i = \frac{q_i N_i}{\sum_k q_k N_k} = \frac{q_i N_i}{qN} = \frac{\phi_i s_i}{\sum_k \phi_k s_k} = \frac{\phi_i s_i}{s} \quad (8)$$

For the correlation of our experimental data we need the equation of state and the equations for the chemical potentials for each component i , which are equal in all phases at equilibrium. The equation of state of our mixture has the following form:

$$\tilde{P} + \tilde{T} \left[\ln(1 - \tilde{\rho}) - \tilde{\rho} \left(\sum_i \phi_i \frac{l_i}{r_i} - v_H \right) - \frac{\tilde{z}}{2} \ln \left(1 - \tilde{\rho} + \frac{q}{r} \tilde{\rho} \right) + \frac{\tilde{z}}{2} \ln \Gamma_{00} \right] = 0 \quad (9)$$

while the chemical potential for the component 1 is given by

$$\begin{aligned} \frac{\mu_1}{RT} = & \ln \frac{\phi_1}{\delta_1 r_1} - r_1 \tilde{\rho} \sum_j \frac{\phi_j l_j}{r_j} + \ln \tilde{\rho} - \frac{\tilde{z}}{2} q_1 \ln \left[1 - \tilde{\rho} + \frac{q}{r} \tilde{\rho} \right] \\ & + \frac{\tilde{z} q_1}{2} [\ln \Gamma_{rr}] - \frac{q_1}{\tilde{T}} - 2q_1 \Theta_r \Gamma_{rr} \frac{\theta_1 \varepsilon_1^* + \theta_2 \varepsilon_{12}^* - \varepsilon^*}{RT} \\ & + r_1 \frac{\tilde{P} \tilde{v}}{\tilde{T}} \left[\frac{v_1^*}{v^*} + \tilde{\rho} - 1 \right] + \frac{\mu_{H,1}}{RT} \end{aligned} \quad (10)$$

where

$$\tilde{T} = \frac{T}{T^*}, \quad \tilde{P} = \frac{P}{P^*}, \quad \tilde{\rho} = \frac{\rho}{\rho^*} = \frac{1}{\tilde{v}} \quad (11)$$

$$l_i = \frac{1}{2} z(r_i - q_i) - (r_i - 1) \quad (12)$$

and

$$\Theta_r = 1 - \Theta_0 = \frac{q/r}{q/r + \tilde{v} - 1} \quad (13)$$

δ_i is a characteristic quantity for each fluid i that takes into account the flexibility and symmetry of the molecule. This parameter cancels out in all applications of our interest. Furthermore, Γ_{00} and Γ_{rr} are factors for the non-random distribution of empty sites around an empty site and for the distribution of molecular segments around a central molecular segment, respectively. These non-randomness factors are obtained through Guggenheim's quasi-chemical condition [12–14] and are given by

$$\Theta_0 \Gamma_{00} + \Theta_r \Gamma_{r0} = 1, \quad \Theta_r \Gamma_{rr} + \Theta_0 \Gamma_{r0} = 1 \quad (14)$$

and

$$\Gamma_{r0} = \frac{2}{1 + [1 - 4\Theta_0 \Theta_r (1 - A)]^{1/2}} \quad (15)$$

where

$$A = \frac{4\Gamma_{rr} \Gamma_{00}}{\Gamma_{r0}^2} = \exp \left(\frac{2^* \varepsilon^* / z}{RT} \right) \quad (16)$$

Hydrogen bonding occurs in the CO₂ + ethanol system, where ethanol is self-associated. In this case the average per segment number of hydrogen bonds is given by

$$v_H = \frac{N_H}{rN} = \frac{2 + C - \sqrt{C(C+4)}}{2r} \quad (17)$$

where

$$C = r\tilde{v} \exp \left(\frac{G_H}{RT} \right) \quad (18)$$

G_H being the Gibbs energy change upon formation of 1 mol of OH--OH hydrogen bonds. G_H may be written as

$$G_H = E_H + PV_H - TS_H \quad (19)$$

where E_H , S_H , and V_H are the energy, entropy, and volume change, respectively, upon hydrogen bond formation.

The hydrogen bonding contribution to the chemical potential of ethanol takes the form:

$$\frac{\mu_{H,ethanol}}{RT} = r v_H + 2 \ln(1 - r v_H) \quad (20)$$

while for CO₂ it is

$$\frac{\mu_{H,CO_2}}{RT} = r v_H \quad (21)$$

The hydrogen bonding parameters for the self-association of ethanol are shown in Table 6.

Table 6
Parameters for OH≡OH hydrogen bonding [12]

Hydrogen bond	E_H (J mol ⁻¹)	S_H (JK ⁻¹ mol ⁻¹)	V_H (cm ³ mol ⁻¹)
OH--OH	-25100	-26.5	0.0

Table 7

Binary interaction parameters and average absolute deviation (AAD%) between experimental and calculated data

System	k_{12}	λ_{12}	AAD (%) in pressure ^a	AAD (%) in y^a	AAD (%) in saturated densities ^a
CO ₂ –ethanol	−0.0217	−0.0270	1.71	1.27	3.23
CO ₂ –dichloromethane	0.0086	−0.1020	0.97	2.87	6.30

$$^a \text{AAD (\%)} = (1/n) \sum_i |(X_i^{\text{cal}} - X_i^{\text{exp}}) / X_i^{\text{exp}}| \times 100.$$

Eqs. (9) and (17) must be solved simultaneously in an iterative scheme in order to obtain, both, the density, $\tilde{\rho}$, and the number of hydrogen bonds, ν_{H} . Of course, in the case of the CO₂ + dichloromethane system, the contributions of Eqs. (20) and (21) are zero.

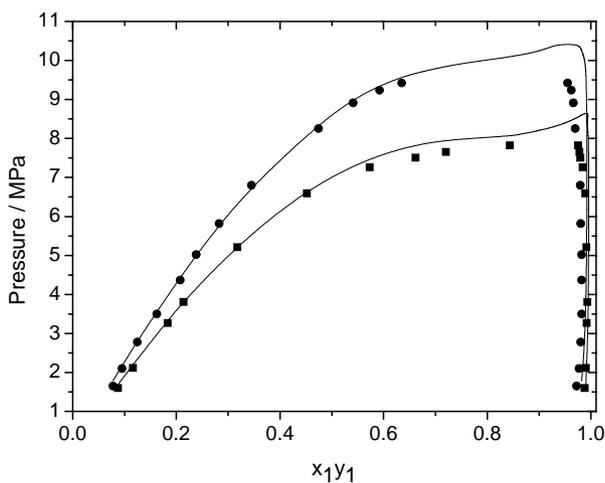


Fig. 4. Phase compositions for the system CO₂ (1)–ethanol (2): (■) experimental ($T = 313.2 \text{ K}$); (●) experimental ($T = 328.2 \text{ K}$); the lines were calculated by the QCHB model.

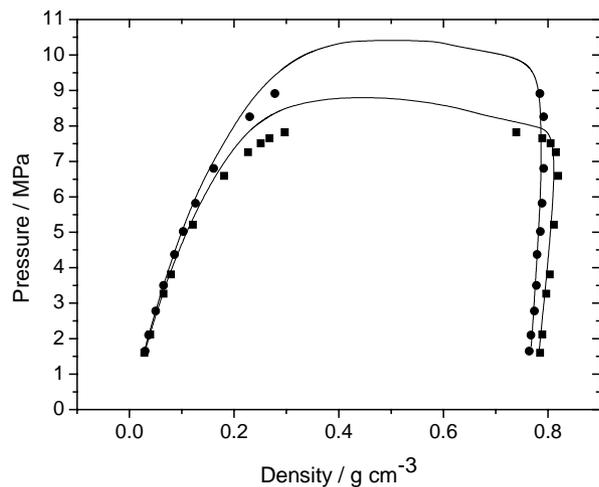


Fig. 5. Saturated densities for the system CO₂ (1)–ethanol (2): (■) experimental ($T = 313.2 \text{ K}$); (●) experimental ($T = 328.2 \text{ K}$); the lines were calculated by the QCHB model.

4.2. Correlation of experimental data

All experimental data reported in Tables 1–4 were correlated with the QCHB model. One single set of binary adjustable parameters, independent of temperature, was used for each binary system. These regressed binary parameters are reported in Table 7. In the same table are also reported the average absolute percent deviations (AAD) between experimental and calculated pressure, vapor composition, and saturated vapor and liquid densities. For given temperature

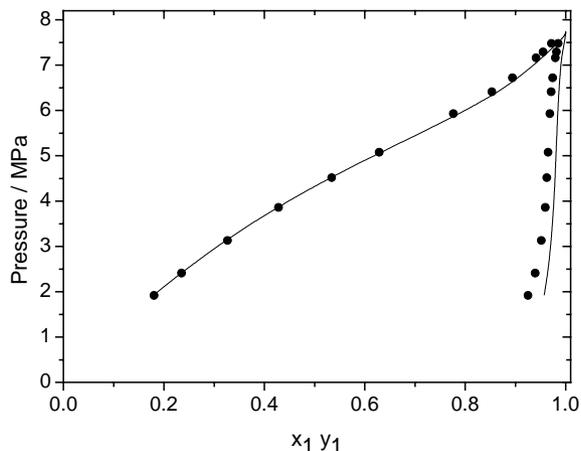


Fig. 6. Phase compositions for the system CO₂ (1)–dichloromethane (2) at 308.2 K: (●) experimental; (—) calculated.

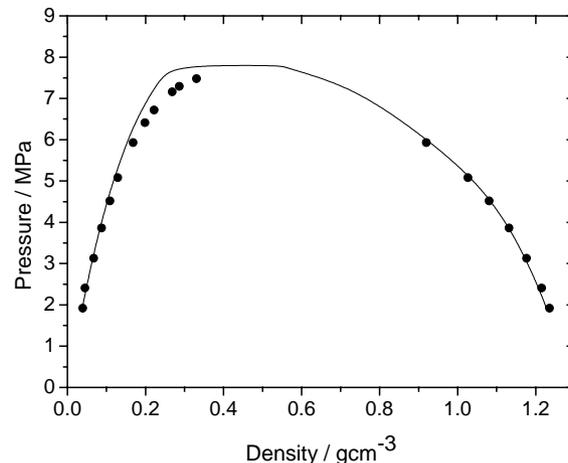


Fig. 7. Saturated densities for the system CO₂ (1)–dichloromethane (2) at 308.2 K: (●) experimental; (—) calculated.

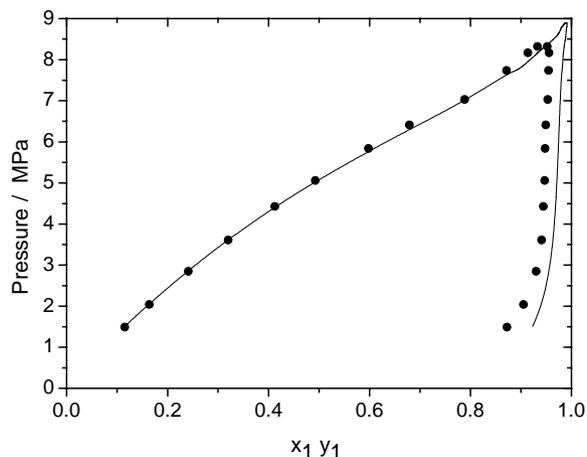


Fig. 8. Phase compositions for the system CO₂ (1)–dichloromethane (2) at 318.2 K: (●) experimental; (—) calculated.

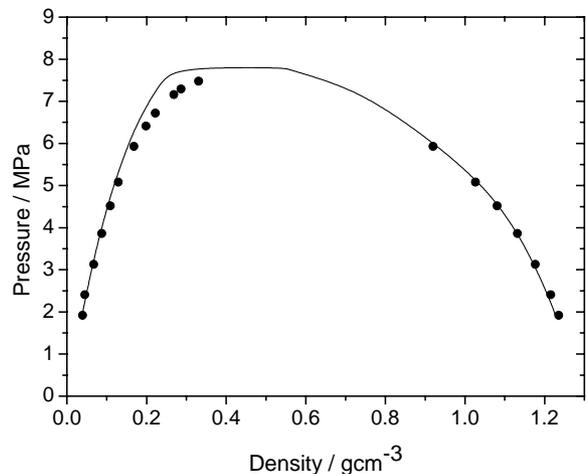


Fig. 9. Saturated densities for the system CO₂ (1)–dichloromethane (2) at 318.2 K: (●) experimental; (—) calculated.

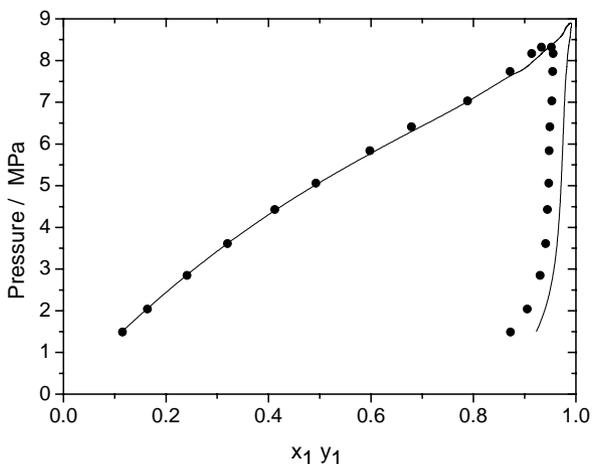


Fig. 10. Phase compositions for the system CO₂ (1)–dichloromethane (2) at 328.2 K: (●) experimental; (—) calculated.

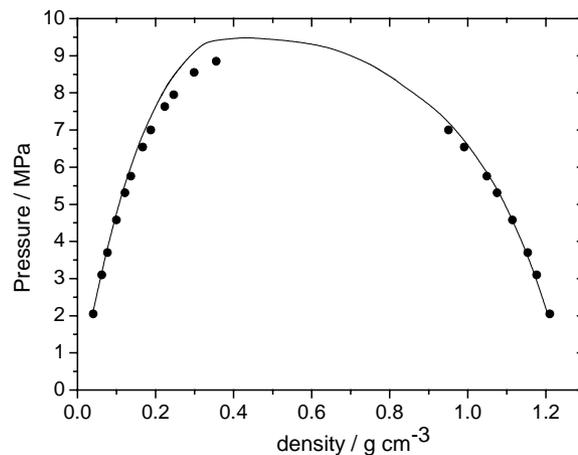


Fig. 11. Saturated densities for the system CO₂ (1)–dichloromethane (2) at 328.2 K: (●) experimental; (—) calculated.

and liquid composition, the model was calculating the pressure at equilibrium, the composition of the vapor phase, and the densities of the two phases at equilibrium.

The experimental and calculated data for the CO₂ + ethanol system are shown in Figs. 4 and 5. As observed, the QCHB model can simultaneously correlate, rather satisfactorily, the phase compositions as well as the saturated densities for this system.

A similar comparison is made in Figs. 6–11 for the CO₂ + dichloromethane system.

5. Discussion and conclusions

The new apparatus that was presented in this work, can be used for reliable experimental measurements of compositions and densities of the vapor and liquid phases at equilibrium for mixtures of fluids over an extended range of external temperature and pressure. Two representative systems were studied, one without and the other with hydrogen bonds. The first system, CO₂ + ethanol, was also used for testing the reliability of our measurements. Although data on phase compositions can be found rather easily in the literature, simultaneous data on the densities of the phases at equilibrium are rather scarce.

The experimental measurements of this work are ideally suited for testing equation-of-state models for the thermodynamic behavior of mixtures of polar and hydrogen bonded fluids. The measured data could be correlated with the QCHB model rather satisfactorily. The hydrogen-bonded system could be correlated almost quantitatively. One single set of binary parameters was used for all temperatures for both systems. It is worth pointing out that one binary parameter would have been sufficient if only the phase composition data were to be correlated. The second parameter deemed necessary for a more satisfactory correlation of the saturated densities.

List of symbols

A	parameter defined by Eq. (16)
C	parameter defined by Eq. (18)
E	energy
G	Gibbs energy
k	binary interaction parameter
K, B	densitometer's constants
l	parameter defined by Eq. (12)
n	number of experimental points
N	number of molecules
N_H	number of hydrogen bonds
N_r	total number of lattice sites
N_0	number of empty lattice sites
P	pressure
r	number of segments per molecule
R	gas constant
s	surface to volume fraction
S	entropy
T	temperature
v	average segmental volume
V	volume
x	mole fraction in liquid phase
X_i	physical quantity at point i
y	mole fraction in vapor phase
z	lattice coordination number
zq	average number of external contacts per molecule

Greek letters

Γ	non-random factor
δ_i	flex constant, characteristic for each fluid i
ε	interaction energy
θ	hole-free surface (contact) fraction
Θ	surface fraction
λ	binary interaction parameter
μ	chemical potential
ν_H	average per segment number of hydrogen bonds
ρ	density
τ	vibration period
φ	segment fraction

Superscripts

l	liquid phase
v	vapor phase

\sim	reduced quantity
*	scaling constant

Subscripts

H	hydrogen bond
i	component of type i
r	property pertinent to molecular segments
0	property pertinent to holes

Acknowledgements

Financial support for this work has been provided by the Greek GSRT/PENED 2001.

References

- [1] D.W. Jennings, R.-J. Lee, A.S. Teja, J. Chem. Eng. Data 36 (1991) 303–307.
- [2] A. Engwicht, U. Girreser, B.W. Muller, Biomaterials 21 (2000) 1587–1593.
- [3] A.D. Edwards, B.Y. Shekunov, A. Kordikowski, R.T. Forbes, P. York, J. Pharm. Sci. 90 (2000) 1115–1124.
- [4] J.-H. Yoon, H.-S. Lee, H. Lee, J. Chem. Eng. Data 38 (1993) 53–55.
- [5] L.A. Galicia-Luna, A. Ortega-Rodriguez, J. Chem. Eng. Data 45 (2000) 265–271.
- [6] K. Suzuki, H. Sue, M. Itou, R.L. Smith, H. Inomata, K. Arai, S. Saito, J. Chem. Eng. Data 35 (1990) 63–66.
- [7] S.N. Joung, W.Y. Chang, H.Y. Shin, S.Y. Kim, K.-P. Yoo, C.S. Lee, W.S. Huh, Fluid Phase Equilib. 185 (2001) 219–230.
- [8] H. Tanaka, M. Kato, J. Chem. Eng. Jpn. 28 (1995) 263–266.
- [9] C.J. Chang, C.-Y. Day, C.-M. Ko, K.-L. Chiu, Fluid Phase Equilib. 131 (1997) 243–258.
- [10] C.J. Chang, K.-L. Chiu, C.-Y. Day, J. Supercrit. Fluids 12 (1998) 223–237.
- [11] A.V. Gonzalez, R. Tufeu, P. Subra, J. Chem. Eng. Data 47 (2002) 492–495.
- [12] C. Panayiotou, J. Chem. Thermodyn. 35 (2003) 349–381.
- [13] C. Panayiotou, E. Stefanis, I. Tsivintzelis, M. Pantoula, I. Economou, Ind. Eng. Chem. Res., in press.
- [14] D. Missopolinou, C. Panayiotou, Fluid Phase Equilib. 110 (1995) 73–88.
- [15] IUPAC, International Thermodynamic Tables of the Fluid State – Carbon dioxide, Pergamon Press, Oxford, 1973.