

MEASUREMENT AND MODELING OF HIGH PRESSURE VAPOR-LIQUID EQUILIBRIA OF CO₂ + ALCOHOL BINARY SYSTEMS

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ABSTRACT

A new apparatus based on a static-analytic method was developed in this work to perform high-pressure vapor-liquid equilibria measurements up to 68 MPa and 373 K. In order to validate this new apparatus, vapor-liquid equilibria of the binary system CO₂ + ethanol was measured at temperatures of 313, 323 and 338 K and pressures from 1.2 to 11 MPa. Results were compared with data from the literature, differences for the mol fractions of liquid and vapor phases were $\leq 3\%$. Vapor-liquid equilibria for the binary systems CO₂ + 1-propanol, CO₂ + 2-methyl-1-propanol, CO₂ + 3-methyl-1-butanol and CO₂ + 1-pentanol at 313 K, 323 K and 333 K, and pressures in the range of 2-12 MPa was measured and modeled with the Peng-Robinson equation of state with the quadratic mixing rules of van der Waals with two adjustable parameters. The results shown that the average absolute deviations for the mol fractions were lower than 7% and 2% for the liquid and vapor phase, respectively.

INTRODUCTION

Environmentally friendly extraction processes with inert, innocuous, and low-boiling solvents, for selective recovery of high-purity active principles from biological substrates are being currently demanded. The use of supercritical carbon dioxide (SC-CO₂) as solvent is an alternative for biological substrates because it is non corrosive, non flammable, and of limited reactivity and toxicity; it is available in a highly purified form at low cost; and, it can be employed at near-environmental temperatures [1]. The solvent power of CO₂ is limited even at a very high pressures, as an alternative the use of mixtures of CO₂ + polar components (called co-solvents) can increase the solubility maintaining the selectivity for active principles relevant for food, pharmaceutical and cosmetic industries. Among others polar compounds, alcohols are selected as co-solvents because, they are suitable for human consumption [2]. In addition, alcohols can be used as solvents for bio-actives compounds contained in a solid matrix in the first step of a recovery process, where the CO₂ is used as an antisolvent to precipitate selectively the components of the extract [3].

Thermodynamic constraints as the mutual solubility of CO₂ and alcohol *i.e.*, vapor-liquid equilibria (VLE) of the binary system CO₂ + alcohol, have to be established to optimize the design and operational conditions of an extraction process using alcohols as a solvents or a co-solvents, and CO₂. Furthermore, thermodynamic models based on equation of state for the VLE can be used for interpolation purposes, and to estimate process conditions when experimental data are not available [4].

The objective of this work has been to measure and modeling the high pressure VLE for the binary systems CO₂ + alcohol (1-propanol, 2-methyl-1-propanol, 3-methyl-1-butanol and 1-pentanol).

MATERIALS AND METHODS

Materials

Carbon dioxide was supplied by AGA (Santiago, Chile), with a purity of 99.99 %. Analytical grade ethanol (purity, 99.9 %), 3-methyl-1-butanol (purity, $\geq 99\%$), 1-propanol (purity, $\geq 99.5\%$), and 2-methyl-1-propanol (purity, $\geq 99.9\%$) were obtained from Merck. 1-pentanol ($>99\%$ pure) by Sigma-Aldrich was purchased from Sigal (Santiago, Chile). All substances were used without further purification.

Experimental apparatus and technique

A schematic diagram of the new experimental apparatus used in this work to measure high-pressure VLE of CO_2 + alcohol systems, is shown in Figure 1. The equipment originally designed to operate with a static-synthetic method was modified incorporating a sampling and analysis arrangement to quantify the phase compositions (static-analytic method). The main component of the system was a high-pressure equilibrium view-cell (2.12 VID ViewCell, Thar Technologies, Pittsburgh, PA) which had a movable piston to adjust its pressure and/or volume ($0.1\text{-}0.3\text{ dm}^3$). The piston was driven by a manual pressure generator (HiP 87-6-5, Erie, PA) using water as the pressurizing fluid. The equilibrium pressure was measured using a pressure transducer (Heise, Shelton, CT) with a precision of 0.01 MPa. The temperature inside the cell was measured and adjusted to within 0.1 K of the set values with a PID controller (Digi-Sense, Vernon Hills, IL) that was connected to four electrical resistances on the cell (1000 W). A needle valve (HiP-11AF1 model 15, Erie, PA, USA) or a syringe pump (Teledyne ISCO, 206D, Lincoln, NE, USA) were used to feed CO_2 to the apparatus. The sampling arrangement for each phase included heating resistances to preheat the lines to avoid condensation of alcohol, a needle valve (HiP model 15-11AF1, Erie, PA, USA), an expansion and flow control valve (Butech, SFPMMV26V, Erie, PA, USA), a cold trap (home made) for the phase separations, and a wet-test meter (Ritter, TG 05/5, Bochum, Germany) to measure CO_2 content. The experimental equipment can be operated up to 373 K and 68 MPa.

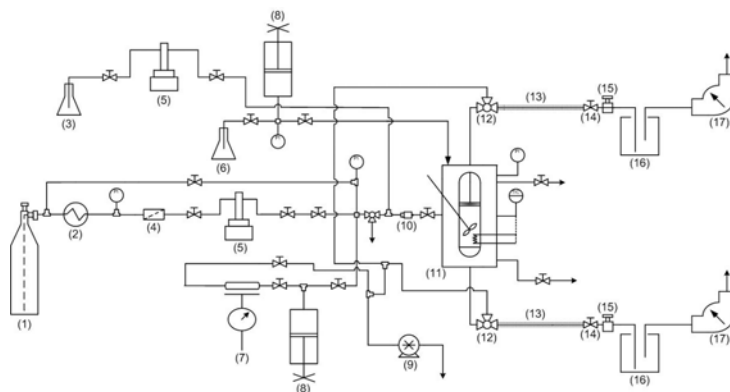


Figure 1. Schematic diagram of the experimental apparatus (1) CO_2 tank, (2) cooler, (3) hydroethanolic solution flask, (4) in-line filter, (5) syringe pump, (6) water flask, (7) analytical balance, (8) manual compressor, (9) vacuum pump, (10) check valve, (11) equilibrium view cell, (12) three way valve, (13) heating resistances, (14) needle valve, (15) sampling valve, (16) cold trap, (17) gas meter.

The experimental procedure was as follows; to start an experiment the equilibrium cell was cleaned and dried using ethanol and CO_2 . The amount of liquid component (alcohol) fed through the top window of the cell was determined gravimetrically. Usually, the volume of alcohol added was *ca.* 50% of the total volume of the cell ($\sim 0.15\text{ dm}^3$). The residual air remaining was removed from the cell with low-pressure CO_2 . The CO_2 was fed to the cell manually at pressure $\leq 6\text{ MPa}$ from the supply tank through the needle valve. For pressures > 6

MPa the feed of CO₂ was carried out assisted by the syringe pump operated at constant flow in the range of 20-40 cm³/min. With both components loaded to the cell, and after the system reached the desired temperature, the pressure was registered in periods of approximately 75 min. The equilibrium condition was reached when two consecutive measurement in pressure had a deviation <0.5 %. Two samples were withdrawn from the liquid and vapor phases through the preheated lines (at 5 K over the temperature of the cell) using the needle valves and the flow control valves. Both samples were expanded into the cold-traps placed in ice baths at 273 K where the alcohol (condensable component) and CO₂ (no-condensable component) were separated. The phase composition was calculated from the weight of the mass of alcohol collected in the trap and the volume measured for the CO₂ in the wet-test meter plus CO₂ density data.

RESULTS

CO₂ + ethanol binary system

In order to verify the operation of the modified static-analytic set-up, isothermal measurements of VLE for the binary system CO₂ (1) + ethanol (2) were performed at three temperatures 313, 323 and 338 K. This system was selected based on the large amount of experimental data available in literature at the conditions of interest in this work. Figure 2 shows the molar fraction of CO₂ in vapor (y_1) and liquid (x_1) phases as a function of temperature (T) and pressure (P) measured in this work. Each data point in Figure 2 for the vapor and liquid molar fractions measured was calculated as the average of four experimental measurements with deviations <1%. Data from literature [5,6,7] were also included in Figure 2 for comparison. At 313 K there was good agreement between the results obtained in this work and the results reported by Joung *et al.* [5] and Tsivintzelis *et al.* [6]. The average deviations from both data sets for the molar fractions were <3% for the liquid phase, and <5% for the vapor phase. In order to reduce these deviations a modification was made to the sampling system. The temperature of the heating resistances was increased, and the lines that connected the cold traps with the wet-test meters were replaced with shorter and no permeable lines. As a result of this modification, at 323 K the deviations between the molar fractions measured in this work from values reported by Joung *et al.* [5] decreased to <3% for both phases. A similar average value for the deviations was obtained from the comparison of data from Jennings *et al.* [7] at 337 K and Joung *et al.* [5] at 339 K with this study at 338 K. According to this analysis, a value of 3% was adopted as the uncertainty for the results measured using the experimental apparatus described in this work.

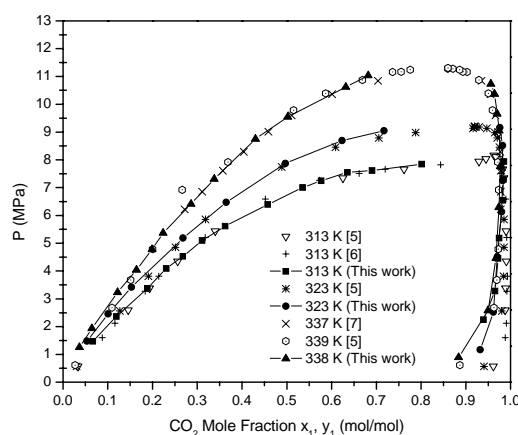


Figure 2: Comparison of VLE data for the CO₂ + ethanol system at 313, 323 and 338 K.

CO₂ + alcohol binary systems

Figure 3 shows the VLE data measured in this work at 313, 323 and 333 K for the binary systems containing CO₂ (1) + alcohol (2), with 1-propanol (A), 2-methyl-1-propanol (B), 3-methyl-1-butanol (C) and 1-pentanol (D). Values for the molar fractions were calculated as the average of two measurements with deviations <1 % for both vapor and liquid phase.

The mixtures CO₂ + alcohol show important differences in the critical temperatures and pressures; CO₂: 304.1 K, 7.37 MPa; 1-propanol: 536.8 K, 5.17 MPa; 2-methyl-1-propanol: 547.8 K, 4.30 MPa; 3-methyl-1-butanol: 579.4 K, 3.90 MPa; 1-pentanol: 588.2 K, 3.91 MPa. The behavior of the VLE is characterized by a liquid phase rich in the heavy component and was able to dissolve more CO₂ as the pressure increased (at constant temperature), or as the temperature decrease (at constant pressure). For the vapor phase, rich in CO₂, the isothermal increment in the pressure for $P < 7.37$ MPa affected negatively the presence of alcohol in this phase. However, for pressures $P > 7.37$ MPa the solvent power of the SC-CO₂ increased as the pressure increased because of the increment in the density of CO₂. At constant pressure the molar fraction of alcohol in the vapor phase increased as the temperature increased. The effect of the vapor pressure of the alcohol over its solubility in the vapor phase surpassed the reduction in the density of the CO₂. In this work, for all systems in Figure 3 was visually monitored that there was no partial liquid miscibility at the temperatures and pressures studied.

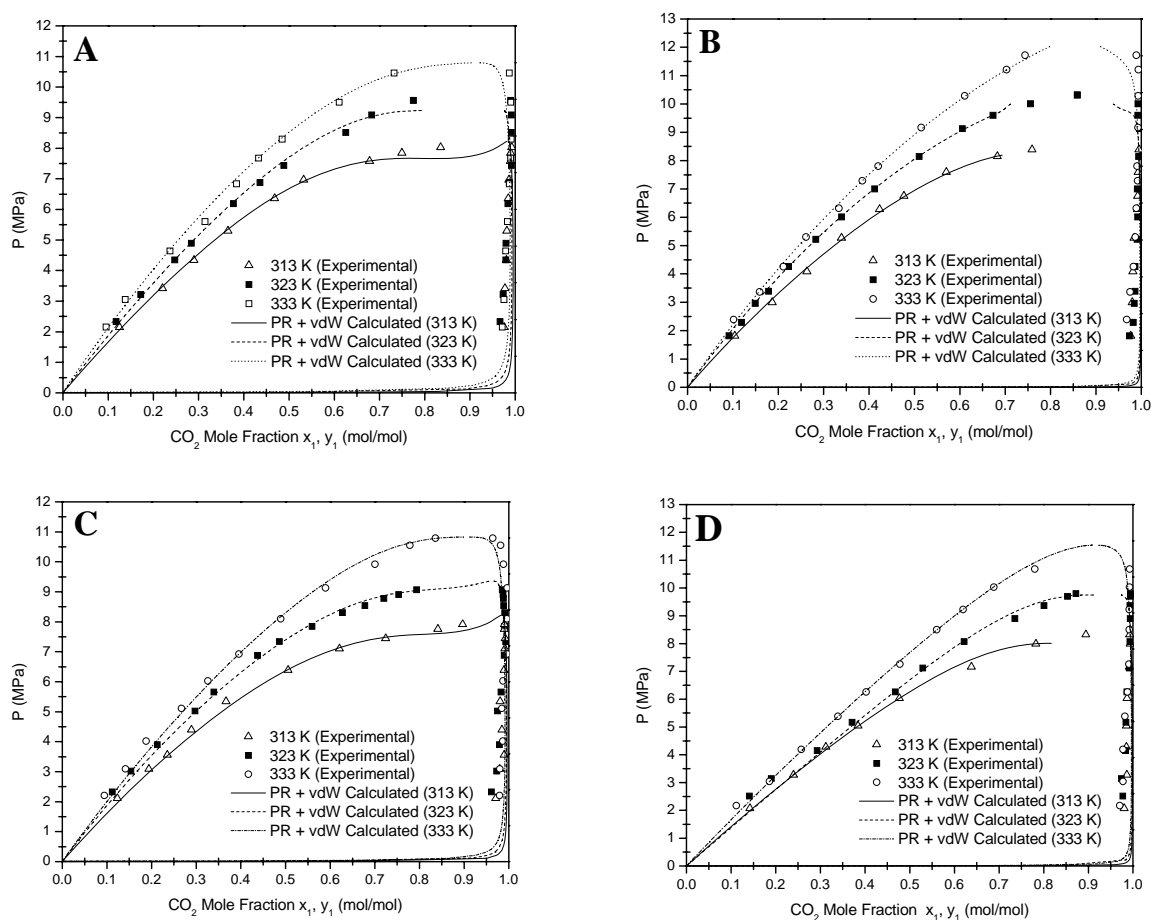


Figure 3: Experimental and calculated VLE compositions. **A:** CO₂ + 1-propanol; **B:** CO₂ + 2-methyl-1-propanol; **C:** CO₂ + 3-methyl-1-butanol; **D:** CO₂ + 1-pentanol.

VLE data from the literature for binary systems of Figure 3 were compared with our data for the three isotherms, 313, 323 and 333 K. For CO₂ + 1-propanol [8;9;10] and CO₂ + 1-pentanol [11,12,13] deviations were <3%. For the system CO₂ + 2-methyl-1-propanol [14,15,16] difference with data from the literature were <5%, showing the largest discrepancies for the molar fraction of the liquid phase. The comparison with data published for CO₂ + 3-methyl-1-butanol [14,16,17,18] indicated deviations <1%.

The experimental VLE data in Figure 3 was modeled using the Peng-Robinson EoS (PR-EoS) [19], Equation (1). We used the quadratic van der Waals mixing rules [20] for the energetic (a) and co-volume (b) parameters, with two adjustable coefficients k_{ij} and l_{ij} , equations (2) and (3). The sum of the average absolute deviations (AAD) between the values measured and correlated for the vapor and liquid phase molar fractions was defined as the objective function (OF) for minimization, Equation (4), where NP represents the total number of experimental values.

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

$$a = \sum_i \sum_j z_i z_j a_{ij} \quad a_{ij} = \sqrt{a_{ii} a_{jj}} (1 - k_{ij}) \quad (2)$$

$$b = \sum_i \sum_j z_i z_j b_{ij} \quad b_{ij} = \frac{b_{ii} + b_{jj}}{2} (1 - l_{ij}) \quad (3)$$

$$OF = \frac{100}{NP} \sum_{i=1}^{NP} \left| \frac{x_i^{cal.} - x_i^{exp.}}{x_i^{exp.}} \right| + \frac{100}{NP} \sum_{i=1}^{NP} \left| \frac{y_i^{cal.} - y_i^{exp.}}{y_i^{exp.}} \right| \quad (4)$$

Table 1 summarizes the results of the correlation using equations (1)-(4) in terms of binary coefficients parameters along with the average absolute deviations for the liquid and vapor phase (AAD_x , AAD_y).

Table 1: Binary interaction parameters and average absolute deviations (AAD_x , AAD_y).

T (K)	k_{12}	l_{12}	AAD_x (%)	AAD_y (%)
CO₂ + 1-Propanol				
313	0.0880	-0.0190	5.98	0.98
323	0.0851	-0.0223	2.74	1.15
333	0.0737	-0.0348	3.07	0.98
CO₂ + 1-Pentanol				
313	0.0894	-0.0391	1.57	1.15
323	0.0824	-0.0499	1.88	1.43
333	0.0768	-0.0518	1.69	1.50
CO₂ + 2-Methyl-1-Propanol				
313	0.0912	-0.0329	4.46	0.88
323	0.0882	-0.0401	3.93	0.93
333	0.0865	-0.0395	5.86	1.04
CO₂ + 3-Methyl-1-Butanol				
313	0.0846	-0.0219	2.13	1.08
323	0.0740	-0.0166	6.76	1.12
333	0.0670	-0.0279	2.86	1.09

In Figure 3, the correlation of the VLE data was represented using tie lines. Good agreement was observed between the values measured and predicted with the PR-EoS for the four binary systems studied. The optimized values for the binary interactions coefficients and $AADs$ were

in the same order of magnitude. However, the capability of the PR-EoS to represent the experimental data follows the order: CO₂ + 1-Pentanol < CO₂ + 1-Propanol < CO₂ + 3-Methyl-1-Butanol < CO₂ + 2-Methyl-1-Propanol as shown in Table 1. The k_{12} parameters were positive and ten times larger than the absolute values of l_{12} parameters (negatives) for the twelve isotherms studied. This indicates that the non-idealities of CO₂ + alcohol mixtures are due to energetic interactions between unlike molecules than differences related to its size or shape. Values of k_{12} decreased systematically as the temperature increased, a similar behavior was observed for the absolute values of l_{12} . Deviations in the liquid phase compositions were $1.7\% \leq ADD_x \leq 6.8\%$ lower than the deviations for the vapor phase, $0.88\% \leq ADD_y \leq 1.5\%$, specially at low pressures. A poor representation was observed for the critical region. The equation of state and mixing rules selected were not able to represent the phase envelope at the highest pressure due to the high asymmetry between the CO₂ and alcohol molecules.

CONCLUSIONS

The high-pressure vapor-liquid equilibrium data for the binary systems CO₂ + 1-propanol, CO₂ + 2-methyl-1-propanol, CO₂ + 3-methyl-1-butanol, and CO₂ + 1-pentanol were measured at temperatures of 313, 323 and 333 K and pressures from 2 MPa to 12 MPa, using a new experimental apparatus. Experimental uncertainty for the mol fractions for both liquid and vapor phases $\leq 3\%$. The Peng-Robinson equation of state with the quadratic mixing rules of van der Waals with two adjustable parameters were used to correlate the vapor-liquid equilibria data for the four CO₂ + alcohol systems with average absolute deviations for the mol fraction of the liquid and vapor phase of $\leq 7\%$ and $\leq 2\%$, respectively.

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