High pressure phase equilibrium measurements for binary systems CO_2 + 1-pentanol and CO_2 + 1-hexanol

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ABSTRACT

This work reports phase equilibrium measurements for the systems $CO_2(1)$ + 1-pentanol(2) and $CO_2(1)$ + 1-hexanol(2). Experiments were carried out using a high pressure variable-volume view cell with operating temperatures ranged from 303.15 K to 373.15 K and pressures up to 17.05 MPa for the system CO_2 + 1-pentanol, and 303.15 K to 353.15 K with pressures up to 16.2 MPa for the system CO_2 + 1-hexanol. The CO_2 molar fractions were ranged from 0.3987 to 0.9192 for the system $CO_2(1)$ + 1-pentanol(2) and from 0.3926 to 0.9800 for the system $CO_2(1)$ + 1-hexanol(2), respectively. Only vapor–liquid (VL) phase transitions were observed for the system $CO_2(1)$ + 1-pentanol(2), while for the system with 1-hexanol(2) vapor–liquid (VL), liquid–liquid (LL) and vapor–liquid–liquid (VLL) phase transition were observed. The experimental data sets were modeled using the Peng–Robinson equation of state with a classical van der Waals quadratic mixing rule (PR-vdW2) and with Wong–Sandler (PR-WS) mixing rule, and they were compared with predicted values using the Predictive Soave–Redlich–Kwong (PSRK) equation of state. PR-WS model provided a better fitting to experimental data for both systems modeled.

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1. Introduction

In the last years has been great interest on the development and application of supercritical fluids in many fields of science and engineering, mainly due to the green chemistry concept [1]. The carbon dioxide (CO_2) is the most widely used fluid as a supercritical solvent due to their unique attractive properties such as, inexpensive, nonflammable, nontoxic, inert, naturally abundant and its critical condition is reached in a relatively easy way, at 304.15 K and 7.38 MPa [1–3], and it can be mentioned that the CO_2 present a high solubility with organic compounds, and generally lower solubility in polar, ionic and polymeric compounds [3].

A variety of potential applications of supercritical carbon dioxide in chemical and food engineering can be mentioned, mainly in oils and fats manufacturing and derivatives, and it has been extensively studied in the past three decades [4–10]. Supercritical fluid (SCF) technology has received great attention in the application and development of new processes and products. Some of these applications are the use of SCFs as solvent in several chemical reactions [1,11–17], chromatographic analysis [18],

polymer processing [19,20] pharmaceutical and food processing [19], coal and petroleum processing [21], environmental applications [12,19,22] and micro and nanoparticles production [23–25]. One of most important characteristic of SCFs lies on it as an alternative medium for chemical reactions due to their unique properties, such as gas-like transport properties and liquid-like densities that can be easily manipulated by changing the pressure and temperature. Besides environmental advantages, one additional attractive feature of SCFs as a medium for chemical reactions is that they can decrease mass transfer limitations and allow a better control of selectivity and reaction yield. In general way, the SCFs application can permit advantageous combination of the reaction, separation, and purification steps [1,16,19,22].

As mentioned by Gutiérrez et al. [3], the addition of a co-solvent into the mixture (with SCF) becomes necessary and interesting [26–28]. For example, the use of CO_2 + polar compounds (called co-solvent) mixtures can increase the solubility, maintain the selectivity for active principles of specific components and significantly increase the performance of the process [3]. As mentioned before, among others, polar compounds, such as low molar mass alcohols (C1–C6) can be used as co-solvents in several processes with supercritical fluids involving natural compounds extraction, enzyme-catalyzed reaction, liquid–liquid separations, biofuel production, natural gas reforming and, specifically C5 and C6 alcohols, as hydrate formation inhibitors in the crude oil storage and transportation. In all areas where the mixtures CO_2 + alcohol are

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relevant, the phase behavior of the system has central role. Furthermore, phase equilibrium data are essential in designing, modeling and optimization of supercritical processes. Since it is not always possible to carry out experiments at all possible temperatures and pressures, generally thermodynamic models based on equations of state are used for prediction of phase behavior and phase equilibria of several complex mixture at high pressures.

Regarding the thermodynamic modeling of phase equilibrium at high pressure systems the cubic equations of state with van der Waals and/or Gibbs free energy-based mixing rules can be a powerful tool. These type of thermodynamic models (cubic EoS) present the advantage that are easily implemented, computational effort is low and are reliable in to predict the phase behavior for systems CO_2 + short alcohols [2–34]. Furthermore, molecular modeling has been successful used for modeling the phase behavior of systems with alcohols [33,34]. In terms of simulation, control and optimization of supercritical processes the application of cubic type equation as thermodynamic model is an interesting and desirable option due to their relative low computation effort.

The phase equilibrium behavior for CO_2 + alcohols systems at high pressures have been widely studied, in which methanol and ethanol are alcohols that present the most experimental data (VLE data) published, and ethanol and iso-propanol are commonly selected as co-solvents. Gutiérrez et al. [3] presented a summarized review on the VLE data for CO_2 + alcohols (C1–C5) presented in the literature. Recently, Secuianu et al. [29], Beier et al. [35], Elizalde-Solis et al. [36] presented VLE, LLE and VLLE data for the system CO_2 + 1-hexanol at temperatures of 293.15–432.15 K. For CO_2 + 1-pentanol system phase equilibrium data have been presented by several authors at temperature range of 293.15–426.86 K [3,37–40]. It can be observed that, besides a considerable number of publications regarding phase equilibrium for CO_2 with 1-hexanol and 1-pentanol and thermodynamic modeling with cubic equation of state, experimental data of these systems obtained close to the critical point of the mixture are rarely presented in the literature. Besides, it is important to mention that the most data presented were obtained using an analytical method for phase equilibrium measurement at high pressures.

In this context, a complementary new set of vapor–liquid, liquid–liquid and vapor–liquid–liquid equilibrium measurement for the two systems CO_2 + 1-pentanol and CO_2 + 1-hexanol, at different temperatures, is presented in this work. Also, for the thermodynamic modeling of these two systems the Peng–Robinson equation of state, with quadratic van der Waals (vdW2) and Wong–Sandler (WS) mixing rules, and the Predictive Soave–Redlich–Kwong (PSRK) equation of state are used to correlate and model the experimental data obtained.

2. Experimental

2.1. Materials

Carbon dioxide (99.9 wt% in the liquid phase) was supplied by White Martins S.A (Curitiba/PR/Brazil). 1-Pentanol (99.8%) and 1-hexanol were supplied by Sigma–Aldrich (São Paulo/SP/Brazil). All compounds were used without further treatment.

2.2. Apparatus and experimental procedure

Experimental apparatus and procedure used in this work were the same used in the early works presented by our group [31,32,41–43,6], in which the phase equilibrium transitions data were measured in a high pressure variable-volume view cell. The experimental setup consists of a variable-volume view cell with two sapphire windows for visual observation, an absolute pressure

transducer (Smar, model LD 301), with an uncertainty of ±0.03 MPa, a pressure indicator (Novus, model N1500) for pressure transition measure and a syringe pump (ISCO, model 260D). In this work, an amount of the alcohol (1-pentanol or 1-hexanol) was loaded with a syringe into the equilibrium cell. The solute (alcohol) was weighed on a precision balance scale (Marte, model AM220), with 0.0001 g accuracy. The load of a known amount of CO_2 was performed with the help of the syringe pump (ISCO, model 260D) resulting in an uncertainty of ±0.005 g in CO_2 loadings. Based on the uncertainty associated with the CO_2 loading and the weighing of solute (alcohols), we estimate that the uncertainties associated to the global concentrations of the mixtures were lower than 0.5%, in mass basis. The cell content was then continuously stirred with a magnetic stirrer using a Teflon-coated stirring bar. After loaded the cell, the temperature controller was then turned on and, once the desired temperature was reached, it was successfully controlled to within 0.5 K; the pressure inside the cell was then increased until a one-phase system was visually observed. The system was kept at this point for at least 20 min to allow stabilization, afterwards the pressure was slowly decreased (typically at a rate of 0.3–0.5 MPa min^{-1}) until the formation of a new phase was observed [41–43]. This procedure was repeated at least three times for each temperature and global composition and then the average value of pressure transition was obtained. The procedure used for obtaining vapor-liquid-liquid equilibrium data was similar to that early presented [32,43]. After finding a pressure condition in which the system consisted of two fluid phases, the pressure was continuously decreased up to the observation of the appearance of a third (vapor) phase.

3. Thermodynamic modeling

The thermodynamic modeling of the experimental data obtained in this work was performed using the Predictive Soave–Redlich–Kwong equation of state [44], and also by correlating the experimental data with the Peng–Robinson equation of state (PR-EoS) [45], with the conventional quadratic mixing rule of van der Waals (vdW2) and Wong–Sandler mixing rule (WS) [46,47]. As briefly presented in our previous works [31,32,41,48,49] the mixture parameter for vdW2 can be summarized as:

$$a = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j a_{ij} \tag{1}$$

$$b = \sum_{i=1}^{n}\sum_{j=1}^{n} x_i x_j b_{ij} \tag{2}$$

with,

$$a_{ij} = (a_i a_j)^{1/2}(1 - k_{ij}) \tag{3}$$

and

$$b_{ij} = \frac{1}{2}(b_i + b_j)(1 - l_{ij}) \tag{4}$$

where the a_i and b_i are parameters of pure compounds [45] and l_{ij} and k_{ij} are adjustable parameters.

The mixture parameters a and b for the WS mixing rule are given by Refs. [46,47]:

$$\frac{a}{RT} = Q\frac{D}{1 - D} \tag{5}$$

$$b = \frac{Q}{1 - D} \tag{6}$$

where,

$$Q = \sum_i \sum_i x_i x_j \left(b_{ij} - \frac{a_{ij}}{RT} \right) \tag{7}$$