The Journal of Supercritical Fluids 135 (2018) 69–77

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu

High pressure phase equilibria for binary mixtures of CO_2 + 2-pentanol, vinyl butyrate, 2-pentyl butyrate or butyric acid systems

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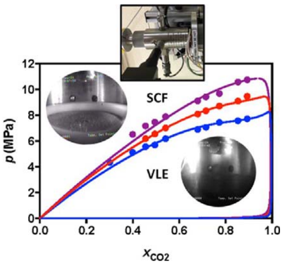
GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
High-pressure phase equilibrium
Supercritical carbon dioxide
Equation of state
Mixing rule

ABSTRACT

High pressure phase equilibrium for four binary systems, (CO_2 + 2-pentanol, CO_2 + vinyl butyrate, CO_2 + 2-pentyl butyrate and CO_2 + butyric acid), were measured at three temperatures of (313.15, 323.15 and 333.15) K and pressures up to 11 MPa. These four organic compounds are those involved in the kinetic resolution of *rac*-2-pentanol and their phase equilibria play a significant role in the separation processes of the reaction compounds. Phase behaviour measurements were taken using a synthetic method in a variable volume high-pressure cell. It was checked that the solubility of CO_2 in the four systems decreases with increases in temperature at a constant pressure and all systems present type-I phase behaviour within scope of this work. Modifications of Henry's Law and Peng-Robinson and Soave-Redlich-Kwong equations of state combined with the Quadratic mixing rule were used to correlate experimental equilibrium data to determine the phase behaviour of these systems.

1. Introduction

Supercritical carbon dioxide ($scCO_2$) is well known as a "green" alternative to organic solvents because of its non-toxic nature. In addition, it presents accessible critical parameters (T_c = 304.2 K, p_c = 72.9 bar), a low cost and non-flammability. The high-pressure phase equilibrium of mixtures with $scCO_2$ and other compounds plays an essential role in an extensive group of applications such as supercritical fluid extraction, reaction, fractionation, nanoparticle formation, the separation of non-volatile mixtures, supercritical fluid chromatography, hydrothermal crystal growth, the hydrothermal destruction of hazardous waste, polymer processing, etc. [1]. The experimental data obtained by phase equilibrium assays must be accurate and reliable because of the severe conditions of any possible applications [2].

The numerous applications of supercritical carbon dioxide have led many authors to attempt a comprehensive understanding of the phase behaviour of (CO_2 + organic compounds) systems. Many papers are related to binary systems of CO_2 and different alcohols in which the

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https://doi.org/10.1016/j.supflu.2018.01.003
Received 13 December 2017; Received in revised form 2 January 2018; Accepted 3 January 2018

high-pressure phase equilibrium is studied [1,3–10]. Such studies of ($scCO_2$ + alcohol) systems are of interest because of the high number of chemical processes in which they are involved, such as the supercritical extraction of thermal labile compounds, the dehydration of alcohols and extraction of natural products [1]. Other interesting families of organic compounds have been mentioned in high-pressure phase equilibrium studies, including alkanes [11], acids [12], amides [13], ketones [13], aromatic compounds like pyrrole [14,15], furans [16] and nitriles [17,18]. Several reviews have attempted to compile the great number of studies related to high-pressure phase equilibrium experimental data in different systems in the last decades [19–21]. These reviews classify the results according to the experimental method used to obtain them and most experimental data are related to binary systems in which one of the components is CO_2.

The (CO_2 + organic compound) systems studied in this work have not been widely investigated. In fact, to the best of our knowledge only the (CO_2 + 2-pentanol) and (CO_2 + butyric acid) systems appears in the literature in conditions of high pressure. Lee and Lee [22] obtained the high pressure vapour-liquid equilibrium for the (CO_2 + 2-pentanol) system at 313.2 K and the experimental data were correlated by several equations of state and mixing rules. Furthermore, Silva-Oliver et al. [2] and Bejarano et al. [9] measured the vapour-liquid equilibrium of the same system. Byun et al. [23] worked with the (CO_2 + butyric acid) system in a wide range of temperatures (313–393 K). The rest of the systems studied in this work have not been studied previously.

Density-based and equation of state (EoS) models are the most common approaches used for the correlation and prediction of the phase equilibria and properties of mixtures [1], and mixing rules are necessary to precisely extend EoS to mixtures. Many authors have published studies using EoSs and mixing rules to obtain thermodynamic models of high-pressure fluid phase equilibria [1,13,14,24–29].

The organic compounds studied in this work are the components involved in the racemic resolution of *rac*-2-pentanol by transesterification with a vinyl ester catalysed by a biocatalyst (lipase). Fig. 1 shows the stoichiometric scheme of the reaction. (*S*)-2-pentanol is a chiral intermediate in the synthesis of several drugs for the potential treatment of diseases like Alzheimer, which inhibits the release and synthesis of the β-amyloid peptide [30]. The kinetic resolution of a mixture of two enantiomers, such as (*R*, *S*)-2-pentanol, is simply based on the difference in their enzymatic transformation rate [31]. The biocatalyst acts selectively by promoting only the reaction of (*R*)-2-pentanol with the vinyl ester to yield the (*R*)-2-pentyl ester, hence facilitating the separation of both enantiomers.

It has long been known that $scCO_2$ has excellent properties for extracting, dissolving and transporting chemicals compounds due to its high diffusivity. For this reason, the knowledge of the high-pressure phase equilibrium data of (CO_2 + 2-pentanol, vinyl butyrate, 2-pentyl butyrate or butyric acid) binary mixtures would allow the relative solubility between CO_2 and the organic compounds to be determined and hence the capability of CO_2 to separate the reaction products by means of its tuning solvent power. CO_2 constitutes a promising alternative to organic solvents due to it can contribute to the integration of reaction/separation processes in a single step for reactions like that shown in Fig. 1. However, $scCO_2$ could have a denaturing and deactivation effect on enzymes mainly due to pressurization/depressurization cycles, a decrease in the pH of the enzyme microenvironment and covalent modification of free amino groups on the surface of the protein forming carbamates [32]. To solve these difficulties, a biocatalytic ionic liquid/$scCO_2$ biphasic system can be used because ionic liquids, which are also considered as “green” solvents, contribute to the stabilization of the enzymes and are excellent non-aqueous environments for enzyme catalysis, resulting in more environmentally benign and efficient processes [33]. The success of this biphasic system is based on the great solubility of the $scCO_2$ in the ionic liquid phase, while the ionic liquid is practically insoluble in the $scCO_2$ phase. Therefore, $scCO_2$ can extract organic substances from ionic liquids without any cross-contamination of the chemical with the ionic liquid [34,35].

Because binary system measurements provide information that would allow the prediction of phase behaviour of multicomponent systems, the first aim of this paper was to obtain the experimental high pressure phase equilibrium data for (CO_2 + 2-pentanol), (CO_2 + vinyl butyrate), (CO_2 + 2-pentyl butyrate) and (CO_2 + butyric acid) systems by testing mixtures of CO_2 with these four components at the temperatures of 313.15, 323.15 and 333.15 K. In this way, our group will contribute to expanding the available databases, which is a necessary task for designing and optimizing the supercritical fluid reaction/extraction processes. The second objective was to correlate the experimental high pressure data by density-based models and by the well-known Peng-Robinson (PR) [36] and Soave-Redlich-Kwong (SRK) [37] EoS coupled with Quadratic mixing rule in a semi-predictive approach to describe the phase equilibrium topology of the four binary mixtures. Consequently, the behaviour of these systems may be predicted or inferred. The critical pressure and temperature (p_c, T_c) of the organic compounds were taken from literature or the Joback group contribution method was used to estimate them. The acentric factor (ω) was estimated by the Lee-Kessler group contribution method.

2. Experimental

2.1. Materials

Carbon dioxide (mass fraction purity $>$ 0.999) was purchased from Linde Abelló S.A. (Barcelona, Spain) and used as received. The organic compounds, 2-pentanol (mass fraction purity: 0.98; CAS RN 6032-29-7), butyric acid (mass fraction purity: 0.99; CAS RN 107-92-6), vinyl butyrate (mass fraction purity: $>$ 0.99; CAS RN 123-20-6) and 2-pentyl butyrate (mass fraction purity: 0.99; CAS RN 60415-61-4), were purchased from Sigma-Aldrich (Germany). Acetone (mass fraction purity $>$ 0.999), used for the validation of the experimental method, and hexane (purity $>$ 0.990), used as solvent for the cleaning of the system, were also purchased from Sigma-Aldrich (Germany). All compounds used in this work were used without further purification and are summarized in Table 1.

2.2. Apparatus and procedure

Fig. 2 represents a schematic diagram of the commercial Super Phase Monitor system (SPM system, Thar Technologies, Inc., USA) used in this work to measure the phase behaviour of 2-pentanol, vinyl butyrate, 2-pentyl butyrate and butyric acid in $scCO_2$. The main components of the SPM system, which was controlled by the software provided from the supplier, are a variable volume view cell, high-pressure

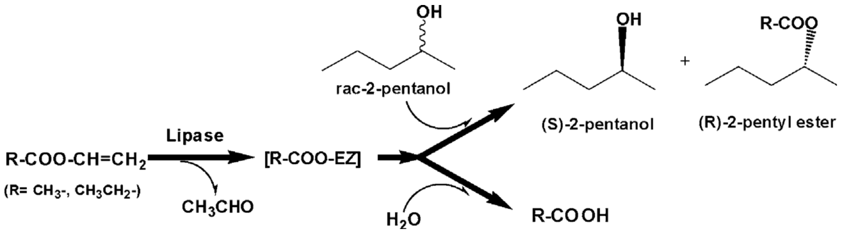

Fig. 1. Stoichiometric scheme of racemic resolution of *rac*-2-pentanol catalysed by a lipase [31].