

High pressure phase equilibria for binary mixtures of CO₂ + 2-pentanol, vinyl butyrate, 2-pentyl butyrate or butyric acid systems

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ABSTRACT

High pressure phase equilibrium for four binary systems, (CO₂ + 2-pentanol, CO₂ + vinyl butyrate, CO₂ + 2-pentyl butyrate and CO₂ + 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 CO₂ 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.

KEYWORDS: High-pressure phase equilibrium, supercritical carbon dioxide, equation of state, mixing rule.

1. INTRODUCTION

Supercritical carbon dioxide (scCO₂) 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 scCO₂ 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 (CO₂ + organic compounds) systems. Many papers are related to binary systems of CO₂ and different alcohols in which the high-pressure phase equilibrium is studied [1, 3-10]. Such studies of (scCO₂ + 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 CO₂.

The (CO₂ + organic compound) systems studied in this work have not been widely investigated. In fact, to the best of our knowledge only the (CO₂ + 2-pentanol) and (CO₂ + 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 (CO₂ + 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 (CO₂ + 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.

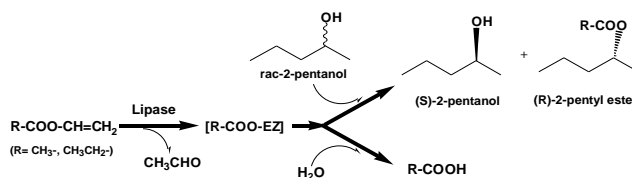


Figure 1. Stoichiometric scheme of racemic resolution of *rac*-2-pentanol catalysed by a lipase [31].

It has long been known that scCO₂ has excellent properties for extracting, dissolving and transporting chemical compounds due to its high diffusivity. For this reason, the knowledge of the high-pressure phase equilibrium data of (CO₂ + 2-pentanol, vinyl butyrate, 2-pentyl butyrate or butyric acid) binary mixtures would allow the relative solubility between CO₂ and the organic compounds to be determined and hence the capability of CO₂ to separate the reaction products by means of its tuning solvent power. CO₂ 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, scCO₂ 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/scCO₂ 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 scCO₂ in the ionic liquid phase, while the ionic liquid is practically insoluble in the scCO₂ phase. Therefore, scCO₂ 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 (CO₂ + 2-pentanol), (CO₂ + vinyl butyrate), (CO₂ + 2-pentyl butyrate) and (CO₂ + butyric acid) systems by testing mixtures of CO₂ 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.

Table 1. Specifications of chemical compounds used in this work.

Chemical Name	Source	Mass Fraction Purity ^a	Purification Method	Analysis Method ^a
Carbon Dioxide	Linde Abelló (Spain)	>0.99	None	-
Acetone	Sigma-Aldrich (Germany)	>0.99	None	GC ^b
2-Pentanol	Sigma-Aldrich (Germany)	0.98	None	GC ^b
Butyric Acid	Sigma-Aldrich (Germany)	0.99	None	GC ^b
Vinyl Butyrate	Sigma-Aldrich (Germany)	>0.99	None	GC ^b
2-Pentyl Butyrate	Sigma-Aldrich (Germany)	0.99	None	GC ^b

^a Mass fraction purity and analysis method were provided by the suppliers.

^b Gas Chromatography.

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 scCO₂. 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 generator and visual apparatus. The cell is a high-pressure cell with a maximum capacity of 26.5 mL which supports a maximum pressure of approximately 69 MPa and is equipped with electric heating rods coupled to a thermostat, which maintains the temperature constant. The stability of the thermostat was estimated as ± 0.2 K. In addition, the cell has a pressure

transducer (Stellar Technology, model ST1560, USA) and a digital thermometer (Yokogawa, model 7563, USA) connected to a four-wire class A RTD probe (Conax, USA). The standard uncertainty of both sensors was estimated at 0.02 MPa and 0.2 K, respectively, i.e. $u(p) = 0.02$ MPa and $u(T) = 0.2$ K. The cell, stirred by means of an integral stirrer, is based on a piston-cylinder, which is moved with a hydraulic pump. The position of the piston-cylinder position determines the cell volume. The entrance of CO₂ into the cell is controlled by the high-pressure generator formed by two syringe pumps (Teledyne ISCO, model 500D, USA), whose pressure is controlled by its own controller. These pumps are connected to a water bath cooling system (Frigiterm, J.P. Selecta S.A., Spain) to liquefy and store CO₂ from a cylinder. A sapphire window with a camera and an illumination source allows visual observation of the cell and a video system brings the image to a computer screen.

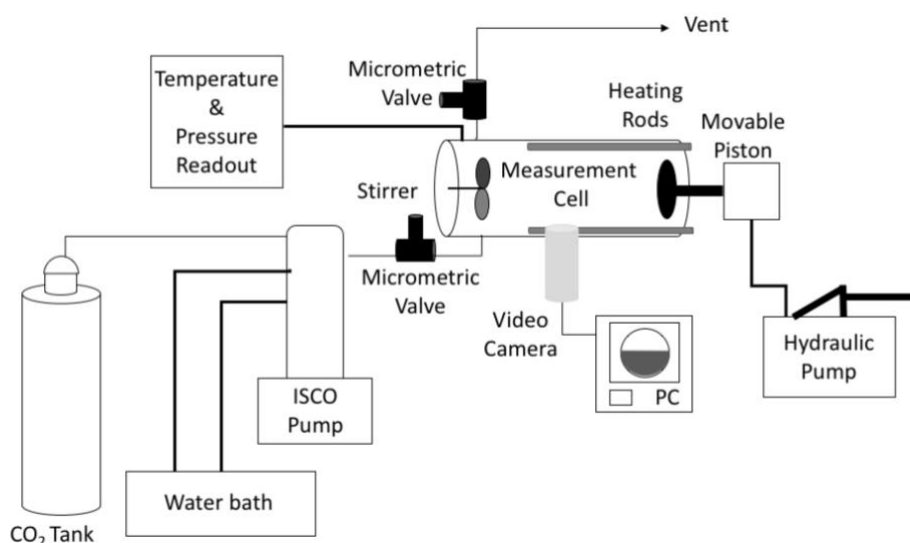


Figure 2. Scheme of the high-pressure phase equilibrium apparatus.

The phase behaviour was determined following a synthetic method. The organic compound was loaded into the cell with a syringe after weighing with an analytical scale (Sartorius, model ED 1245, Germany) with an accuracy of 0.1 mg. Before each experiment, the cell was purged with CO₂ at low pressure by opening the bypass valve to

remove traces of air. Then, compressed CO₂ was introduced into the cell using the syringe pump. To determine the mole fraction of the binary mixture inside the cell, the loaded mass of CO₂ was calculated by the volume displacement of the pump and CO₂ density obtained from NIST [38] at the pressure and temperature values chosen. The mass of the CO₂ remaining after the purge was calculated to be <1% and was ignored. The mole fraction standard uncertainty was estimated to be 0.001, i.e. $u(x) = 0.001$.

Once the components were loaded inside the cell, the pressure of the binary mixture was raised by the reduction of the volume of the cell by moving the piston until only one phase was observed at a fixed temperature value. Then, the system was kept as a homogeneous mixture for at least 30 minutes under stirring to ensure phase equilibrium. Once in equilibrium, the pressure of the cell was decreased in a stepwise manner by increasing the cell volume (by moving of the piston) until a second phase was observed. The pressure was recorded for every increase of 80 μ L volume. For a given load (CO₂ + organic compound) of the cell, the experiments were repeated at least twice. In order to determine the bubble points, the pressure was plotted vs. volume, obtaining a two-section graph. The change in slope determined the equilibrium pressure, as described by Thamanavat et al. [39], the change denoting a switch in compressibility module, meaning that a new gas phase was formed. This procedure was repeated at 313.15, 323.15 and 333.15 K in order to generate isothermal curves.

2.3. Validation of experimental method

The experimental technique used in this study was first validated using the well-studied (CO₂ + acetone) system. The bubble point pressures measured for the system were compared with data obtained by other authors: e.g. Hsieh and Vrabec [40], Stievano and Elvassore [41] and Day et al. [42]. The first two authors used a synthetic method, while

the third one used an analytical method. Fig. 3 shows the results obtained in this work for the (CO₂ + acetone) system at 313.15 K compared with those measured by the three authors cited. As can be seen from Fig. 3 our experimental data were in good agreement (average deviation of ± 0.1 MPa in experimental pressure points) with the data published in the literature even taking into account the different methods used to obtain the bubble points. The small discrepancies between the different sources and the experimental data can be mainly attributed to uncertainties in the different experimental methods used. Our experimental data can contribute to extending the mole fraction range studied by other researchers.

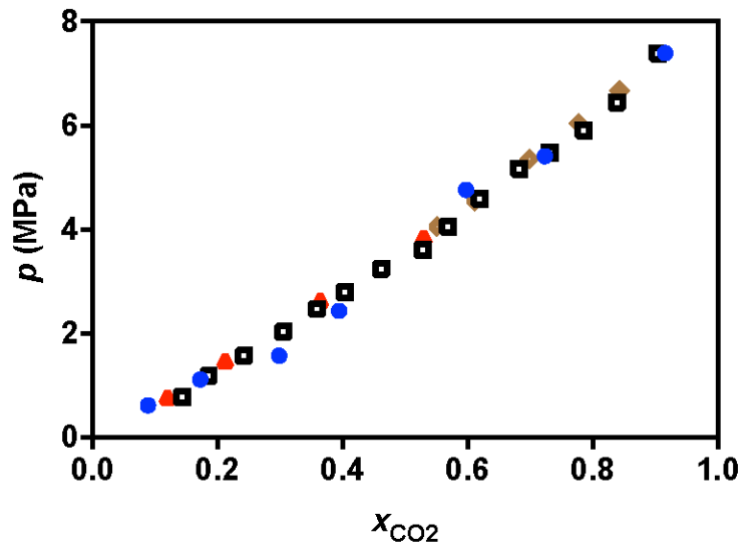


Figure 3. Phase equilibrium diagram for the (CO₂ + acetone) system at 313.15 K. ● This work; ◆ Hsieh and Vrabec [40]; ▲ Stievano and Elvassore [41]; ■ Day et al. [42].

3. RESULTS AND DISCUSSION

3.1. Experimental phase equilibrium data

Experimental pressure-composition (p, x) isotherms obtained for the (CO₂ + 2-pentanol, vinyl butyrate, 2-pentyl butyrate or butyric acid) systems at 313.15, 323.15 and 333.15 K are presented in Tables 2-5, respectively. The results obtained for (CO₂ + 2-pentanol) and

(CO₂ + butyric acid) are in good agreement with those previously published in the literature [2, 9, 22, 23] as there are no major deviations (average deviation of 0.3 MPa approximately). Fig. 4.a and Fig. 4.b show the comparison between literature data and our experimental results for the (CO₂ + 2-pentanol) and (CO₂ + butyric acid) systems, respectively. The bubble (or equilibrium) points measured for each system and their phase equilibrium topology are presented in Figs. 5 and 6. Mixture critical points were not measured within the range of the CO₂ mole fraction of this study. For all the binary systems studied (Figs. 5 and 6), the bubble pressure increased as the CO₂ mole fraction increased at a fixed temperature, meaning that the liquid phase (rich in organic compound) is able to dissolve more CO₂. However, CO₂ solubility in the liquid phase decreased in all systems when the temperature rose under a constant pressure. Three phases were not observed for the tested temperatures or mole fractions ranges of this study, but all systems showed critical mixture curves with a maximum in pressure-temperature space between the critical temperatures of CO₂ and the component. For these reasons, phase behaviour of these systems, according to Scott and Konyenburg [43], can be established as Type-I in the conditions of this work. Type-I behaviour is the simplest case and means that only one phase is present throughout the phase diagram. It is represented by a continuous critical curve, which connects both critical points of the pure compounds in a p - T phase diagram.

Table 2. Phase equilibrium experimental data for (CO₂ + 2-pentanol) system at 313.15, 323.15 and 333.15 K.^a

CO ₂ mole fraction	Pressure (MPa)	CO ₂ mole fraction	Pressure (MPa)	CO ₂ mole fraction	Pressure (MPa)
T=313.15 K		T=323.15 K		T=333.15 K	
0.893	7.73	0.893	9.48	0.893	10.75
0.853	7.58	0.853	9.10	0.853	10.58
0.773	7.45	0.773	8.71	0.773	9.69
0.715	7.07	0.715	8.34	0.715	9.42
0.679	6.90	0.679	8.09	0.679	9.12
0.542	6.19	0.542	7.02	0.542	7.89
0.495	5.70	0.495	6.56	0.495	7.47
0.455	5.57	0.455	6.20	0.455	7.18
0.399	5.12			0.399	6.52
0.302	4.35				

^a Standard uncertainties, u , are $u(p) = 0.02$ MPa; $u(T) = 0.2$ K; $u(x) = 0.001$.

Table 3. Phase equilibrium experimental data for (CO₂ + vinyl butyrate) system at 313.15, 323.15 and 333.15 K.^a

CO ₂ mole fraction	Pressure (MPa)	CO ₂ mole fraction	Pressure (MPa)	CO ₂ mole fraction	Pressure (MPa)
T=313.15 K		T=323.15 K		T=333.15 K	
0.932	6.77	0.963	8.23	0.862	8.95
0.825	5.88	0.957	8.08	0.786	7.21
0.791	5.63	0.912	7.69	0.753	6.79
0.753	5.06	0.882	7.04	0.643	5.60
0.700	4.63	0.840	6.56	0.592	4.89
0.662	4.34	0.793	6.18	0.517	4.24
0.634	4.14	0.699	5.21	0.461	3.79
0.624	4.07	0.658	4.72	0.411	3.34
0.583	3.80	0.613	4.38	0.356	2.92
0.582	3.79	0.558	4.04	0.278	2.30
0.500	3.30	0.512	3.64		
0.427	2.92	0.456	3.19		
0.361	2.62	0.395	2.86		
0.305	2.41	0.325	2.48		
		0.245	2.05		

^a Standard uncertainties, u , are $u(p) = 0.02$ MPa; $u(T) = 0.2$ K; $u(x) = 0.001$.

Table 4. Phase equilibrium experimental data for (CO₂ + 2-pentyl butyrate) system at 313.15, 323.15 and 333.15 K.^a

CO ₂ mole fraction	Pressure (MPa)	CO ₂ mole fraction	Pressure (MPa)	CO ₂ mole fraction	Pressure (MPa)
T=313.15 K		T=323.15 K		T=333.15 K	
0.886	6.52	0.932	7.58	0.923	8.84
0.860	6.37	0.897	7.46	0.886	8.47
0.839	6.17	0.875	6.95	0.838	7.62
0.804	5.89	0.844	6.71	0.807	7.10
0.769	5.55	0.767	5.98	0.784	6.94
0.747	5.32	0.727	5.63	0.738	6.53
0.734	5.28	0.668	5.25	0.736	6.46
0.704	5.01	0.651	5.12	0.717	6.25
0.669	4.65	0.624	4.92	0.686	6.10
0.633	4.33	0.577	4.59	0.624	5.78
0.593	4.07	0.538	4.22	0.553	5.14
0.537	3.49	0.491	4.05	0.468	4.54
0.469	3.09	0.420	3.72	0.436	4.32
0.365	2.61	0.333	3.26	0.396	4.09
		0.220	2.63	0.354	3.86
				0.303	3.59

^a Standard uncertainties, u , are $u(p) = 0.02$ MPa; $u(T) = 0.2$ K; $u(x) = 0.001$.

Table 5. Phase equilibrium experimental data for (CO₂ + butyric acid) system at 313.15, 323.15 and 333.15 K.^a

CO ₂ mole fraction	Pressure (MPa)	CO ₂ mole fraction	Pressure (MPa)	CO ₂ mole fraction	Pressure (MPa)
T=313.15 K		T=323.15 K		T=333.15 K	
0.933	7.59	0.919	9.32	0.899	10.88
0.910	7.44	0.877	8.66	0.882	10.66
0.875	7.23	0.849	8.18	0.859	10.33
0.818	6.87	0.837	8.07	0.797	9.79
0.708	6.17	0.834	7.97	0.752	9.25
0.658	5.90	0.796	7.65	0.703	8.58
0.553	5.03	0.763	7.39	0.670	8.18
0.500	4.59	0.666	6.66	0.587	7.54
0.452	4.38	0.540	5.99	0.529	7.02
0.399	3.99	0.425	5.05	0.472	6.51
0.350	3.54	0.364	4.73	0.436	6.18
0.277	3.01	0.302	4.43	0.395	5.78
		0.241	3.99		
		0.157	3.43		

^a Standard uncertainties, u , are $u(p) = 0.02$ MPa; $u(T) = 0.2$ K; $u(x) = 0.001$.

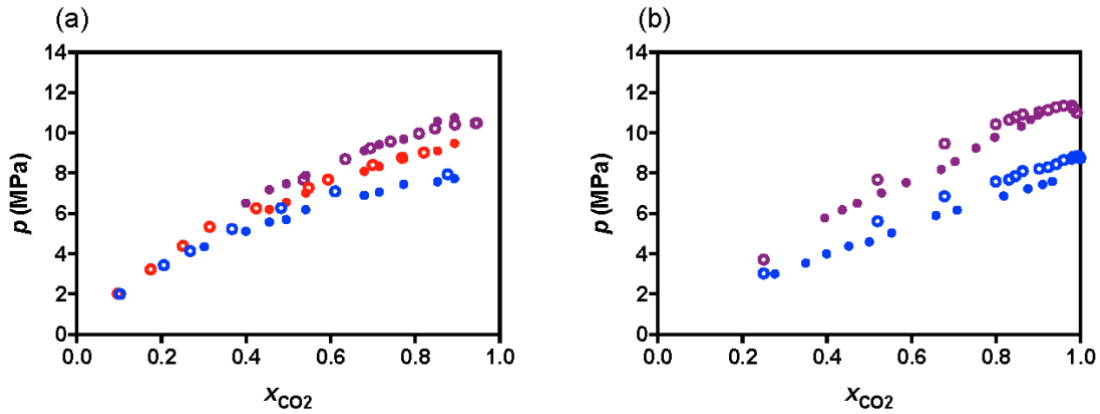


Figure 4. Comparison of phase equilibrium data found in literature with the results obtained in this work. a) CO₂ + 2-pentanol system; (●) 313.15 K, this work, (●) 323.15 K, this work, (●) 333.15 K, this work, (○) 313.15 K, Bejarano et al. [9], (○) 323.15 K, Bejarano et al. [9], (○) 333.15 K, Silva-Oliver et al. [2], b) CO₂ + butyric acid system; (●) 313.15 K, this work, (●) 333.15 K, this work, (○) 313.15 K, Byun et al. [23], (○) 333.15 K, Byun et al. [23].

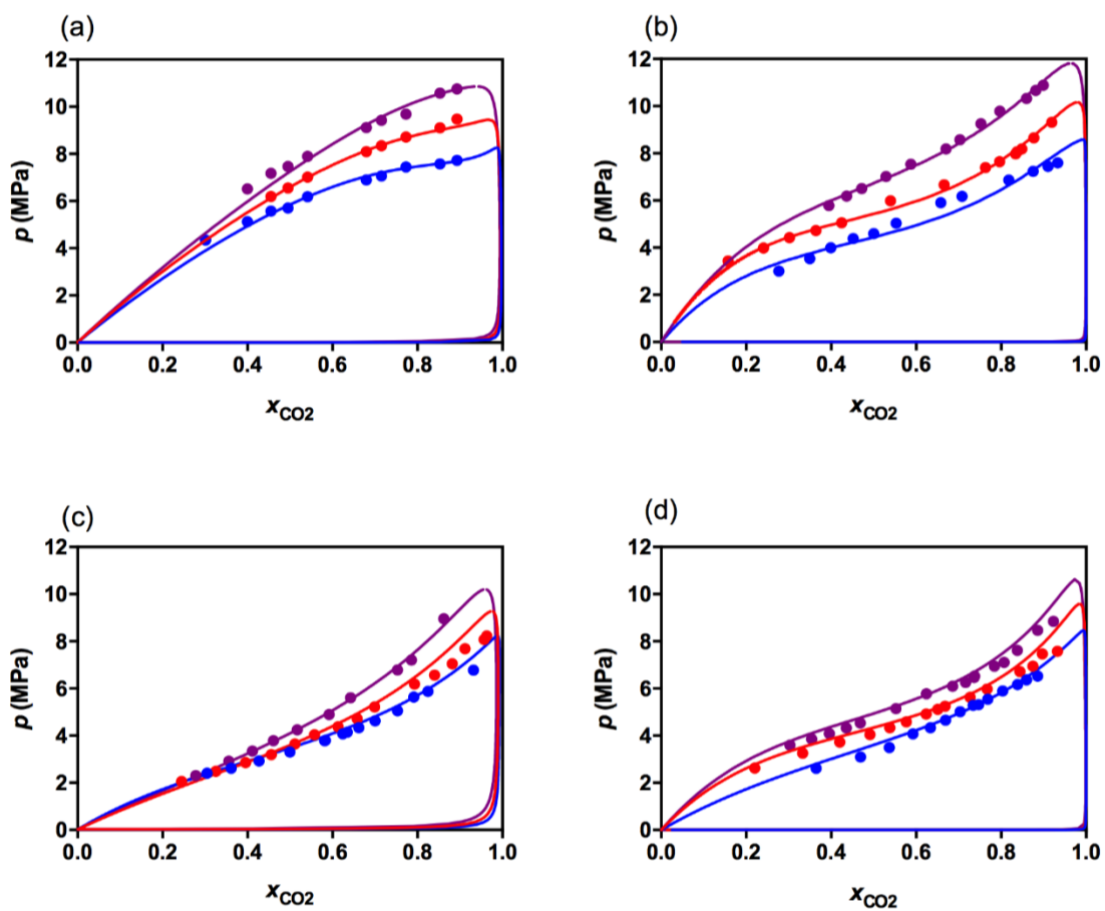


Figure 5. Phase equilibria in the (CO_2 + organic compound) binary system at: (●) 313.15 K, (●) 323.15 K and (●) 333.15 K. (a) 2-pentanol; (b) butyric acid; (c) vinyl butyrate; (d) 2-pentyl butyrate. Curves show the results of the thermodynamic modelling using the Peng-Robinson EoS and the Quadratic mixing rule as described in the text.

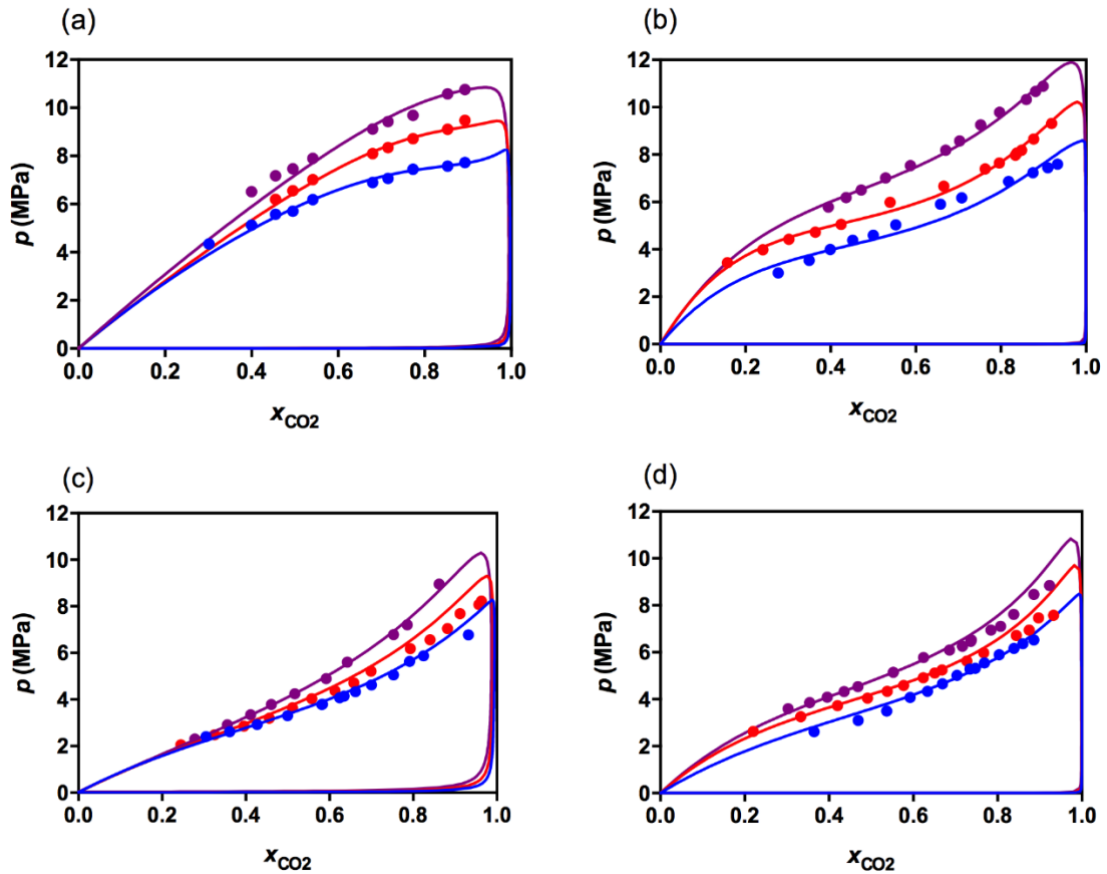


Figure 6. Phase equilibria in the (CO₂ + organic compound) binary system at: (●) 313.15 K, (●) 323.15 K and (●) 333.15 K. (a) 2-pentanol; (b) butyric acid; (c) vinyl butyrate; (d) 2-pentyl butyrate. Curves show the results of the thermodynamic modelling using the Soave-Redlich-Kwong EoS and the Quadratic mixing rule as described in the text.

3.2. Density-based models

CO₂ density has a dominant effect on its solubility in organic compounds. Chrastil [44] presented an equation based on a solvato model capable of correlating the composition (solubility) balance of a solute in the supercritical phase for the binary vapour-liquid or solid-vapour equilibria. This is a linear dependency, in logarithmic basis, between the solute solubility and the supercritical fluid density. The Chrastil equation has been applied to dilute gaseous solutions (i.e., low concentration of solute in the supercritical phase)

and it has been also used to determine the quality of the experimental measurements of solubility.

The solubility of a gas in a liquid is usually described by the use of the Henry's law, which establishes that the amount of gas dissolved in a liquid has a linear dependence with its partial pressure. Nevertheless, for high pressures, deviations from Henry's law can become noticeable and hence this law is frequently not adequate to represent the solubility of supercritical fluids in organic liquids. Hernández et al. [45] have developed two semiempirical dependent correlations, based on a modification of Henry's law, to represent the solubility of a supercritical fluid in a liquid. The supercritical fluid mole fraction in the liquid phase was given by the Eqs. (1) and (2) for binary mixtures. These authors found that Eq. (1) presents better results when the mixture exhibits positive deviations to Henry's law and the Eq. (2) correlates better for binary mixtures which exhibit negative deviations to Henry's law.

$$\ln(x_{scCO_2}) = A \ln(\rho_{scCO_2}) + B \quad (\text{constant temperature}) \quad (1)$$

$$\ln(x_{scCO_2}) = A' \frac{\ln(\rho_{scCO_2})}{p} + B' \quad (\text{constant temperature}) \quad (2)$$

where x_{scCO_2} is the mole fraction of supercritical carbon dioxide, p is the pressure (MPa), ρ_{scCO_2} is the supercritical carbon dioxide density (kg/m³) and A , B , A' and B' are the fitting parameters which are regressed from the experimental data. Table 6 presents the values of the fitting parameters and the regression coefficient, R^2 , obtained from the regression for the investigated systems.

Table 6. Regression parameters of Eqs. (1) and (2) for (CO₂ + 2-pentanol, butyric acid, vinyl butyrate or 2-pentyl butyrate) binary systems at 313.15, 323.15 and 333.15 K.

Compound	<i>T</i> (K)	CO ₂ density range (kg·m ⁻³)	<i>A</i>	<i>-B</i>	<i>R</i> ²	<i>-A'</i>	<i>B'</i>	<i>R</i> ^{2'}
2-Pentanol	313.15	93.4-250.7	1.0647	5.9939	0.9949	3.2701	2.1380	0.9750
	323.15	142.0-327.7	0.8269	4.8724	0.9965	3.5596	2.0295	0.9864
	333.15	140.3-339.6	0.9068	5.3782	0.9929	3.7674	1.9017	0.9940
Butyric acid	313.15	59.1-238.7	0.8498	4.6715	0.9895	1.9381	1.2714	0.9876
	323.15	65.5-312.4	1.1091	6.1856	0.9334	2.9343	1.7907	0.9958
	333.15	118.8-349.0	0.7498	4.4433	0.9751	2.8796	1.4424	0.9989
Vinyl butyrate	313.15	45.7-185.1	0.7676	3.9554	0.9393	1.3095	0.9444	0.9944
	323.15	36.5-232.2	0.6835	3.6511	0.9504	1.2351	0.7730	0.9991
	333.15	39.9-233.1	0.6537	3.5833	0.9651	1.1726	0.5646	0.9976
2-Pentyl butyrate	313.15	50.1-172.4	0.6571	3.4738	0.9746	1.1812	0.7841	0.9945
	323.15	48.2-197.7	0.9353	4.8913	0.9328	1.8270	1.2287	0.9953
	333.15	65.8-227.8	0.8914	4.7735	0.9474	2.0089	1.2002	0.9934

As can be observed in Table 6, the regression coefficients are generally higher by using Eq. (2). Nevertheless, for the (CO₂ + 2-pentanol) system, better regression coefficients have been obtained with Eq. (1), as reported in Table 6. This fact was also observed by Bejarano et al. [9] for the same system, who estimated values of the Henry constant indicating positive deviations to Henry's law, in agreement with our results. Fig. 7 depicts the results of the regressions at 313.15, 323.15 and 333.15 K. CO₂ solubility in the organic compounds can be established for the three temperature values studied in the order 2-pentanol > butyric acid > esters. The differences in the CO₂ solubility in the organic compounds may be mainly attributed to their relative polarity [27]. The fact that the CO₂ solubility is greater in 2-pentanol than in the rest of the organic compounds involved in the racemic resolution of *rac*-2-pentanol is of great interest, because it would allow the

recovery of the unreacted (*S*)-2-pentanol (Fig. 1) in a biphasic ionic liquid/CO₂ system, allowing the separation of the racemic mixture.

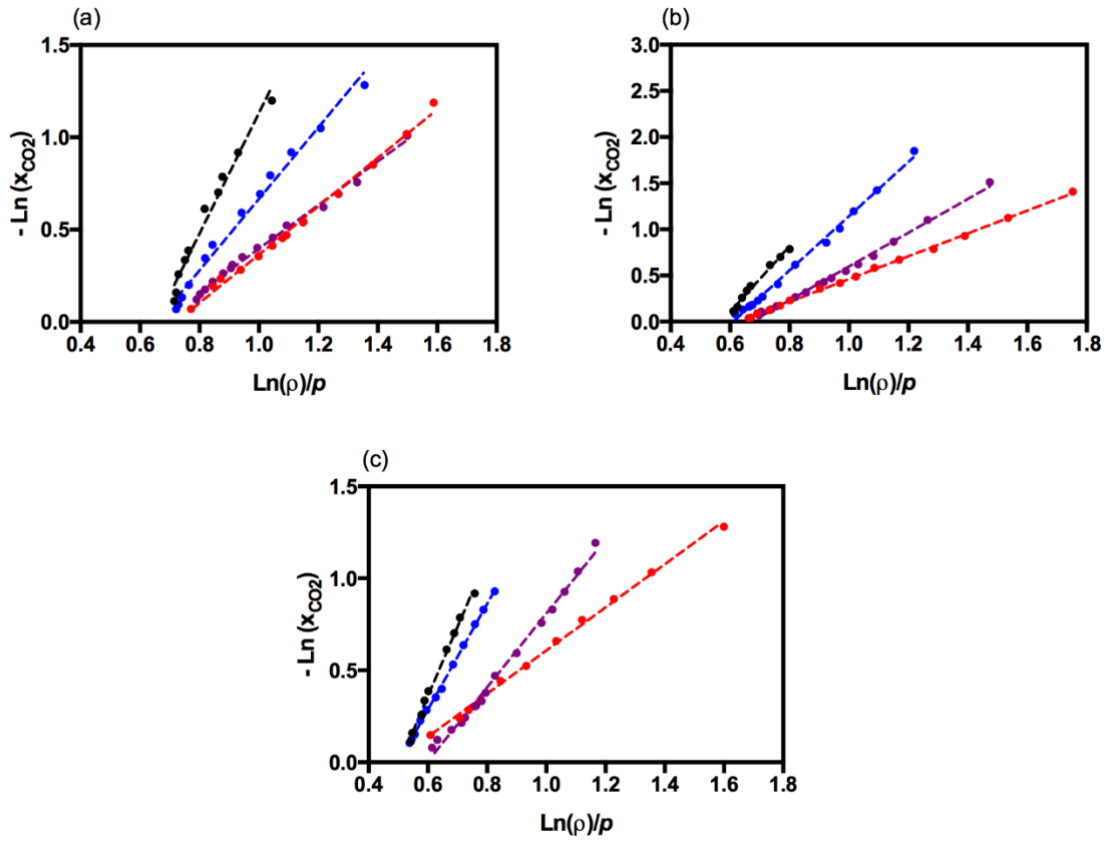


Figure 7. Linear correlation between $\ln(x_{CO_2})$ and $\ln(\rho_{CO_2}/p)$ for binary mixtures of CO₂ with 2-pentanol (●), butyric acid (●), vinyl butyrate (●) and 2-pentyl butyrate (●) at a) 313.15 K; b) 323.15 K; c) 333.15 K.

3.3. Thermodynamic modeling

A great variety of EoS to predict phase behaviour of binary mixtures can be found in the literature. Among them, cubic EoS, such as Peng-Robinson [36] and Soave-Redlich-Kwong [37] EoS, have been widely studied because they are simple and accurate. In this work, the experimental data were correlated using these two EoS combined with Quadratic (Q) mixing rules which include two binary interaction parameters (BIP) named as k_{ij} , l_{ij} .

The Peng-Robinson EoS for a pure compound is expressed as follows:

$$p = \frac{RT}{V - b} - \frac{a[T]}{V(V + b) + b(V - b)} \quad (3)$$

where p , T , V and R are the pressure, temperature, molar volume and the ideal gas constant, respectively, while $a[T]$ and b are obtained from the critical temperature (T_c), critical pressure (p_c) and acentric factor (ω) as describe below for pure compounds:

$$a[T] = 0.45724 \left(\frac{R^2 T_c^2}{p_c} \right) \alpha[T_r] \quad (4)$$

$$T_r = \frac{T}{T_c} \quad (5)$$

$$\alpha[T_r] = (1 + m[1 - T_r^{0.5}])^2 \quad (6)$$

$$m = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (7)$$

$$b = 0.0778 \left(\frac{RT_c}{p_c} \right) \quad (8)$$

For its part, the Soave-Redlich-Kwong EoS is defined by the following equations:

$$p = \frac{RT}{V - b} - \frac{a[T]}{V(V + b)} \quad (9)$$

$$a[T] = 0.42747 \left(\frac{R^2 T_c^2}{p_c} \right) \alpha[T_r] \quad (10)$$

$$m = 0.48 + 1.574\omega - 0.176\omega^2 \quad (11)$$

$$b = 0.08664 \left(\frac{RT_c}{p_c} \right) \quad (12)$$

where T_r and $\alpha[T_r]$ are calculated with Eqs. (5) and (6), respectively.

In order to adapt the Peng-Robinson and Soave-Redlich-Kwong EoS to a binary mixture, the Quadratic van der Waals one fluid mixing rule was used. The equations below show how to combine a and b parameters of the pure compounds to obtain a_{mix} and b_{mix} :

$$a_{mix} = \sum_i \sum_j x_i x_j a_{ij} \quad (13)$$

$$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij}) \quad (14)$$

$$b_{mix} = \sum_i \sum_j x_i x_j b_{ij} \quad (15)$$

$$b_{ij} = \frac{b_i + b_j}{2} (1 - l_{ij}) \quad (16)$$

where a_i , a_j , b_i and b_j are pure component parameters calculated with Eqs. (4) and (8) for Peng-Robinson EoS and Eqs. (10) and (12) for Soave-Redlich-Kwong EoS. k_{ij} and l_{ij} are defined as the BIP obtained from correlation of the experimental data.

Correlations for the (CO₂ + 2-pentanol), (CO₂ + vinyl butyrate), (CO₂ + 2-pentyl butyrate) and (CO₂ + butyric acid) binary systems studied were obtained with the software Phase Equilibria 2000 (PE2000) developed by Brunner et al. [46]. PE2000 uses the Simplex-Nelder-Mead algorithm [47] to optimize the BIP and the results are shown in Figs. 5 and 6. The critical parameters and acentric factors needed to solve the Peng-Robinson and Soave-Redlich-Kwong EoS were estimated with the Joback [48] or taken from the literature [49-52] and Lee-Kessler [53] group contribution methods, respectively. The values used for the critical parameters are shown in table 7.

Table 7. Critical parameters (p_c, T_c) and acentric factor (ω) of the pure compounds used for thermodynamic modelling.

Compound	Mw (g/mol)	p_c (MPa)	T_c (K)	ω
Carbon Dioxide	44.10	7.38 ^a	304.2 ^a	0.225 ^a
Acetone	58.08	4.70 ^b	508.1 ^b	0.306 ^{**}
2-Pentanol	88.20	3.68 ^c	560.3 ^c	0.557 ^{**}
Butyric Acid	88.11	4.06 ^d	615.2 ^d	0.690 ^{**}
Vinyl Butyrate	114.14	3.56 [*]	539.9 [*]	0.394 ^{**}
2-Pentyl Butyrate	158.24	2.34 [*]	618.7 [*]	0.565 ^{**}

^a Retrieved from DIPPR database [49].

^b Retrieved from Ambrose et al. [50]

^c Retrieved from Gude and Teja [51]

^d Retrieved from Andereya and Chase [52]

^{*} Estimated with Joback method.

^{**} Estimated with Lee-Kessler method.

Table 8 shows the BIP used with the Peng-Robinson and Soave-Redlich-Kwong EoS for each system and temperature. The suitability of using the modelling approach to correlate the experimental bubble point data with the points calculated by Peng-Robinson and Soave-Redlich-Kwong EoS was assessed from the relative mean square deviation (RMSD) according to Eq. (17):

$$RMSD = \sqrt{\frac{1}{n} \sum_{i=1}^n \left(\frac{p^{exp} - p^{calc}}{p^{calc}} \right)^2} \quad (17)$$

where p is the equilibrium pressure of the coexisting phases at a fixed temperature value for the experimental and calculated points and n is the number of experimental points. The RMSD values obtained for the isothermal curves of the (CO₂ + 2-pentanol), (CO₂ + vinyl butyrate), (CO₂ + 2-pentyl butyrate) and (CO₂ + butyric acid) binary systems with Peng-Robinson and Soave-Redlich-Kwong EoS are summarized in Table 9.

Table 8. BIP (k_{ij} , l_{ji}) used for the thermodynamic modelling of the (CO₂ + 2-pentanol), (CO₂ + vinyl butyrate), (CO₂ + 2-pentyl butyrate) and (CO₂ + butyric acid) binary systems at 313.15, 323.15 and 333.15 K.

<i>T</i> (K)	2-Pentanol		Butyric Acid		Vinyl Butyrate		2-Pentyl Butyrate	
	k_{ij}	l_{ij}	k_{ij}	l_{ij}	k_{ij}	l_{ij}	k_{ij}	l_{ij}
Peng-Robinson - Quadratic								
313.15	0.0821	-0.0328	-0.0618	-0.1007	-0.0499	-0.0998	-0.0212	-0.0425
323.15	0.0747	-0.0371	-0.0650	-0.1178	-0.0683	-0.0706	-0.0613	-0.1196
333.15	0.0688	-0.0348	-0.0402	-0.1007	-0.0627	-0.0557	-0.0636	-0.1237
Soave-Redlich-Kwong - Quadratic								
313.15	0.0898	-0.0351	-0.0723	-0.1028	-0.0505	-0.0858	-0.0300	-0.0700
323.15	0.0873	-0.0255	-0.0743	-0.1205	-0.0631	-0.0728	-0.0501	-0.1001
333.15	0.0814	-0.0290	-0.0467	-0.1012	-0.0644	-0.0562	-0.0501	-0.1003

Table 9. RMSD values (%) obtained for the thermodynamic modelling using Peng-Robinson and Soave-Redlich-Kwong EoS combined with Quadratic mixing rules for the studied systems at 313.15, 323.15 K and 333.15 K.

<i>T</i> (K)	2-Pentanol	Vinyl Butyrate	2-Pentyl butyrate	Butyric Acid
	Peng-Robinson - Quadratic			
313.15	3.91	3.95	4.02	5.88
323.15	1.16	6.51	5.62	3.71
333.15	3.91	2.08	4.78	2.52
Soave-Redlich-Kwong - Quadratic				
313.15	4.01	3.78	3.90	6.18
323.15	1.99	6.46	5.12	4.25
333.15	4.37	2.19	4.79	2.51

Figs. 5 and 6 show the comparison of experimental and calculated data obtained with Peng-Robinson and Soave-Redlich-Kwong EoS, respectively, for the (CO₂ + 2-pentanol), (CO₂ + vinyl butyrate), (CO₂ + 2-pentyl butyrate) and (CO₂ + butyric acid) binary systems. Highly good agreement between experimental and calculated data was found for all the systems with both EoS. As shown in Table , the RMSD values ranged from 1.16

to 6.51 % and from 1.99 to 6.46 % for the thermodynamic modelling using Peng-Robinson and Soave-Redlich-Kwong EoS, respectively. The (CO₂ + 2-pentanol) system at 323.15 K showed the best fit with RMSD < 2% using both EoS.

Although neither the critical point of the mixture nor dew points were experimentally measured in this work, the calculated data from Peng-Robinson and Soave-Redlich-Kwong EoS gave an insight of both. For all systems, at pressures near the critical point of the mixture, the mole fraction of the organic compound in the vapour phase increased as the temperature increased isobarically. This is mainly due to two reasons. Firstly, the increase in the solvation capacity of the vapor phase (rich in CO₂), as its density rises to reach the mixture critical point. And, secondly, an increase in temperature leads to an increase in the chemical potential of the organic compound. From Figs. 5 and 6, it can be inferred that the critical point of the mixture calculated from the fitting curves increased with temperature and that no three-phase regions are present, pointing the type-I phase behaviour for all the studied systems which is in good agreement with experimental observations.

From the experimental data as well as from density-based and the thermodynamic models (Peng-Robinson and Soave-Redlich-Kwong EoS), it can be concluded that the differences in the CO₂ solubility in the organic compounds at different temperatures may be used for the kinetic resolution of the mixture of (*R*, *S*)-2-pentanol. By lipase-catalyzed reaction, the (*S*)-2-pentanol isomer did not react with vinyl butyrate and may be solubilized in scCO₂ until reach their equilibrium concentration. On the contrary, the (*R*)-2-pentanol reacts with the vinyl ester in ionic liquid reaction media to form the (*R*)-2-pentylbutyrate. Nevertheless, it should be mentioned that the previous conclusion has been inferred for binary mixtures and it does not take into account solute-solute interactions. Therefore, further studies involving mixtures with the four organic components and CO₂ are needed.

4. CONCLUSIONS

The high-pressure phase equilibria of (CO₂ + 2-pentanol), (CO₂ + vinyl butyrate), (CO₂ + 2-pentyl butyrate) and (CO₂ + butyric acid) binary systems were measured at temperatures of 313.15 K, 323.15 K and 333.15 K using a synthetic method. The well-known phase equilibrium diagram of the (CO₂ + acetone) binary system was used to validate the experimental method and good agreement was found with the results previously published, being average deviation of ± 0.1 MPa in experimental pressure points. No coexisting three phases were observed and type-I behaviour was observed for the conditions used in this study.

The new modification of Henry's Law developed by Hernández et al. [45] has been used to correlate the solubility of scCO₂, expressed in terms of CO₂ mole fraction, in the organic compounds as a function of solely the CO₂ density with similar accuracy than EoS-based models. These correlations indicate that the CO₂ solubility in the organic compounds for the three temperature values studied follows the order 2-pentanol > butyric acid > esters, allowing the recovery of the unreacted (*S*)-2-pentanol in a biphasic ionic liquid/CO₂ system and facilitating the separation of the racemic mixture.

As regards the thermodynamic modelling, a reasonably highly good correlation was obtained for the experimental data using the Peng-Robinson and Soave-Redlich-Kwong EoS applied with Quadratic mixing rules and two BIP. The RMSD values found were lower than 6.46 % in all cases. The experimental and calculated data presented show good agreement to be used in a first engineering approach in the pressure and temperature range studied.

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