Phase Equilibrium Measurements and Data Correlation for the Ternary System Oleic Acid + 1-Octanol + Carbon Dioxide

Chiara Giulia Laudani, Mateja Primožič, Željko Knez,* and Maja Habulin

University of Maribor, Faculty of Chemistry and Chemical Engineering, Laboratory for Separation Processes and Product Design, Smetanova ul. 17, SI-2000 Maribor, Slovenia

Abstract. A study of the high-pressure phase equilibria in the ternary system oleic acid/1-octanol/supercritical CO_2 was performed to obtain information for optimization of enzymatic synthesis of *n*-octyl oleate. Equilibrium data were measured at temperatures of 308.15, 323.15 and 343.15 K over a pressure range from 1 to 25 MPa. Two different apparatuses: a Variable Volume View Cell and a Batch Stirred Tank were used employing synthetic and static-analytic measurement methods, respectively. The measured solubility of dense CO_2 in the binary liquid mixture oleic acid/1-octanol covered the range from 0.0781 to 0.7686 of CO_2 molar fraction. CO_2 solubility increased with increasing pressure up to 10 MPa. At higher pressures, no significant increase was observed. The Soave-Redlich-Kwong equation-of-state (SRK-EoS) with quadratic mixing rules was successfully used for data correlation in the whole *P-T-x* region studied.

Keywords: data correlation, 1-octanol, oleic acid, supercritical carbon dioxide, Soave-Redlich-Kwong equation-of-state, vapor-liquid equilibria

INTRODUCTION

Supercritical fluid processes are emerging as important alternatives to conventional techniques in many fields, such as extraction, fractionation, micronization, cleaning, and materials processing. Supercritical fluids (SCFs) have also been considered as an alternative medium to organic solvents for carrying out enzymatic reactions.[1–3] Among the SCFs, carbon dioxide (SC-CO_2) is largely chosen, being environmentally friendly, not flammable, not toxic and cheap. Its critical pressure (7.38 MPa) and temperature (304.25 K) are consistent with the use of enzymes and/or labile solutes. Improvements of biocatalysts and a better understanding of biocatalysis assisted by SC-CO_2 are expected to influence the production of fine chemicals, natural products, food ingredients and pharmaceuticals. For the design of chemical processes, such as enzymatic reactions, phase equilibrium data of the studied system provide important information for the success of the application. In the presence of the SCF in the reaction bulk, the mass transport resistance is minimized and an efficient and fast diffusion of the reactive mixture on the biocatalyst surface is obtained, facilitating the reaction and increasing the desired products yield. Moreover, SC-CO_2 can act as a separation medium after the reaction, due to its tunable solvating power, allowing thus the integration of the bio-reaction and product separation in a single step. As the reaction proceeds, the key issue in the supercritical process is to ensure a good solubility of the CO_2 in the reactive mixture in contact with the solid catalyst. For this purpose, it is prerequisite to know the phase behavior for the reactive system in the region of interest in terms of pressure, temperature and composition, to determine the most favorable process conditions.

Wax esters, obtained from the esterification reaction between long-chained fatty alcohols and fatty acids, have high significance in lubricant, pharmaceutical and cosmetics applications. Particularly, *n*-octyl oleate, derived from oleic acid and 1-octanol, is a light transparent oil liquid consumed in manufacturing of industrial polymer plasticizers, lubricants and oiling agents for textile industry; it is widely used as emollient, principally in skin creams for its well-recognized softening and smoothing effect. Phase equilibria information on the ternary system oleic acid/1-octanol/CO_2 is relevant for the high yield of the *n*-octyl oleate production by direct lipase-catalyzed esterification of oleic acid with 1-octanol in dense CO_2. Informations available in the literature on the phase behavior are related only to the

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* Author to whom correspondence should be addressed. (E-mail: zeljko.knez@uni-mb.si)
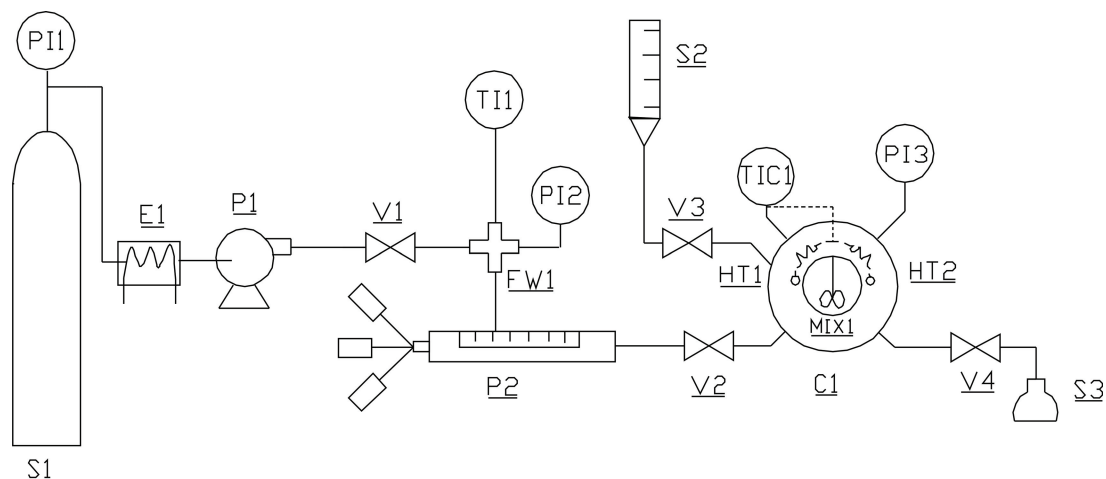
Figure 1. Sketch of the View Cell apparatus: S1 – CO₂ cylinder; E1 – cooler; P1 – high pressure membrane pump; P2 – manual pump; S2 – liquid charge vessel; C1 – view cell; HT1, HT2 – electrical heaters; MIX1 – stirrer; V1, V3, V4 – high pressure valves; V2 – one-way valve; PI – pressure indicator; TI – temperature indicator; TIC – temperature indicator and controller; S3 – sample collector.

oleic acid/CO₂ and 1-octanol/CO₂ binary systems. Weng and Lee[4] reported the vapor-liquid equilibrium data for 1-octanol/CO₂ at temperatures from 348 to 453 K. More recently, Chang *et al.*[5] obtained experimental data on *P-x-y* diagrams and Henry's constants for 1-octanol/CO₂, calculated from density measurements. Zou *et al.*[6] and Yu *et al.*[7] measured densities and equilibrium compositions of both vapor and liquid phases for the binary mixture oleic acid/CO₂ at pressures up to 13 MPa and temperatures from 313.15 to 333.15 K. Foster *et al.*[8] determined the solubility of oleic acid in SC-CO₂ at 318.15 and 328.15 K. Škerget *et al.*[9] measured the solubility of oleic acid in dense CO₂ at 303.15, 313.15 and 323.15 K in the pressure range from 10 to 30 MPa, providing a data correlation by a density model. However, there is still a lack of experimental data for the ternary system oleic acid/1-octanol/CO₂.

The aim of the work was to provide vapor-liquid equilibrium experimental data on the oleic acid/1-octanol/CO₂ system and correlate the data using an equation of state. Particularly, this study allows coupling the kinetic experimental observations with thermodynamic arguments, in order to relate the different reaction performance observed to the position of the process operating point with respect to the location of vapor and liquid phase boundaries of the oleic acid/1-octanol/CO₂ system.

EXPERIMENTAL

Materials

1-Octanol (purity 98 %) was supplied by Aldrich Chemical Co. (Milwaukee, WI, USA). Oleic acid (purity 99 %) was purchased by Merck (Darmstadt, Germany).

Carbon dioxide (purity 99.998 %) was provided by Messer MG (Ruše, Slovenia).

Apparatuses and Procedures

Phase equilibrium measurements of the system oleic acid/1-octanol/CO₂ were performed using two different apparatuses. First, the number of phases at given pressure and temperature conditions at a known composition of the ternary mixture was determined in the Variable-Volume View Cell, which operates in accordance to the synthetic method. A second series of experiments was carried out in a second apparatus, the Batch Stirred Tank, to obtain direct information about the compositions of the vapor- and liquid-phase at equilibrium using a static method. A temperature region between 308.15 and 343.15 K (typical for enzymatic reactions) and pressures up to 25 MPa were covered in both series of experimental runs.

The reason for experimental errors could be in determination of carbon dioxide composition in the mixture, pressure fluctuation during sampling and temperature fluctuation in the pump during carbon dioxide loading.

Variable-Volume View Cell apparatus.

A sketch of the view cell apparatus is shown in Figure 1. The apparatus consists of a variable-volume view cell (NWA GmbH, Lorrach, Germany) that allows observing phase separation of the mixture. The cell, made of stainless steel (AISI 316), was designed to operate up to 75 MPa and 473.15 K. Its internal volume may be varied between 30 and 62 cm³ by means of a piston connected to a hydraulic pressurization system. The piston position was determined measuring the electric resistance through a cable sealed to the piston and connected
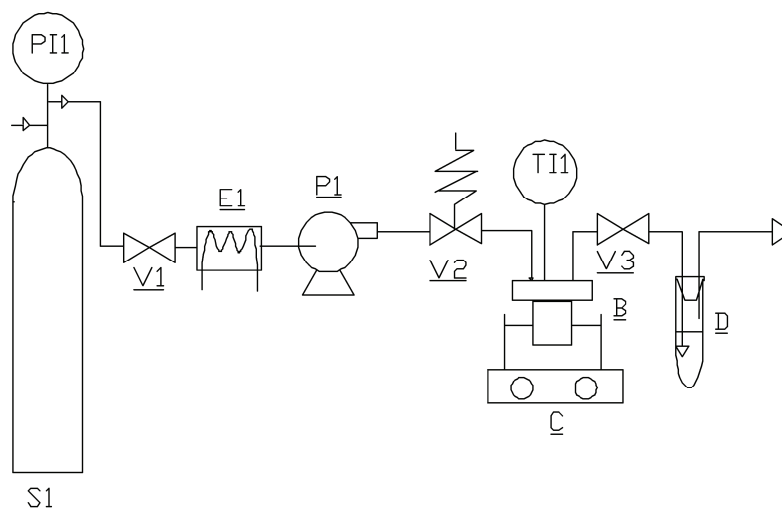
Figure 2. Sketch of the Batch Stirred Tank apparatus: S1 – CO_2 cylinder; E1 – cooler; P1 – high pressure membrane pump; B – vessel in oil bath; C – electrical heater and magnetic mixer; D – testing tube; V1, V3 – high-pressure valves (needle valves); V2 – safety valve; PI – pressure indicator; TI – temperature indicator.

to an ohmmeter (mod. 2210, MISCO - Systemax Europe Ltd, Wellingborough, United Kingdom). The cell was equipped with a blade-turbine stirrer to mix the phases in the cell, eliminate stagnant zones and favor mass transfer. Cell heating was obtained using two stainless steel cartridge heaters (mod. Firerod, WATLOW, Missouri, USA) having a length of 60 mm and lodged in cavities of the metallic body of the cell. A TIC controller (mod. 2216, EUROTHERM Controls Inc, Virginia, USA) controlled the temperature. Bulk temperature inside the cell was measured by a K-type thermocouple (WATLOW, Missouri, USA). Pressure was measured by using a Bourdon type manometer (mod. MQ1, OMET S.R.L., Milano, Italia). Two supply lines allowed to feed the liquid solution and CO_2. During measurements, the cell was isolated by the rest of the apparatus by means of a high-pressure valve (mod. 100VM-4073, Autoclave Engineers, Pennsylvania, USA) located on the CO_2 feed line and an ON/OFF valve (mod. 2AB-2LJ2-SSP, PARKER, Devon, England) situated on the discharge line. A micrometric valve (mod. 710.3022, SITEC, Zurich, Switzerland) on the discharge line allowed the regulation of the outgoing flow during release. Liquid CO_2 was pumped by a manual pump (mod. 750.1100, SITEC, Zurich, Switzerland) equipped with a cooling jacket connected to a thermostatic bath (mod RE 106, LAUDA GmbH, Lauda-Königshofen, Germany). To monitor the temperature and pressure of the liquefied gas, the manual pump was equipped with a J-type thermocouple (WATLOW, Missouri, USA) and a Bourdon type manometer (mod. MQ1, OMET S.R.L., Milano, Italia). Experiments in the view cell were performed to obtain the location of vapor- and liquid-phase boundaries and define equilibrium pressure and temperature at a known composition of the mixture at which

phase separation occurred by using the synthetic method. In all measurements, the cell was first filled with a known amount of the oleic acid/1-octanol solution. Then, a known amount of CO_2 was added using the manual pump, equipped with a piston to reduce the internal volume during the manually induced movement. A graduate scale showed the cell internal volume reduction. Each turn of the manual actuator corresponded to a volume of 0.6 mL. The volume of CO_2 introduced in the cell during pumping was evaluated from the actuator rotations number. Temperature, pressure and volume values were used to calculate the amount of CO_2 introduced in the cell by the Bender equation.[10,11] To promote mass transfer the system was stirred for 1 hour. Afterwards the stirrer was stopped for at least 1 hour to allow complete phase separation. Finally, the observation of the number of phases at the given conditions was possible. To trace the vapor-liquid equilibrium boundaries at a given temperature, the pressure was increased at constant composition by means of a volume reduction of the cell. The experimental protocol was repeated by increasing the pressure until the vapor-liquid phase separation meniscus disappeared and only one phase was present inside the cell.

Batch Stirred Tank (BST) apparatus

A second apparatus (Batch Stirred Tank) was used to perform measurements by the static-analytic method. Analogous apparatus was proposed by Knez and coworkers elsewhere.[9,12] The high-pressure vessel apparatus used for measurements is analogous to the vessel used for the bio-reaction tests.[13,14] The vessel, with internal volume of about 72 mL, was designed for operation up to 30 MPa and 473.15 K. The BST sketch is reported in Figure 2. The equilibrium reactor was filled

Table 1. Measured vapor-liquid equilibrium data for the ternary system oleic acid/1-octanol/CO$_2$ – liquid phase CO$_2$ molar fraction at three selected temperatures (308.15, 323.15 and 343.15 K)

308.15 K		323.15 K		343.15 K	
P / MPa	$x(CO_2)$	P / MPa	$x(CO_2)$	P / MPa	$x(CO_2)$
1.13	0.1715	1.17	0.1174	1.07	0.0871
2.34	0.3051	4.20	0.3958	3.04	0.2171
3.50	0.4194	5.18	0.4568	4.21	0.3022
4.10	0.4525	6.12	0.5134	5.47	0.3698
5.72	0.5803	7.60	0.5870	7.05	0.4507
6.26	0.6081	9.19	0.6460	9.28	0.5551
7.04	0.6560	10.37	0.6766	12.08	0.6432
7.29	0.6654	11.19	0.6876	13.20	0.6691
8.03	0.6884	13.13	0.7101	15.28	0.7039
8.97	0.7016	15.80	0.7381	16.67	0.7255
11.06	0.7297	17.12	0.7509	18.42	0.7447
13.52	0.7408	19.96	0.7550	19.51	0.7512
14.41	0.7457	23.48	0.7672	21.95	0.7616
15.52	0.7527			23.65	0.7661
16.06	0.7562				
18.34	0.7624				
20.04	0.7637				
24.22	0.7686				

with a sufficient amount of liquid mixture (20 mL of oleic acid and 9.96 mL of 1-octanol). In all experiments, oleic acid/1-octanol equimolar mixture upon addition of SC-CO$_2$ was used, as the oleic acid/1-octanol molar ratio equal to 1 was the condition of interest in the studied enzymatic esterification. Liquid CO$_2$ cooled from the supply tank was pumped by a high-pressure pump (PM-101, NWA GmbH, Lorrach, Germany). Pressure was measured by using a Digibar manometer (mod. PE 200, HBM GmbH, Darmstadt, Germany). The equilibrium vessel was dipped into an oil bath and heated up by means of a rotating mixing and heating system (Rotamix 550 MMH, Tehtnica, Železniki, Slovenia). Bulk temperature inside the vessel was monitored by means of a digital thermometer (mod. GTH 1150, Greisinger Electronic GmbH, Regenstauf, Germany) equipped with a K-type thermocouple (WATLOW, Missouri, USA). Once the constant operating conditions were reached, the ternary oleic acid/1-octanol/CO$_2$ mixture was mixed for 1 hour, tuned at agitation speed of 500 rpm, until the equilibrium was reached. After leaving the system for another hour to obtain phase separation, samples of both the vapor and liquid phase were collected by means of high-pressure valves (mod. 100VM-4073, Autoclave Engineers, Pennsylvania, USA) into a glass trap. The sampling lines volumes were negligible compared with the volume of sample and the sample amount was suitably small compared to the equilibrium vessel volume to avoid altering the equilibrium conditions of the system. At least two experiments were run at each tested *P-T-x*

condition. The amounts of the sampled mixture were determined by weighing the traps on a high precision balance (mod. AG 204, Mettler Toledo, Greifensee, Switzerland). Then, the glass trap was opened and left at environmental conditions for 2 hours to allow the CO$_2$ release and evaluation of the oleic acid/1-octanol content in the sample. Identification of the equilibrium composition of vapor and liquid phase was performed by a Gas Chromatograph (mod. 5890 Hewlett-Packard, Pittsburg, PA, USA) equipped with a hydrogen Flame Ionization Detector (FID) and a HP-FFAP column (30 m × 0.25 mm × 0.25 μm), designed for the analysis of fatty acids without derivatization. FID temperature was set at 573.15 K. The oven time-temperature profile was as following: 353.15 K (1 min), 25 K / min to 453.15 K (1 min), 5 K / min to 493.15K (10 min) 5 K/min to 503.15K (30 min). Nitrogen was used as carrier gas at a total flow rate through the column of 61 mL/min. The samples were analyzed in hexane solution. Each sample was analyzed at least 3 times and the relative deviation was within ±1 % of the sample weight.

RESULTS AND DISCUSSION

Vapor-liquid equilibrium experimental data of the system oleic acid/1-octanol/CO$_2$ at three selected temperatures, 308.15, 323.15 and 343.15 K, over a pressure range from 1 to 25 MPa are reported in Tables 1 and 2. In all *P-T-x* conditions tested, a split of the system into the two vapor and liquid phases was registered. Ternary

Table 2. Measured vapor-liquid equilibrium data for ternary system oleic acid/1-octanol/CO_2 – vapor phase CO_2 molar fraction at three selected temperatures (308.15, 323.15 and 343.15 K).

308.15 K		323.15 K		343.15 K	
P/MPa	$y(CO_2)$	P/MPa	$y(CO_2)$	P/MPa	$y(CO_2)$
1.56	0.9999	2.60	0.9999	0.81	0.9999
2.41	0.9999	3.91	0.9998	1.57	1.0000
3.50	1.0000	5.29	0.9999	2.23	0.9998
4.31	0.9999	6.88	0.9999	3.63	0.9996
5.08	0.9996	8.00	0.9997	4.47	0.9999
5.89	0.9999	10.80	0.9974	5.20	0.9999
6.92	0.9998	11.81	0.9963	6.10	0.9998
7.47	0.9997	14.75	0.9936	6.80	0.9998
7.56	0.9991	16.96	0.9906	7.42	0.9999
8.51	0.9964	17.79	0.9900	8.55	0.9994
10.32	0.9949	19.75	0.9881	9.19	0.9996
12.82	0.9919	21.77	0.9866	9.83	0.9995
20.73	0.9865	23.09	0.9856	10.60	0.9995
22.53	0.9852	24.10	0.9856	11.02	0.9997
24.69	0.9812	25.37	0.9842	11.63	0.9994
				12.93	0.9976
				14.10	0.9968
				15.16	0.9951
				16.05	0.9935
				19.71	0.9903
				20.75	0.9898
				23.55	0.9920
				25.41	0.9912

system thermodynamic data were represented on a pseudo-binary pressure/composition (*P*/*x*) diagram (Figure 3) for easier comparison with the binary systems data and to point out directly the information of interest about the solubility of CO_2 in the oleic acid/1-octanol mixture. The scale for the gas phase was enlarged to evidence the right hand side of the diagram due to the very low solubility of the liquid mixture in the dense gas. From the graph, it is clear that CO_2 solubility in the liquid phase markedly increased with pressure up to 10 MPa. Under the investigated *P-T-x* conditions, the solubility of dense CO_2 in the binary liquid mixture oleic acid/1-octanol was evaluated in the range of 0.0781–0.7686 CO_2 molar fraction. A larger amount of CO_2 dissolved in the liquid oleic acid/1-octanol mixture when pressure was set at values of around 10 MPa at different values of temperature. At higher pressures, no significant increase in the CO_2 solubility in the liquid phase was observed, whereas CO_2 content marginally decreased in the vapor phase. Upon increasing the temperature from 308.15 to 343.15 K, a decrease of CO_2 molar fraction in the liquid phase was registered. However, the temperature effect on the CO_2 solubility in the liquid phase was negligible at pressures higher than 15 MPa. Vapor phase composition variations with the tem-

perature were not important. The results showed that, in
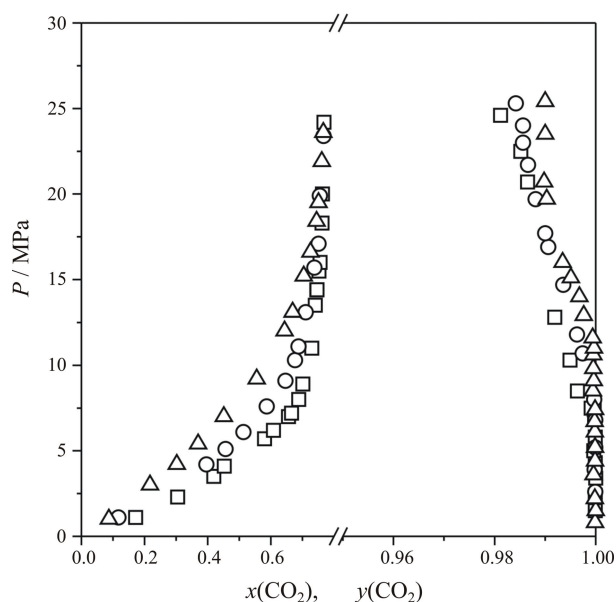
Figure 3. Pseudo-binary representation of the ternary system oleic acid/1-octanol/CO_2 at a oleic acid/1-octanol molar ratio equal to 1 at three selected temperatures: □ 308.15 K; ○ 323.15 K; Δ 343.15 K.

order to maximize the amount of CO_2 dissolved in the liquid reaction bulk, it is suitable to work at low temperatures or at high pressures. Oleic acid and 1-octanol amounts contained in the vapor phase were low enough not to constitute a limitation in the choice of the working conditions for the enzymatic reaction. Most of the low-volatility components remained in the liquid phase, since their solubility in the gas phase was very low. From the comparison of the equilibrium data of the ternary system oleic acid/1-octanol/CO_2 with the solubility data of the binary oleic acid/CO_2 and 1-octanol/CO_2 systems, it resulted that the solubility of CO_2 in 1-octanol was lowered in the presence of oleic acid, while the solubility of CO_2 in oleic acid was slightly modified by the presence of 1-octanol.

DATA CORRELATION

The ternary system experimental data has been correlated by the Soave-Redlich-Kwong equation-of-state (SRK-EoS):[15]

$$P = \frac{RT}{v-b} - \frac{a\alpha}{v(v+b)} \tag{1}$$

with

$$\alpha = [1 + (0.48 + 1.57\omega - 0.17\omega^2)(1 - T_r^{0.5})]^2 \tag{2}$$

Quadratic mixing rules[16] were used to calculate the parameters a and b in Eq. (1):

$$a = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j \sqrt{a_i a_j}(1-k_{ij}) \tag{3}$$

$$b = \sum_{i=1}^{N}\sum_{j=1}^{N} x_i x_j \frac{b_i + b_j}{2}(1-l_{ij}) \tag{4}$$

The binary interaction parameters k_{ij} and l_{ij} for the binary systems were required for this computation. The interaction parameters of the binary system 1-

Table 3. Critical temperature T_c, critical pressure P_c and acentric factor ω of oleic acid, 1-octanol and CO_2

Component	T_c/K	P_c/MPa	ω
Oleic acid[7,19,20]	781.0	1.39	1.187
1-Octanol[5,18]	652.5	2.86	0.587
CO_2[18]	304.1	7.38	0.239

octanol/oleic acid were set to zero due to the complete miscibility of the two components. Binary interaction parameter calculations for the oleic acid/CO_2 and 1-octanol/CO_2 systems were performed by correlating the experimental vapor-liquid equilibrium data available in literature[5,7] with equation of state predictions. A good fit between experimental points and calculated values was achieved by calculating the parameter values that minimize the relative molar fraction deviation:

$$obf = \sum_{i=1}^{N}\left(\frac{x_{calc} - x_{exp}}{x_{exp}}\right)^2 \tag{5}$$

where N is the number of isothermal data points considered. Calculations were performed using "Phase Equilibria" software, developed at the Technical University of Hamburg by Pfohl *et al.*[17] Pure component critical constants and acentric factors used for calculations were found in literature[5,7,18–20] and are shown in Table 3. The fitted binary interaction parameters and the average relative deviation (in terms of mole fractions of liquid phase) between calculated and binary system experimental data are listed in Table 4. Phase equilibrium calculations for the ternary system were performed using the process simulation program SIMSCI PRO/II (PRO/II Software, Invensys Systems, Inc. SimSci-Esscor). The calculated binary interaction parameters were inserted in the input specification file of the program. In addition, the properties of the pure components were modified according to the values used in the binary system computation. Through equilibrium evaluation, the program computed the compositions of vapor and liquid phase. By running the calculation at different

Table 4. SRK-EoS optimized parameters for the binary systems oleic acid/CO_2 and 1-octanol/CO_2

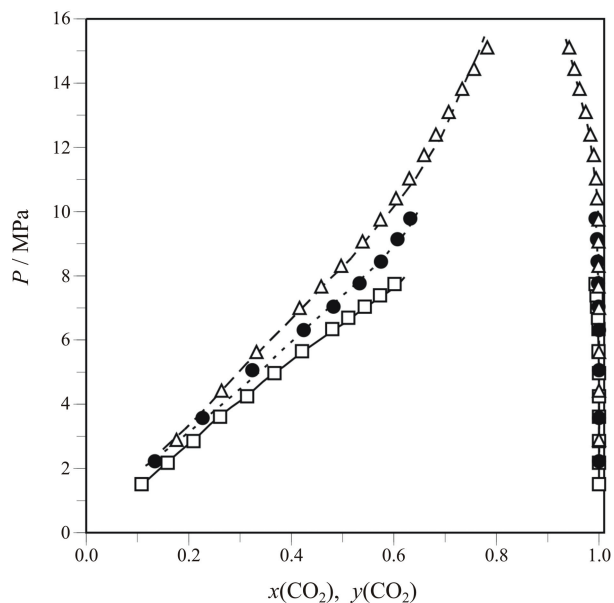| System	T/K	k_{12}	l_{12}	Relative deviation (%) liquid phase
Oleic acid/CO_2[7]	313.15	0.0821	0.0036	0.1021
	333.15	0.0880	-0.0168	0.0661
1-Octanol/CO_2[5]	308.15	0.1033	-0.0298	0.1150
	318.19	0.1000	-0.0305	0.1572
	328.15	0.0944	-0.0335	0.1629

Figure 4. Comparison of literature values (Chang and co-workers[5]) with calculated equilibrium data (this work) of the binary system 1-octanol/CO₂: □ ⎯⎯ 308.15 K; ● ----318.19 K; Δ − − − 328.15 K.
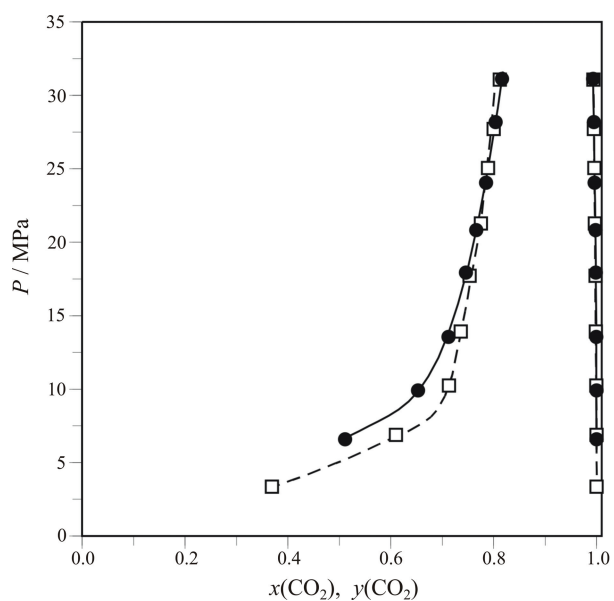

Figure 5. Comparison of literature values (Yu and coworkers[7]) with calculated equilibrium data (this work) for the binary system oleic acid/CO₂: □ − − − 313.15 K; ● ⎯⎯ 333.15 K.

pressures, the desired thermodynamic vapor-liquid equilibrium data for the ternary system were obtained. It was found that SRK-EoS fitted satisfactorily the experimental data of the two binary systems, oleic acid/CO₂[7] and 1-octanol/CO₂,[5] and of the ternary system oleic acid/1-octanol/CO₂.

Peng-Robinson-EoS (PR-EoS) was also tested:

$$P = \frac{RT}{v-b} - \frac{a\alpha}{v^2 + 2bv - b^2} \qquad (6)$$

with

$$\alpha = \left(1 + A\left(1 - T_r^{0.5}\right)\right)^2$$
$$A = 0.37464 + 1.54226\omega - 0.26992\omega^2 \qquad (7)$$

$$T_r = \frac{T}{T_c} \qquad (8)$$

The both cubic equations-of-state (SRK-EoS and PR-EoS) in combination with mixing rules are currently the most widely used models for the calculations of solubilities of components in SCF. Both EoS are suitable for the modelling of systems vapour-liquid and liquid-liquid. The form of the mixing rules that extend the use of equations of state developed for pure fluids to mixtures is more important than the particular *P-V-T* relationship embodied in EoS.[21]

PR-EoS described satisfactorily only the binary systems behavior, whilst applied to the ternary system it did not fit the experimental data.

Calculated solubility data for the binary system oleic acid/CO₂ and 1-octanol/CO₂ are compared with experimental data reported in literature[5,7] in the Figures 4 and 5. Comparisons of ternary system oleic acid/1-octanol/CO₂ experimental points with calculated solubility data values of the SRK-EoS at three selected temperatures, 308.15, 313.15 and 343.15 K, are shown in Figures 6, 7 and 8, respectively. In Figure 9 liquid-phase
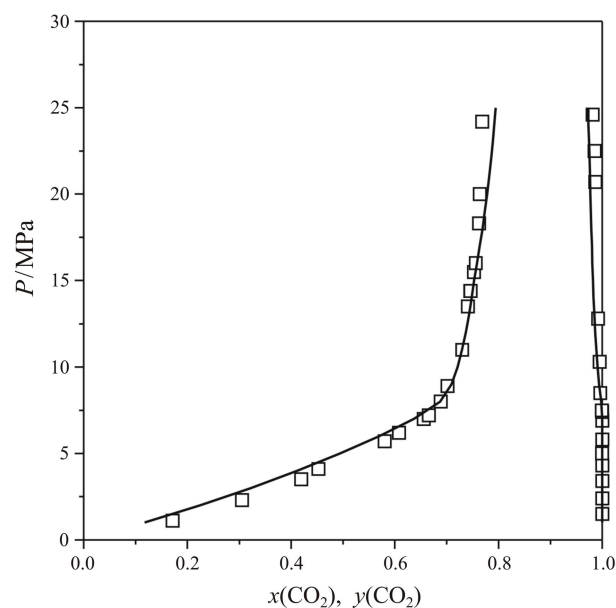

Figure 6. Measured and calculated vapor-liquid equilibrium data of the ternary system oleic acid/1-octanol/CO₂ at 308.15 K: □ experimental points; ⎯⎯ calculated.
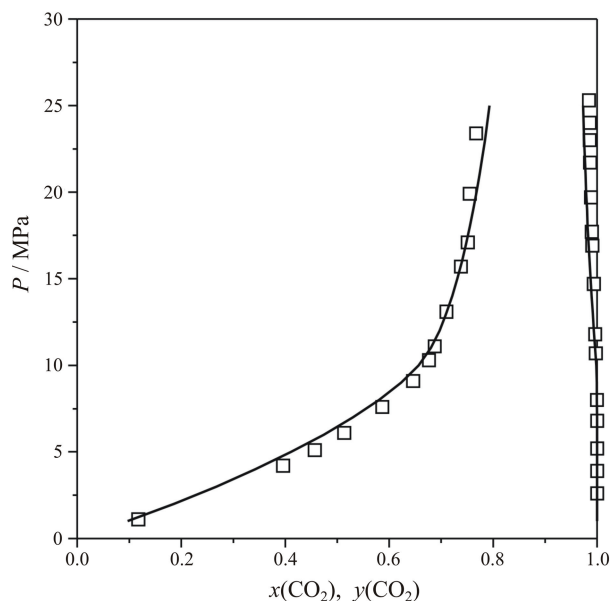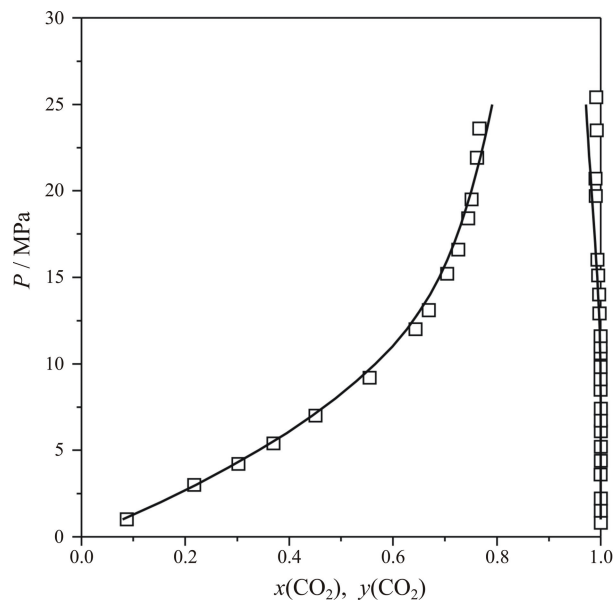
Figure 7. Measured and calculated vapor-liquid equilibrium data of the ternary system oleic acid/1-octanol/CO$_2$ at 323.15 K: □ experimental points; —— calculated.

Figure 8. Measured and calculated vapor-liquid equilibrium data of the ternary system oleic acid/1-octanol/CO$_2$ at 343.15 K: □ experimental points; —— calculated.

oleic acid content points at three selected temperatures experimental are depicted. The relative deviations are listed in Table 5. According to the results, the proposed model describes satisfactorily the phase behavior of the ternary system oleic acid/1-octanol/CO$_2$. The deviation of the calculated mole fractions from the experimentally determined data was of the order of magnitude of experimental errors. The maximum relative deviations were evaluated at 0.91% and 2.58% for the vapor and liquid phase, respectively. However, at higher pressures an increase in the deviation between model and experimental data was registered. For this reason, model extrapolation to pressures higher than those experimentally inves-

tigated in this work could be not reliable.

CONCLUSION

The phase equilibrium of the ternary system oleic acid/1-octanol/CO$_2$ was studied at 308.15, 323.15 and 343.15 K, over a pressure range from 1 to 25 MPa. This study is useful in determination of the optimum reaction conditions for the *n*-octyl oleate enzymatic synthesis by direct lipase-catalyzed esterification of oleic acid with 1-octanol in SC-CO$_2$. A larger amount of CO$_2$ dissolved in the liquid reaction bulk at pressures close to 10 MPa. At higher pressures, no significant increase in the CO$_2$

Table 5. Relative deviations between experimental and calculated data of oleic acid, 1-octanol and CO$_2$ molar fraction for liquid and vapor phase at three selected temperatures

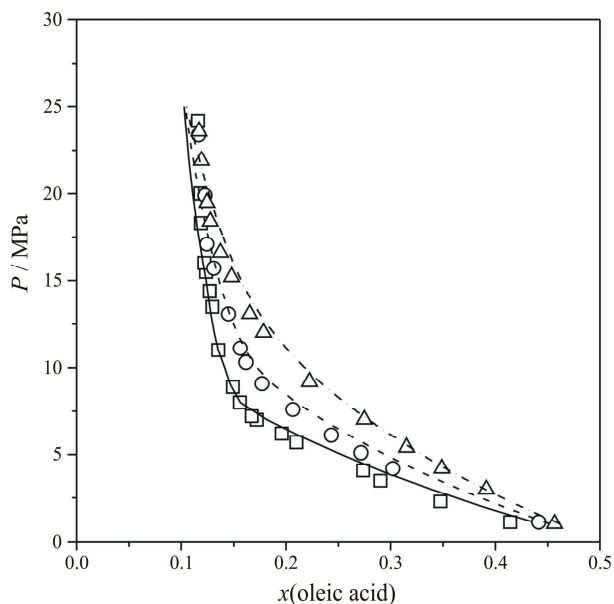| Component	T/K	Relative deviation (%) liquid phase	Relative deviation (%) vapor phase
Oleic acid	308.15	1.3	0.2
	323.15	1.8	0.3
	343.15	0.8	0.2
1-Octanol	308.15	1.3	0.3
	323.15	1.1	0.9
	343.15	0.7	0.8
CO$_2$	308.15	2.6	0.5
	323.15	2.1	0.7
	343.15	1.5	0.7

Figure 9. Measured and calculated oleic acid liquid-phase equilibrium data for the ternary system oleic acid/1-octanol/CO_2 at three selected temperatures: □——308.15 K; ○——— 328.15 K; Δ—··—348.15 K.

solubility in the liquid phase was observed. At the investigated pressure and temperature conditions, the phase equilibrium of the ternary system oleic acid/1-octanol/CO_2 can successfully be described by the SRK-EoS.

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SAŽETAK

Fazne ravnoteže i korelacija podataka za ternarni sustav oleinska kiselina+ 1-oktanol + ugljikov dioksid

Chiara Giulia Laudani, Mateja Primožič, Željko Knez i Maja Habulin

University of Maribor, Faculty of Chemistry and Chemical Engineering, Laboratory for Separation Processes and Product Design, Smetanova ul. 17, SI-2000 Maribor, Slovenia

Kako bi se dobili podaci potrebni za optimalizaciju enzimske sinteze *n*-oktil-oleata, proučavane su fazne ravnoteže u sustavu: oleinska kiselina + 1-oktanol + ugljikov dioksid, i to pri temperaturama od 309,15 K, 323,15 K i 343,15 K te pri tlakovima u rasponu od 1 MPa do 25 MPa, služeći se sintetičkim i statičko-analitičkim metodama. Topljivost ugljikova dioksida u tekućim binarnim smjesama oleinske kiseline i 1-oktanola raste s povećanjem tlaka sve do 10 MPa. Za korelaciju mjernih podataka uspješno je primijenjena jednadžba stanja Suave-Redlich-Kwong (s kvadratnim pravilima miješanja), u cijelomu području istraživanih parametara *p-T-x*.