Phase behaviour of the pseudo-ternary system carbon dioxide + ethanol + fish oil at high pressures

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ABSTRACT

This work provides experimental fluid phase equilibrium data of the pseudo-ternary mixture CO_2 + ethanol + fish oil, a system of interest in pharmaceutical and food-industry applications such as the production of omega-3-enriched lipid derivatives at mild, non-oxidative conditions. Experimental tie-lines were obtained by means of an analytical isothermal method with recirculation of the vapour phase. Measurements were carried out in the temperature range 323.15 K-343.15 K and at pressures from 10 MPa to 30 MPa. The Peng-Robinson equation of state coupled with the conventional van der Waals mixing rules with two adjustable parameters was used for experimental data correlation.

Keywords

Phase equilibrium, Supercritical carbon dioxide, Ethanol, Fish oil, Thermodynamic modelling, Peng-Robinson equation of state.

1. INTRODUCTION

Dense carbon dioxide is expected to play an important role as a reaction medium in ecologically friendly processing. Enzyme-catalysed ethanolysis of lipid sources in supercritical carbon dioxide (SC-CO_2) or CO_2-expanded media can be used to improve the production of lipid derivatives, including concentrates of omega 3 polyunsaturated fatty acids (n-3 PUFAs) from fish oil [1,2]. However, the relatively low solubility of the reactants in SC-CO_2 limits the reaction performance in this medium; thus, a CO_2-expanded media is preferred to minimise mass transfer limitations [3]. Understanding the phase behaviour of the ethanol + fish oil substrate mixture with CO_2 would help in the selection of adequate ethanolysis conditions (pressure, temperature, ethanol-to-oil ratio, and amount of dissolved CO_2 in the reaction mixture). This knowledge can be also extended to other potential applications and may be of interest in the fish oil industry, since SC-CO_2 or CO_2-expanded media can be used throughout all the n-3 PUFA concentration process, including the supercritical extraction of the fish oil [4], the refining step [5], the separation and fractionation of the reaction products [6,7], or the formulation of the final product by means of particle formation techniques [8].

Experimental data related with high-pressure phase equilibrium of the binary system CO_2 + ethanol are extensively reported in the literature [9–14]. Besides, ternary and higher systems comprising CO_2 and pure triglycerides, other lipid derivatives and their mixtures have been also investigated [15]. However, only a few data regarding the phase equilibrium of pseudo-ternary mixtures of CO_2, ethanol, and edible oils can be found in the literature, and these data are usually related to the solubility of the lipid compounds in CO_2 with ethanol as a co-solvent [16].

Several publications have previously reported fluid phase equilibrium of pseudo-ternary mixtures of CO_2 + ethanol + vegetable oils. However, to our knowledge, this is the first work

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dealing with oils rich in n-3 PUFAs from animal sources, such as fish oil. Geana and Steiner [17] reported fluid phase equilibrium data for the pseudo-ternary system CO_2 + ethanol + rapeseed oil in the temperature range 313 K-353 K and at pressures from 6 MPa to 12 MPa, satisfactorily correlating the phase behaviour with the Peng-Robinson equation of state (PR EoS) [18] coupled with the conventional van der Waals mixing rules with two adjustable parameters (vdW2). Ndiaye et al. [19] studied the fluid phase equilibria of binary and ternary mixtures involving CO_2, ethanol, soybean oil, castor oil, and their fatty acid ethyl esters. The pseudo-ternary system CO_2 + ethanol + castor oil was studied at fixed ethanol-to-oil ratios, temperatures ranging from 313.15 K to 343.15 K and pressures from 2.13 MPa to 27.13 MPa. Experimental data were correlated both with PR EoS vdW2 and the Statistical Associating Fluid Theory (SAFT) [20] with one binary interaction parameter. Among these two models, the authors considered that SAFT EoS described better the phase behaviour of the pseudo-ternary system, yet they pointed out at some deviations from their experimental results, such as the over-prediction of the cloud point pressure at high ethanol ratios [20]. Hernández et al. [21] investigated the fluid phase equilibrium behaviour of the pseudo-ternary mixture CO_2 + ethanol + sunflower oil at two different conditions of temperature and pressure (313.15 K and 13 MPa; 333.15 K and 20 MPa). A group contribution equation of state (GC EoS) [22] was used to correlate the experimental data. Two different sets of parameters were adopted for the interaction between the triglyceride and the alcohol groups, one of them corresponding to the Liquid + Liquid (L1+L2) 2-phase region, and the other to the Vapour + Liquid (V+L2) 2-phase region. More recently, Dalmolin et al. [23] studied the phase transitions in the system CO_2 + ethanol + rapeseed oil, at temperatures in the range 313.15 K-343.15 K and pressures up to 22.53 MPa. They found a 3-phase region with a Vapour + Liquid + Liquid (V+L1+L2) phase transition that occurred at higher pressures when increasing temperature, and satisfactorily explained their experimental results with the PR EoS vdW2 model.

In this work, the phase behaviour of the pseudo-ternary mixture CO_2 + ethanol + fish oil in the temperature range from 323.15 K to 343.15 K and pressures from 10 MPa to 30 MPa has been determined by means of an analytical isothermal method with recirculation of the vapour phase (AnTVcir, as described by Dohrn and Brunner [24]). The main goal of the study involves a contribution towards understanding the phase behaviour of systems containing CO_2, ethanol, and oils rich in n-3 PUFAs. The knowledge obtained will be useful in the development of applications involving these pseudo-ternary mixtures, such as the previously mentioned enzymatic reactions, supercritical extraction and fractionation, and particle formation techniques.

2. EXPERIMENTAL

2.1. Materials

Fish oil was provided by AFAMSA S.A. (Pontevedra, Spain) being a mixture of tuna (*Thunnus* sp.) and sardine (*Sardina pilchardus*) refined oils. The fatty acid profile and free fatty acid content of the fish oil have been determined according to AOCS methods [25]. The fatty acid profile has been previously reported [26] and is also provided in Table 1. Free fatty acid content was found to be 0.29 ± 0.04 % oleic acid. Density of fish oil was also measured in an Anton Paar DMA 5000 instrument, finding values of $\rho^{323.15\ K} = 906.53$ kg·m^{-3} and $\rho^{343.15\ K} = 895.83$ kg·m^{-3} ($u(\rho) = \pm 0.05$ kg·m^{-3}). Absolute ethanol (0.999 mass fraction) was purchased from Merck KGaA. Carbon dioxide (0.999 mass fraction in the liquid phase) was supplied by Air Liquide S.A. (Spain). Compounds have been used as provided by the manufacturers without further purification.

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The potential reactivity of fish oil in contact with ethanol could lead to some extent of trans-esterification and reaction products could be formed during phase equilibria measurements, mainly fatty acid ethyl esters (FAEE). Although reaction in the absence of catalysts is very slow, the presence of FAEE and other intermediate components was analysed after phase equilibria measurements by NP-HPLC. Chromatographic method is reported elsewhere [27]. FAEE content was found less than 0.001 mole fraction and it was considered not to affect the phase equilibria. Hidrolysis of the fish oil was also evaluated by means of the free fatty acid content [25], finding a maximum increase up to 0.81 ± 0.05 % oleic acid at the highest studied temperature (343.15 K). Fatty acid profile was also determined after phase equilibria measurements, finding no significant changes compared to the initial profile (Table 1). Additionally, since fish oil is rich in polyunsaturated fatty acids (Table 1) it is very prone to oxidation. Therefore primary oxidation was evaluated by means of peroxide value analysis [28] before and after phase equilibria measurements. Although PV slightly increased from 2.0 ± 0.2 meq O_2/kg to 3.5 ± 0.1 meq O_2/kg, oxidation products are minor components present in small amounts that would not affect the phase equilibria of the system.

2.2. Apparatus and procedure

A schematic diagram of the high-pressure apparatus used for fluid phase equilibrium measurements is shown in Figure 1. It was built by Eurotechnica GmbH (Germany) and consists of an equilibrium cell made of stainless steel (SS-316) and equipped with a sapphire window for observing the content of the cell during measurements. Internal volume of the cell ranges from 40 to 70 mL, adjustable through a manual screw piston. The cell includes a pressure transducer and an immersed thermocouple. Both of them calibrated and connected to a Data Acquisition System (DAS). The equipment was placed inside an oven that allowed temperature control of the system. Mixing of the components of the system was achieved by

continuously taking the vapour phase and passing it back into the equilibrium cell through the liquid phase by means of a gear pump (Micropump IDEX). A 750 µL loop that could be isolated by means of a 6 way valve (VICI) was placed in the recirculation path for sampling the vapour phase with minimal equilibrium disturbance. Besides, a micro-metering valve was connected to the bottom of the equilibrium cell through a 1/16" capillary for sampling the heavy phase. Pressure drop occurring when sampling the liquid phase was compensated by reducing the volume of the cell through the manual screw piston. Maximum specifications of the apparatus are p = 32 MPa and T = 393 K.

A typical experiment with the high-pressure variable-volume view cell began with the pre-heating of the system up to the desired temperature. When the temperature was achieved, the equilibrium cell was gently purged with low pressure CO_2 to sweep the residual air inside the cell. Immediately afterwards, known volumes of fish oil and ethanol were introduced into the cell by means of a binary HPLC pump (Agilent 1200 Series). A certain amount of CO_2 was then charged into the cell by using a high-pressure syringe pump (ISCO 260D). The exact amounts of fish oil and ethanol were calculated using their respective densities at room temperature, whereas the mass of CO_2 charged into the cell was measured by a Coriolis mass flow meter (Rheonik RHE015). Once the cell was charged and the desired pressure was adjusted by actuating the manual screw piston, the gear pump was connected and recirculation of the vapour phase was performed for at least 2 h to facilitate the mixing of the components and its distribution in the different phases of the system. The system was then let to stand for another 2 h at constant temperature and pressure. Phase separation was visually verified through the sapphire window and samples from the vapour and liquid phases were taken by the 6-way and the micro-metering valve, respectively. Pressure variations up to ±0.1 MPa were observed during sampling, while temperature change was not detected. Overall standard

uncertainties in the equilibrium measurements were $u(p) = \pm 0.15$ MPa, $u(T) = \pm 0.1$ K, and $u(w_i) = \pm 0.005$; being w_i the mass fraction of component i.

Samples were decompressed to atmospheric pressure and released CO_2 was measured by means of a thermal mass flow meter (Bronkhorst F-110C). Ethanol and fish oil were separated from CO_2 and collected in an ice-cooled glass trap. The amount of each component was determined by weighing the vials in a precision analytical balance (accurate to ± 0.0001 g) before and after evaporation of ethanol at T = 373.15 K.

3. RESULTS AND DISCUSSION

3.1. Experimental data

In order to check the reliability of the apparatus and experimental procedure, preliminary measurements of the binary system CO_2 + ethanol were carried out. Experimental high-pressure phase equilibria data of the CO_2 + ethanol binary system are summarised in Table 2. The results obtained were compared with data taken from literature [9,12], finding a good agreement (Figure 2).

Experimental high-pressure phase equilibrium data of the pseudo-ternary system CO_2 + ethanol + fish oil are listed in Tables 3-5. Due to the large differences in molecular weight of the components of the system, compositions are expressed in terms of mass fraction instead of mole fraction.

Experimental results at T = 323.15 K showed two different 2-phase regions for the two pressures investigated (10 MPa and 30 MPa). In one of them, two liquid phases could be distinguished, being the light and heavy phases rich with ethanol and oil, respectively

(L1+L2). In the other 2-phase region, a light vapour phase rich with CO_2 and a heavy liquid phase rich with fish oil (V+L2) were observed. Homogeneous monophasic mixtures were visually and analytically verified, samples taken from the top and bottom of the equilibrium cell were similar with differences smaller than the experimental uncertainty. In the case of the phase equilibrium at T = 343.15 K and p = 10 MPa, three 2-phase regions (L1+L2, V+L1, and V+L2) and a 3-phase region (V+L1+L2) were observed. The appearance of the V+L1 region is consistent with the published phase equilibrium data of the binary system CO_2 + ethanol at T = 343.15 K [9,12].

Results obtained for the binary ethanol + fish oil tie-lines at T = 323.15 K, and pressures of 10 MPa and 30 MPa (Figure 3) are similar to those obtained by Bucio *et al.* in previous works at the same temperature and atmospheric pressure [26], indicating that, in the range investigated, pressure does not significantly affect phase equilibrium of this binary mixture. The composition of the two liquid phases in the L1+L2 region became more similar as more CO_2 is dissolved. The same was true for the V+L2 region, where the compositions of the vapour and liquid phases in equilibrium tend to merge with increasing amounts of dissolved ethanol. A similar trend has been found for other pseudo-ternary mixtures of CO_2 + ethanol + natural lipids, such as castor oil [19] and sunflower oil [21]. The homogeneous monophasic region at p = 30 MPa appears to be slightly larger, although no strong effect of pressure on the phase behaviour of the mixture at T = 323.15 K can be observed.

From the phase diagram at T = 343.15 K and p = 10 MPa (Figure 4), it can be observed that, starting from the binary sides of the phase diagram, increasing amounts of the third component made the tie-lines of the 2-phase regions approach the sides of the 3-phase region triangle. Inside this 3-phase region, theoretical mixtures split in a V+L1+L2 system, each phase with a composition defined by the vertices of the triangle.

Comparing the phase behaviour at T = 343.15 K, p = 10 MPa (Figure 4) with the 323.15 K isotherm at the same pressure (Figure 3a), it is noticeable that the former presents a lower amount of CO_2 dissolved in the liquid phase (V+L2 region), probably because of the temperature-driven increase in the CO_2 vapour pressure. On the contrary, it can be observed that raising temperature from 323.15 to 343.15 K increases the solubility of fish oil in ethanol (L1+L2 region) from near 0.075 mass fraction up to 0.35 mass fraction, yet adding CO_2 has a slight de-entraining effect at 343.15 K since the more CO_2 is dissolved, the wider the tie-lines become.

3.2. Data correlation

In this work, fish oil has been treated as a pseudo-component, assuming that the different triacylglycerols present in the fish oil behave in a similar way, which has been previously verified [26]. Experimental phase equilibrium data of the pseudo-ternary mixture were correlated with the Peng-Robinson equation of state (PR EoS) in combination with the conventional van der Waals mixing rules with two adjustable parameters (vdW2).

The PR EoS, was used as originally defined by Peng and Robinson [18]:

$$p = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)}$$

(1)

where the parameter a is related to the intermolecular attractive forces and b to the size of the molecules. For a pure fluid, constant b takes the value:

$$b = 0.07780 \frac{RT_C}{p_C}$$

(2)

where T_C and p_C are the critical temperature and pressure of the pure fluid, respectively.

$a(T)$ is a function of temperature:

$$a(T) = a(T_C)\alpha(T) \tag{3}$$

where

$$a(T_C) = 0.45724 \frac{(RT_C)^2}{p_C} \tag{4}$$

and $\alpha(T)$ depends on the temperature and acentric factor values of the compound. If $T < T_C$, the conventional expression from Peng-Robinson [18] is used:

$$\alpha(T) = \left(1 + \beta\left(1 - \sqrt{T/T_C}\right)\right)^2 \tag{5}$$

where β depends on the acentric factor ω according to $\beta = 0.37464 + 1.54226\omega - 0.26992\omega^2$ if $\omega \le 0.491$; and $\beta = 0.379642 + 1.48503\omega - 0.164423\omega^2 + 0.016666\omega^3$ if $\omega > 0.491$.

Else, if $T > T_C$, $\alpha(T)$ is calculated as recommended in [29]:

$$\alpha(T) = \left(\exp\left(c(1 - (T/T_C)^d)\right)\right)^2 \tag{6}$$

with

$$d = 1 + \frac{\beta}{2} \tag{7}$$

$$c = 1 - \frac{1}{d} \tag{8}$$

Binary mixture parameters are defined by the quadratic van der Waals mixing rules:

$$a = \sum_i \sum_j z_i z_j a_{ij} = \sum_i \sum_j z_i z_j \left(a_i a_j\right)^{0.5}\left(1 - k_{ij}\right) \tag{9}$$

$$b = \sum_i \sum_j z_i z_j b_{ij} = \sum_i \sum_j z_i z_j \frac{b_i + b_j}{2}\left(1 - l_{ij}\right) \tag{10}$$

here, z is either x or y and k_{ij}, l_{ij} are adjustable binary interaction parameters. For a pure fluid, $k_{ii} = l_{ii} = 0$.

The molecular weight (MW), critical properties (T_C and p_C) and acentric factor (ω) of the components of the system are listed in Table 6. Values for CO_2 and ethanol were obtained from the literature [30] whereas group contribution methods were used to estimate the critical properties and the acentric factor of the pseudo-component fish oil [31,32].

Binary interaction parameters k_{ij}, l_{ij} in Equations 9-10 were estimated and fugacity coefficients φ_i^V and φ_i^L were calculated for each data set according to [18]. Simultaneously, the tie-line compositions that minimized the objective function (Equation 11), satisfied the isofugacity criterion $\left(\varphi_i^V y_i = \varphi_i^L x_i\right)$ for every component i, and the mass balances in each phase, were calculated by the Newton-Raphson method by fixing pressure, temperature, and composition of fish oil in the liquid phase.

A least-square objective function was defined as:

$$OF = \sum_{i=1}^{NC} \sum_{j=1}^{NP} \left(z_{ij}^{exp} - z_{ij}^{calc}\right)^2 \tag{11}$$

where NC = number of components of the system, NP = number of experimental data points and z is either x or y. The superscripts exp and calc refer to experimental and calculated values.

Performance of PR EoS in combination with vdW2 mixing rules can be observed in Figures 3 and 4. The estimated binary interaction parameters for the PR EoS vdW2 model and the OF values (Equation 11) are reported in Table 7. The CO_2 + ethanol interaction parameters (k_{12}, l_{12}) were estimated by correlating binary experimental data obtained in this work (Table 2) together with experimental data taken from literature at 323.15 K and 343.15 K [9,12] to the PR EoS vdW2 model, and were fixed in the calculations of the pseudo-ternary system. Results of this fitting are shown in Figure 2. Experimental data points with deviations larger than 0.0001 from the calculations (according to Equation 11 with $j = 1$) were not taken into account.

The PR EoS vdW2 model was not fully capable of representing the different types of phase equilibrium (L1+L2, V+L1 and V+L2) when the same ethanol + fish oil interaction parameters (k_{23}, l_{23}) were applied in the correlation, thus different sets of binary interaction parameters were adopted for the ethanol + fish oil mixture in each of the 2-phase regions observed. This procedure is similar to the one followed by Hernández *et al.*, who adopted different sets of parameters for the interaction between the triglyceride and the alcohol groups in the correlation of CO_2 + ethanol + sunflower oil phase equilibrium data with GC EoS [21]. The Peng-Robinson equation of state with Wong-Sandler mixing rules [33] (PR WS EoS) was also explored in order to overcome this deficiency. However, no significant improvement in the correlation of experimental data was achieved and therefore we chose the PR EoS vdW2 model due to its simplicity. As Hernández *et al.* [21] pointed out, it is likely that a more extensive set of binary ethanol + fish oil phase equilibrium data would be necessary.

For the V+L1 and V+L2 regions at T = 343.15 K and p = 10 MPa, only the first binary interaction parameter (k_{23}) was included in the calculations, setting $l_{23} = 0$. As it can be seen in Figure 4, this consideration leads to a good agreement between experimental and calculated data, possibly because of the low fractions of fish oil and ethanol in the V+L1 and V+L2 regions, respectively.

As a general trend, the estimated values for the binary CO_2 + ethanol interaction parameters (k_{12} and l_{12}) are similar to those reported in the literature [13,17,19,23]. In the case of the CO_2 + fish oil and ethanol + fish oil binaries, comparison is not an easy task, since interaction parameters for the PR EoS vdW2 model are scarcely reported in the literature, and parameters from different EoS and other mixing rules are not directly related. Geana and Steiner [17] also used the PR EoS vdW2 model to correlate the phase equilibria of the mixture CO_2 + ethanol + rapeseed oil in the temperature range 313 K-353 K and at pressures from 6 MPa to 12 MPa. The estimated interaction parameters for the CO_2 + oil and ethanol + oil binaries are of the same order as the ones obtained in this work. Differences could be attributed to the different fatty acid composition of the oils. Rapeseed oil is composed mainly by C18:1, C18:2 and C18:3 fatty acids [17], whereas fish oil mainly constituents are C16:0, C18:1 and C22:6n-3 [26]. Similar values for these parameters can be also found in other available publications dealing with rapeseed oil [23] and other vegetal oils such as castor oil and soybean oil [19].

3.3. Thermodynamic consistency

Thermodynamic consistency of the experimental data has been tentatively tested by means of the method proposed by Valderrama and Faúndez [34] for high pressure gas-liquid equilibrium data including both phases, which has been adapted to ternary mixtures at

isobaric conditions. This method can be considered as a modeling procedure since a thermodynamic model that can accurately fit the experimental data must be first used to apply the consistency test [34].

The expression of the Gibbs-Duhem equation given in [34] at isothermal, isobaric conditions can be reduced to:

$$\sum_{i=1}^{NC} \left(z_i \mathrm{d} \ln \varphi_i \right) = 0 \quad \text{(isothermal, isobaric conditions } \mathrm{d}T = 0, \mathrm{d}p = 0\text{)} \tag{12}$$

which can lead to an expression similar to that given by Van Ness [35]:

$$\sum_{i=1}^{NC} \mathrm{d}\left(z_i \ln \varphi_i \right) - \sum_{i=1}^{NC} \left(\ln \varphi_i \mathrm{d}z_i \right) = 0 \tag{13}$$

By integrating both terms in the left side of Equation 13 and designating the first by A_1 and the second by A_2, the experimental data can be considered as thermodynamically consistent when the criteria proposed by Wisniak *et al.* [36] is met:

$$A_1 = \sum_{i=1}^{NC} \int \mathrm{d}\left(z_i \ln \varphi_i \right) \tag{14}$$

$$A_2 = \sum_{i=1}^{NC} \int \left(\ln \varphi_i \mathrm{d}z_i \right) \tag{15}$$

$$D = 100 \frac{\left\| |A_1| - |A_2| \right\|}{|A_1| + |A_2|} \leq 2 \tag{16}$$

Overall calculated deviations D are 0.457 for the experimental isothermal-isobaric data set obtained at T = 323.15 K and p = 10 MPa, 0.616 at T = 323.15 K and p = 30 MPa, and 0.104 at T = 343.15 K and p = 10 MPa. Although area tests are usually not considered a sufficient

condition of consistency, these positive results give an idea of the good quality of the phase equilibria data obtained in this work.

4. CONCLUSION

Knowledge of the phase behaviour of oils rich in n-3 PUFAs with ethanol and CO_2 rises as one of the fundamental aspects in the production of n-3 PUFA concentrates at mild, non-oxidative conditions. Experimental phase equilibrium data of the mixture CO_2 + ethanol + fish oil is presented in this work at 3 different p-T combinations. Tie-lines of the pseudo-ternary diagram were obtained by means of an analytical isothermal method with recirculation of the vapour phase in a high-pressure variable-volume view cell. Results showed two 2-phase regions (L1+L2 and V+L2) at T = 323.15 K for both pressures investigated (10 MPa and 30 MPa). An additional V+L1 and a 3-phase region (V+L1+L2) were observed at T = 343.15 K and p = 10 MPa. Experimental data were correlated with the Peng-Robinson equation of state coupled with conventional two-parameter van der Waals mixing rules. The model successfully explained the experimental results, although different sets of binary ethanol + fish oil interaction parameters were required to adequately represent the different types of phase equilibrium. Experimental data can be considered as thermodynamically consistent according to the proposed area test.

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Table 1. Fatty acid composition of the fish oil [26].

Fatty acid		% wt.
myristic	C14:0	3.8
palmitic	C16:0	21.0
palmitoleic	C16:1n-7	6.1
stearic	C18:0	6.0
oleic	C18:1n-9	18.4
vaccenic	C18:1n-7	3.0
linoleic cis (LA)	C18:2n-6	2.4
α-linolenic (ALA)	C18:3n-3	0.7
stearidonic	C18:4n-3	0.9
eicosenoic	C20:1n-9	2.1
eicosatrienoic	C20:3n-3	2.0
eicosapentaenoic (EPA)	C20:5n-3	6.9
docosapentaenoic (DPA)	C22:5n-3	1.8
docosahexaenoic (DHA)	C22:6n-3	24.9

Standard uncertainties are u(percentage) $= \pm 0.5$

Table 2. Vapour + Liquid phase compositions (mole fraction) of the binary system CO_2 (1) + ethanol (2).

p / MPa	x_1	y_1	p / MPa	x_1	y_1
T = 323.15 K			T = 343.15 K		
4.67	0.2647	0.9840	7.01	0.2930	0.9679
5.12	0.2771	0.9859	8.05	0.3785	0.9656
5.34	0.3058	0.9819	9.04	0.4260	0.9614
5.78	0.3128	0.9837	9.98	0.4968	0.9484
7.07	0.4128	0.9814	10.98	0.6130	0.9432
7.69	0.4795	0.9739	11.50	0.6910	0.9060
7.96	0.5069	0.9764			
8.16	0.5455	0.9754			
8.44	0.6348	0.9740			
8.46	0.6279	0.9671			
8.51	0.6535	0.9679			
8.69	0.6875	0.9630			

Standard uncertainties are $u(p) = \pm 0.15$ MPa, $u(T) = \pm 0.1$ K, and $u(w_i) = \pm 0.005$

Table 3. Liquid + Liquid (L1+L2) and Vapour + Liquid (V+L2) phase compositions (weight fraction) of the pseudo-ternary system CO_2 (1) + ethanol (2) + fish oil (3) at T = 323.15 K and p = 10 MPa.

heavy phase			light phase			type of
w_1	w_2	w_3	w_1	w_2	w_3	phase eq.
0.0000	0.2652	0.7348	0.0000	0.9256	0.0744	L1+L2
0.0423	0.2836	0.6741	0.0420	0.8692	0.0888	L1+L2
0.0761	0.2966	0.6273	0.0780	0.7957	0.1263	L1+L2
0.1012	0.3087	0.5901	0.1016	0.7638	0.1346	L1+L2
0.1696	0.3898	0.4406	0.1710	0.6176	0.2114	L1+L2
0.2247	0.0000	0.7754	0.9868	0.0000	0.0132	V+L2
0.2440	0.0272	0.7288	0.9580	0.0280	0.0140	V+L2
0.2776	0.0747	0.6478	0.9003	0.0751	0.0246	V+L2
0.3330	0.1181	0.5490	0.7924	0.1657	0.0419	V+L2
0.3622	0.1541	0.4837	0.7332	0.2193	0.0476	V+L2
0.3730	0.1710	0.4560	0.6949	0.2525	0.0526	V+L2
0.3804	0.1841	0.4355	0.6207	0.3010	0.0783	V+L2
0.2026	0.2224	0.5751	0.2024	0.2222	0.5754	homogeneous
0.2745	0.4691	0.2564	0.2747	0.4689	0.2564	homogeneous
0.3039	0.2838	0.4023	0.3030	0.2844	0.4026	homogeneous
0.4590	0.3640	0.1770	0.4593	0.3638	0.1769	homogeneous

Standard uncertainties are $u(p) = \pm 0.15$ MPa, $u(T) = \pm 0.1$ K, and $u(w_i) = \pm 0.005$

Table 4. Liquid + Liquid (L1+L2) and Vapour + Liquid (V+L2) phase compositions (weight fraction) of the pseudo-ternary system CO_2 (1) + ethanol (2) + fish oil (3) at T = 323.15 K and p = 30 MPa.

heavy phase			light phase			type of
w_1	w_2	w_3	w_1	w_2	w_3	phase eq.
0.0000	0.2219	0.7781	0.0000	0.9066	0.0934	L1+L2
0.0649	0.3010	0.6341	0.0771	0.8185	0.1044	L1+L2
0.1550	0.4288	0.4162	0.1520	0.6654	0.1826	L1+L2
0.2559	0.0000	0.7441	0.9832	0.0000	0.0168	V+L2
0.2843	0.0674	0.6484	0.9089	0.0639	0.0272	V+L2
0.3073	0.1174	0.5753	0.8588	0.1131	0.0281	V+L2
0.3404	0.1401	0.5194	0.8252	0.1417	0.0331	V+L2
0.3844	0.1666	0.4490	0.7079	0.2367	0.0555	V+L2
0.4922	0.2338	0.2740	0.6089	0.3036	0.0875	V+L2
0.2926	0.2224	0.4851	0.2928	0.2219	0.4853	homogeneous
0.2919	0.4499	0.2582	0.2902	0.4488	0.2610	homogeneous
0.4528	0.416	0.1312	0.4481	0.4163	0.1356	homogeneous
0.5219	0.3261	0.1520	0.5198	0.328	0.1522	homogeneous

Standard uncertainties are $u(p) = \pm 0.15$ MPa, $u(T) = \pm 0.1$ K, and $u(w_i) = \pm 0.005$

Table 5. Liquid + Liquid (L1+L2) and Vapour + Liquid (V+L1, V+L2) phase compositions (weight fraction) of the pseudo-ternary system CO_2 (1) + ethanol (2) + fish oil (3) at T = 343.15 K and p = 10 MPa.

heavy phase			light phase			type of phase eq.
w_1	w_2	w_3	w_1	w_2	w_3	
0.0000	0.2829	0.7171	0.0000	0.6497	0.3503	L1+L2
0.0363	0.2327	0.7310	0.0728	0.6418	0.2854	L1+L2
0.0618	0.2102	0.7280	0.1725	0.6291	0.1984	L1+L2
0.0890	0.1851	0.7259	0.3132	0.5677	0.1191	L1+L2
0.1157	0.1607	0.7236	0.4183	0.5088	0.0729	L1+L2
0.1624	0.1162	0.7214	0.4981	0.4199	0.0820	L1+L2
0.4854	0.5146	0.0000	0.9461	0.0539	0.0000	V+L1
0.4850	0.5014	0.0136	0.9239	0.0589	0.0172	V+L1
0.4870	0.4752	0.0378	0.9002	0.0680	0.0318	V+L1
0.1820	0.0000	0.8180	0.9796	0.0000	0.0204	V+L2
0.1843	0.0396	0.7761	0.9455	0.0325	0.0220	V+L2
0.1794	0.0717	0.7489	0.9143	0.0542	0.0315	V+L2
0.1814	0.0957	0.7229	0.9055	0.0607	0.0338	V+L2

Standard uncertainties are $u(p) = \pm 0.15$ MPa, $u(T) = \pm 0.1$ K, and $u(w_i) = \pm 0.005$

Table 6. Molecular weight (MW), critical temperature (T_c), critical pressure (p_c), and acentric factor (ω) of the components of the pseudo-ternary system CO_2 + ethanol + fish oil.

(pseudo-)component	MW / g/mol	T_C / K	p_C / MPa	ω	Ref.
CO_2	44.01	304.1	7.38	0.225	[30]
Ethanol	46.07	513.9	6.14	0.644	[30]
Fish Oil	902.03[a]	945.3	0.643	1.906	[31,32]

[a] Calculated as a weighted average based on the reported fatty acid profile of the fish oil [26].

Table 7. Estimated binary interaction parameters of the PR EoS vdW2 model for the pseudo-ternary system CO_2 + ethanol + fish oil at different temperature and pressure conditions in the different Liquid + Liquid (L1+L2) and Vapour + Liquid (V+L1, V+L2) 2-phase regions.

T / K	p / MPa	type of phase eq.	k_{12}[a]	k_{13}	k_{23}	l_{12}[a]	l_{13}	l_{23}	OF
323.15	10-30	L1+L2	0.0952	0.0695	-0.1026	-0.0248	0.0031	-0.0099	0.0631
		V+L2			0.0208			-0.1026	
343.15	10	L1+L2			-0.0821			-0.0118	
		V+L1	0.0913	0.2268	0.1400	-0.0103	-0.1005	-[b]	0.0408
		V+L2			-0.0355			-[b]	

[a] Estimated from binary experimental data obtained in this work and taken from literature [9,12].
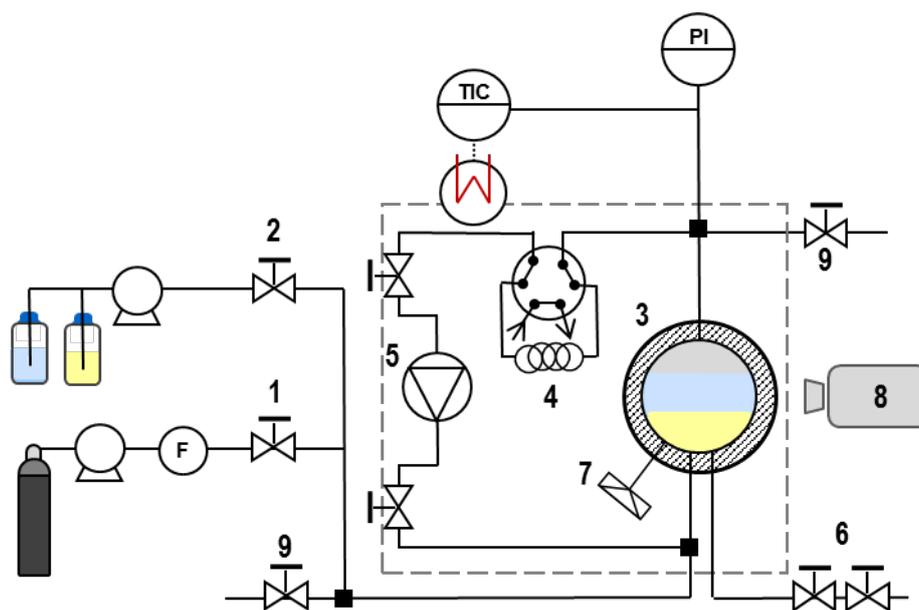[b] not considered ($l_{23} = 0$).

Figure 1. Schematic diagram of the high-pressure apparatus used for the phase equilibrium measurements. 1: CO_2 inlet; 2: Fish oil and ethanol inlet; 3: high-pressure variable volume equilibrium view cell; 4: 6-way valve for light-phase sampling; 5: gear pump; 6: heavy-phase sampling valves; 7: rupture disk; 8: camera endoscope and video recorder; 9: venting valves; F: Coriolis mass flow meter;
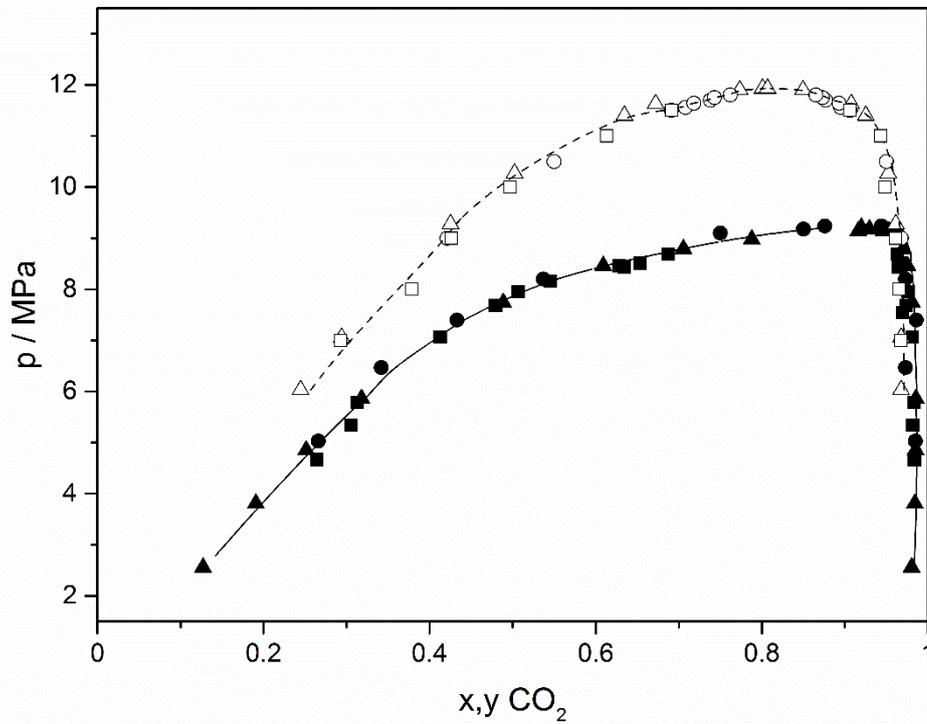
Figure 2. Pressure-composition diagram of the binary system CO_2 + ethanol at T = 323.15 K (full symbols) and T = 343.15 K (hollow symbols). □,■: experimental data obtained in this work; ●,○: data from Lim *et al.* [9]; ▲,△: data from Joung *et al.* [12]. Continuous and dashed lines are calculated values from PR EoS vdW2 model at T = 323.15 K and T = 343.15 K, respectively.
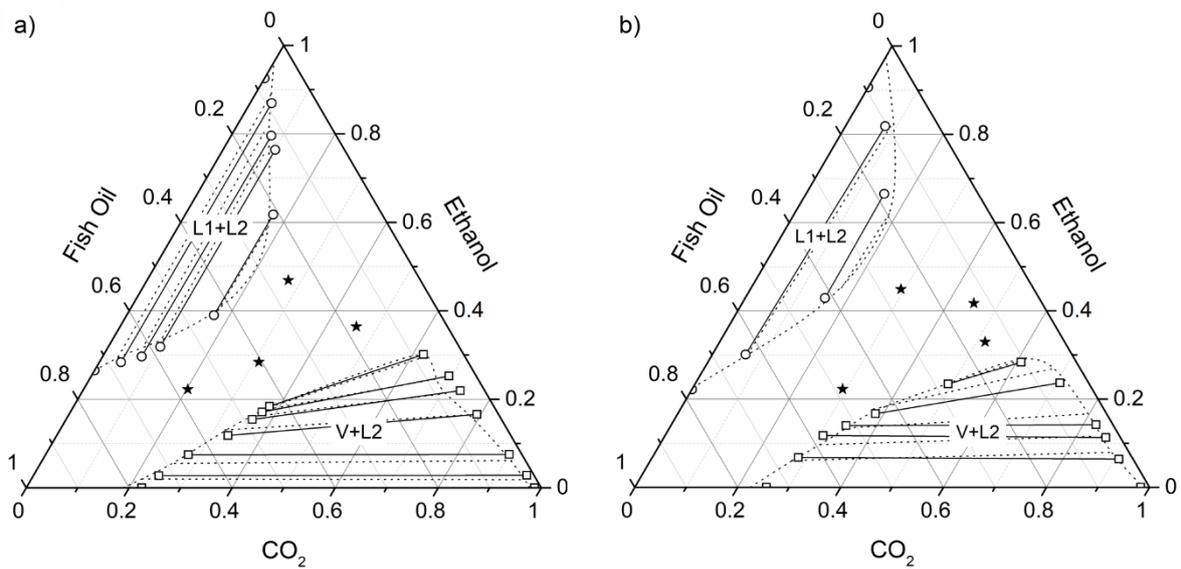
Figure 3. Phase diagram of the pseudo-ternary system CO_2 + ethanol + fish oil.
a) T = 323.15 K, p = 10 MPa; b) T = 323.15 K, p = 30 MPa.-○-: experimental L1+L2 tie-line; -□-: experimental V+L2 tie-line; ★: experimental monophasic mixture; ···· : PR EoS vdW2 model.
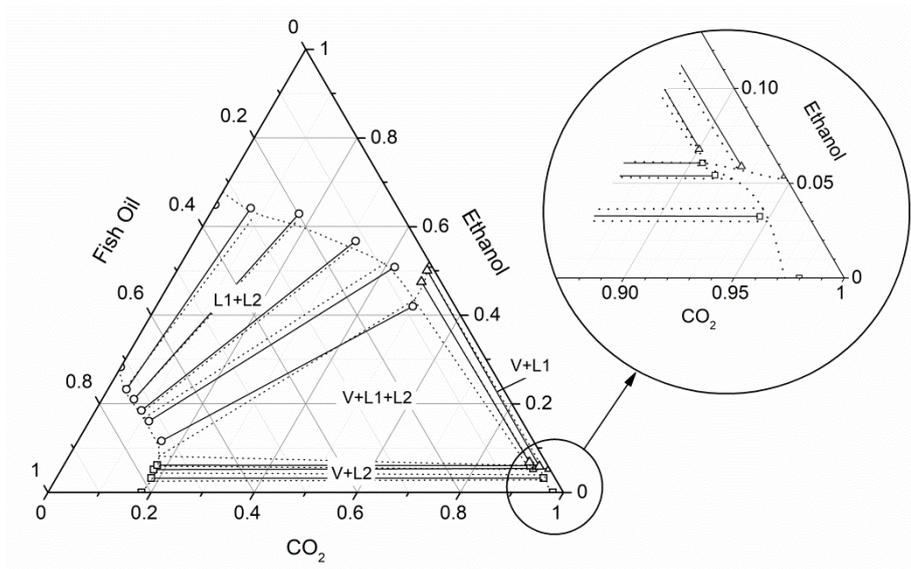
Figure 4. Phase diagram of the pseudo-ternary system CO_2 + ethanol + fish oil at T = 343.15 K and p = 10 MPa. -○-: experimental L1+L2 tie-line; -Δ- experimental V+L1 tie-line; -□-: experimental V+L2 tie-line; ····: PR EoS vdW2 model.