



# Phase equilibria of free fatty acids enriched vegetable oils and carbon dioxide: Experimental data, distribution coefficients and separation factors



Petra Kotnik, Mojca Škerget, Željko Knez\*

University of Maribor, Faculty of Chemistry and Chemical Engineering, Smetanova 17, SI-2000 Maribor, Slovenia

## ARTICLE INFO

### Article history:

Received 14 July 2012

Received in revised form 3 January 2014

Accepted 3 January 2014

### Keywords:

Supercritical carbon dioxide

Free fatty acids

Phase equilibria

Ternary system

Distribution coefficients

Separation factor

## ABSTRACT

In present work, the oils were treated by saponification procedure to release fatty acids from triglycerides to obtain free fatty acids (FFA) enriched oils and glycerol. Phase equilibria data for systems FFA enriched rapeseed oil–CO<sub>2</sub>, FFA enriched corn germ oil–CO<sub>2</sub> and FFA enriched borage oil–CO<sub>2</sub> were determined at temperatures 35, 45, 65 and 85 °C, and in pressure range from 100 to 550 Bar. Experiments using FFA enriched oils were performed using high-pressure variable-volume view cell, where phase inversions were also observed at temperatures 35 and 45 °C. Samples from liquid and vapor phases were analyzed by gas chromatography for the content of free fatty acids, and based on obtained data; the distribution coefficients and the separation factors between FFA and glycerol were calculated.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

Vegetable oils represent an important part in human and animal nutrition, and are used also in biochemical and bio energy production. Crude vegetable oils are recovered from natural material by pressing or solvent extraction procedures. Oils used for human consumptions are refined using complex procedures to remove undesired compounds and to avoid degradation reactions in order to follow strict food normative regulations [1].

Supercritical CO<sub>2</sub> is an advantageous solvent for extraction and fractionation of vegetable oils. To determine the optimal supercritical procedure, the basic equilibrium data are needed. High pressure phase equilibria of systems vegetable oils–CO<sub>2</sub> have not yet been entirely investigated. Vegetable oils usually contain approximately 95 wt.% of triglycerides and up to 5% of free fatty acids, phytosterols, phospholipids and other compounds, so we are dealing with multicomponent mixture. Many authors have investigated the phase equilibria of binary or ternary systems of mixtures of triglycerides [2–6], free fatty acids [2,5–8], fatty acid esters [2,3,9], oil minor components [5–7,10] or/and vegetable oils [2,11–14] in CO<sub>2</sub>. In most literature, the vegetable oils are usually discussed as one of the component in binary mixture with CO<sub>2</sub>. Yu et al. [2]

investigated the solubility of fatty acids, fatty acid esters, triglycerides, fats and oils in supercritical CO<sub>2</sub>. Chen et al. [5] measured VLE equilibrium data for binary systems linoleic acid–CO<sub>2</sub>, triolein–CO<sub>2</sub> and  $\alpha$ -tocopherol–CO<sub>2</sub> at 40 and 60 °C and at pressures up to 242.1 Bar. The review of literature for solubility data of binary systems of pure lipid components in CO<sub>2</sub> was published by Güçlü-Üstündağ et al. [3]. Ronco et al. [6] investigated VLE for binary systems including CO<sub>2</sub> and oleic, linoleic acid, triolein and sunflower oil. It was found, that components behave differently if phase equilibria were measured in systems with single component or with multicomponent mixture and CO<sub>2</sub>. The authors also indicate that solubility in CO<sub>2</sub> decreases with the chain length of lipid molecule. Therefore, the free fatty acids, mono- and diglycerides which are present in oils, are more soluble in CO<sub>2</sub> than triglycerides [2,6,15]. Phase equilibria of those systems have been observed up to pressure 350 Bar and temperatures up to 110 °C. On the other hand, it is reported, that CO<sub>2</sub> has low solvent power in case of vegetable oils [16–18], but the presence of minor components in oils can improve solubility in CO<sub>2</sub>. The solubility of lipid components in vegetable oil decreases with higher molecular mass or longer molecular chain, therefore the solubility is increasing from triglycerides, diglycerides, monoglycerides, fatty acids to methyl esters, as reported by Nilsson et al. [8]. The FFA-enriched vegetable oils should be therefore more soluble as oils with triglycerides as major component.

The aim of this work was to measure the phase equilibria of FFA-enriched oils in SC-CO<sub>2</sub>: rapeseed, corn germ and borage oil, at

\* Corresponding author. Tel.: +386 2 229 4461; fax: +386 2 252 7774.  
E-mail addresses: [zeljko.knez@uni-mb.si](mailto:zeljko.knez@uni-mb.si), [zeljko.knez@um.si](mailto:zeljko.knez@um.si) (Ž. Knez).

temperatures 35, 45, 65 and 85 °C and pressures up to 550 Bar. The experiments were performed in high-pressure variable-volume view cell. Moreover, the content of saturated and unsaturated fatty acids was determined by GC analysis and the distribution coefficients and separation factors between FFA and glycerol were calculated.

## 2. Materials and methods

### 2.1. Materials

The crude oils (rapeseed, corn germ and borage) were obtained from Gea d.d., Slovenia. All chemicals used for analysis were purchased from Sigma–Aldrich, Germany. CO<sub>2</sub> (purity 2.5) was obtained from Messer, Slovenia.

### 2.2. Phase equilibria determination

The phase equilibria determinations of systems saponified rapeseed oil–CO<sub>2</sub>, saponified corn germ oil–CO<sub>2</sub>, and saponified borage oil–CO<sub>2</sub> were performed using variable-volume view cell apparatus. A detail description of apparatus and method can be found in the literature [18]. The apparatus consists of a high-pressure variable volume view cell (NWA GMBh, Lorrach, Germany), which is designed for a pressure of 750 Bar and temperature of 200 °C, with a variable volume between 30 and 60 mL. The isothermal-analytical method in combination with the visual-synthetic method was used for phase behaviour determination. During sampling, the observed pressure change was up to 10 Bar, while the temperature was constant.

### 2.3. Saponification

FFAs were prepared using saponification process suggested by Yi-Hsu Ju et al. [19]. A NaOH solution was prepared by dissolving 48 g NaOH and 0.5 g Na<sub>2</sub>EDTA in 160 mL water. To this solution, 160 mL ethanol was added. To 100 g of oil 200 mL of NaOH solution was added and then heated at 60 °C with magnetic stirring at 550 rpm for 1 h. After 1 h 40 mL water and 400 mL hexane was added and the solution was stirred for 1 h at room temperature. The upper layer containing unsaponifiable matter was removed and discarded. To the lower layer 160 mL water was added and 12N hydrochloric acid was added until the pH equalled 1. The resulting lower layer was removed by a separating funnel and discarded. The FFA-containing upper layer was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, and solvent was evaporated in a vacuum rotary evaporator. FFAs obtained from saponification of oil were immediately analysed. After saponification the oils were used for phase equilibrium determination.

### 2.4. Gas chromatography analysis of FFA

The analyses were performed with GC model 6890 Agilent (USA) with column (HP-FFAP 30 m × 0.25 mm × 0.25 μm) and FID temperature set at 300 °C. The oven time–temperature profile was as follows 120 °C (1 min), 25 °C per min to 180 °C (1 min), 5 °C per min to 220 °C (10 min), 5 °C per min to 230 °C (30 min). The carrier gas was helium with total flow through the column 64.0 mL/min. The samples were analysed in *n*-hexane solutions. The quantification of FFA was made using individual calibration curves.

Each data point represents the average of at least three measurements and the relative standard deviation between measurements was 0.5%.

**Table 1**

Composition of oil after saponification (FFA-enriched oils).

FA composition/oil	Rapeseed	Corn germ	Borage seed
Total FFA (wt.%)	76.41	63.03	61.05
Saturated FFA (%)	8.49	11.93	17.10
Unsaturated FFA (%)	91.51	88.07	82.90

## 3. Results and discussion

The FFA-enriched oils were prepared by the saponification of individual oil and after saponification the oil was used for phase equilibrium determination. In Table 1, the content of FFA in oils is presented.

With the saponification process, fatty acids were released from the glycerides by cleavage of the ester bounds. In all cases, the FFA-enriched oil consist of more than 60 wt.% FFA. In Fig. 1 the schematic separation of fatty acids from triglycerides in oils is presented [20]. Therefore after saponification process in FFA-enriched oils free fatty acids and glycerol are present. The density of the oil during saponification was not changed and was for all used oils between 870 and 880 kg/m<sup>3</sup>.

### 3.1. Phase equilibrium determination

During the phase equilibrium study, the phase inversions in the cell were observed at constant temperature with increasing pressure from 100 to 550 Bar. In Table 2, the conditions of phase inversion are presented for each oil and temperature investigated.

At lower pressure the observed systems are composed of lower oil-rich phase and upper CO<sub>2</sub>-rich phase. At certain pressure the phases were inverted, and lower CO<sub>2</sub>-rich and upper oil-rich phase were obtained. The inversion of phases was visually detected, as shown in Figs. 2 and 3. This phenomenon was already described in detail in our previous work [16].

As can be seen from Table 2, the phase inversions in the pressure range investigated were observed at temperatures 35 °C and 45 °C and pressures higher than 460 Bar for rapeseed and corn germ oil. For the borage oil the phase inversion were observed at pressure 380 Bar and temperature 45 °C. This oil according to Table 1 contains 61.05 wt.% of FFA, where 82.90% of unsaturated FFAs are present. The phase inversions of rapeseed oil and corn germ oil at 45 °C are presented in Figs. 2 and 3, respectively. For the system borage oil–CO<sub>2</sub>, the same results of phase inversion as for other two systems were obtained, and therefore this system is not presented. Although the FFA enriched borage oil has different ratio between saturated and unsaturated FFA as rapeseed oil, the point of phase inversion at temperature 35 °C can be compared to the point observed for system rapeseed oil–CO<sub>2</sub>. At higher temperature, 45 °C, the phase inversion of system borage oil–CO<sub>2</sub> occur at much lower pressure than in system rapeseed oil–CO<sub>2</sub>, because more saturated FFAs are present compared to rapeseed oil.

In Figs. 4–6 the phase equilibria for the systems FFA enriched rapeseed oil–CO<sub>2</sub>, FFA enriched corn germ oil–CO<sub>2</sub> and FFA enriched borage oil–CO<sub>2</sub> are presented, respectively. The mole fraction of CO<sub>2</sub> in lower oil-rich phase is high; more than 0.76 mole fraction of CO<sub>2</sub> is present at pressure 100 Bar and temperature 35 °C.

**Table 2**

Pressure and temperature of phase inversion for investigated oils (isopycnic points).

	35 °C	45 °C	65 °C	85 °C
Rapeseed oil	480	460	Npi <sup>*</sup>	Npi <sup>*</sup>
Corn germ oil	520	480	Npi <sup>*</sup>	Npi <sup>*</sup>
Borage oil	460	380	Npi <sup>*</sup>	Npi <sup>*</sup>

<sup>\*</sup> Npi–no phase inversion was observed up to pressure 550 Bar.

Download English Version:

<https://daneshyari.com/en/article/230639>

Download Persian Version:

<https://daneshyari.com/article/230639>

[Daneshyari.com](https://daneshyari.com)