

Solubility of Binary Solid Mixture β -Carotene–Capsaicin in Dense CO₂

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The equilibrium solubilities of binary solid mixture β -carotene–capsaicin in liquid and supercritical CO₂ were measured using a static–analytic method. The solubilities of solid mixture components in CO₂ were determined at 25 and 40 °C in the pressure range from 100 to 300 bar. Measurements were performed at two mass ratios of solid components [$w(\text{carotene}):w(\text{capsaicin})$ 1:1 or 2:1, respectively] and it was found that the mass ratio of both components did not influence the equilibrium solubility. The equilibrium data of the ternary system β -carotene–capsaicin–CO₂ were compared to the equilibrium solubility data of binary systems β -carotene–CO₂ and capsaicin–CO₂. It could be observed that the solubility of capsaicin was lower in the presence of β -carotene. The solubility of β -carotene in CO₂ did not change in the presence of capsaicin. As shown in the examples in the paper, the data presented are important for designing the separation process of coloring and hot components from paprika.

Keywords: Dense carbon dioxide; solubility data; process parameters; paprika

INTRODUCTION

The solubility data of solid mixtures in supercritical fluid (SCF) are rarely reported in literature. For most of the reported systems it was observed that the solubility of a particular solid component in the ternary system is considerably higher than that in the pure solid–SCF system at the same temperature and pressure (Lee et al., 1988). This was valid for the systems where the solutes were highly soluble in SCF. It was also reported for the system phenanthrene and 2,3-dimethylnaphthalene, the solubilities of which are low in the binary case, that the solubilities of the components decrease in the ternary case (Dobbs et al., 1987). However, the fundamental mechanism of the solubility changes that appear in solid mixtures has not yet been completely understood.

Capsaicin and β -carotene are both components of paprika (*Capsicum annum*), one of the oldest source of natural colorants used in the food and cosmetic industries. β -Carotene is one of several carotenoids found in paprika. Capsaicin is the most important component among various capsaicinoids which causes pungency of paprika and should therefore be removed from coloring compounds (carotenoids). On the other hand, capsaicin is used in stimulation medicine because of its irritating effect on the receptors participating in circulatory and respiratory reflexes. The extraction process of paprika with organic solvents has shown some disadvantages (solvents cannot be completely removed, high temperatures of distillation can cause extract denaturation, extracts contain byproducts as fatty acids, capsaicin, etc.), which were minimized using SCF as an extraction solvent. A process for the production of paprika oleoresin with SC CO₂ is relatively well described in literature (Coenen et al., 1982; Coenen and Kriegel, 1983; Coenen and Hagen, 1983; Knez et al., 1991; Knez and Škerget, 1994).

The solubility data for β -carotene and capsaicin in CO₂ can be found in literature (Sakaki, 1992; Cygn-

arowicz et al., 1990; Škerget et al., 1995; Knez and Steiner, 1992); however, there were no data on the behavior of the ternary system β -carotene–capsaicin–CO₂.

In the present work the solubility of binary solid mixture β -carotene–capsaicin in CO₂ was determined. The obtained data were compared to the solubility of pure solid components in dense CO₂ at the same conditions (Knez and Steiner, 1992; Škerget et al., 1995).

MATERIALS AND METHODS

Apparatus. For the solubility measurements a static–analytic method was used. The detailed description can be found in Knez and Steiner (1992) and Škerget et al. (1995).

Reagents. β -Carotene with a minimum purity of 95% was obtained from Sigma Chemical (St. Louis, MO), Cat. No. C-9750. Capsaicin with a minimum purity of 98% was obtained from Sigma Chemical (St. Louis, MO), Cat. No. M-2028. Chloroform was 99% pure and was obtained from Kemika (Zagreb, CRO). CO₂ was supplied by Linde (Celje, SLO) and was 99.97% pure.

Procedures. The 500 mL equilibrium cell was loaded with a sufficient amount of the β -carotene–capsaicin mixture with appointed mass ratios (0.1 g of each component or 0.2 g of β -carotene and 0.1 g of capsaicin). The CO₂ from the supply tank was cooled to a liquid state and compressed into the equilibrium cell by a high-pressure pump. The temperature in the autoclave was regulated with a heating jacket (accurate to ± 0.5 °C). The component mixture–CO₂ suspension was mixed with a mechanical oscillating device under constant operating conditions until equilibrium was reached. After 1 h of phase separation a sample of the mixture–CO₂ solution (approximately 1 mL) was taken through the sampling valve into a trap with solvent (chloroform) where the components were solubilized. The trap was immersed in a sub-zero ethylene glycol–water bath. The amount of CO₂ released was measured with a rotameter. The pressure observed while taking the samples changed from 0.5 to 1 bar. The temperature change was not detected. The volume of the deadspace between the cell and sampling valve was 1.1×10^{-2} mL, when compared with the volume of sample (approximately 1 mL) was only 1.1%.

Since the quantity of the sample was sufficiently small compared to the volume of the equilibrium cell, further experiments could be done.

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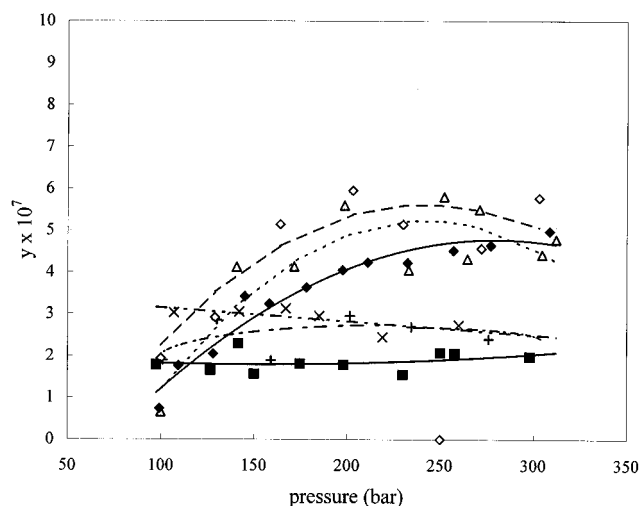


Figure 1. Solubility of β -carotene (C1) in dense CO₂ in binary system and in ternary system with capsaicin (C2) at different mass ratios (w) of both solid components. Symbols represent measurements, lines represent best fits: (x, -.-) 25 °C, $w_{C1}:w_{C2} = 1:1$; (Δ , - - -) 40 °C, $w_{C1}:w_{C2} = 1:1$; (+, -.-) 25 °C, $w_{C1}:w_{C2} = 2:1$; (\diamond , - - -) 40 °C, $w_{C1}:w_{C2} = 2:1$; (\blacksquare , -) 25 °C, pure C1 (Škerget et al., 1995); (\blacklozenge , -) 40 °C, pure C1 (Škerget et al., 1995).

The concentration of solutes in the chloroform was determined by UV spectrophotometry. The absorbance was measured (accurate to ± 0.001) at the absorption maximum of 460 nm for β -carotene and 280 nm for capsaicin. It was found that capsaicin did not influence the absorbance of β -carotene at 460 nm. Low absorbance of β -carotene at 280 nm was considered in the determination of capsaicin concentration. The HPLC was used in order to check the purity of dissolved β -carotene because it is labile against light and heat. The chromatographic conditions were as follows: column, RP18 (ODS, octadecylsilane-coated silica); mobile phase, acetonitrile/dichloromethane/methanol (v/v/v 65/25/1); flow rate of mobile phase, 2.5 mL min⁻¹; wavelength, 450 nm. The stability of capsaicin was tested by TLC (plate, Silica gel 60 F 254; solvent, diethyl ether; reagent for detection, dichloroquinonechloroimide). The method is described by Wagner et al. (1983).

RESULTS AND DISCUSSION

The solubility data of β -carotene and capsaicin in the ternary system β -carotene–capsaicin–CO₂ at two mass ratios of solid components $w(\text{carotene}):w(\text{capsaicin}) = 1:1$ and $2:1$ are presented in Figures 1 and 2. It can be observed that the mass ratio of components has no influence on the equilibrium solubilities. The comparisons of binary and ternary solubility data for each component show that the solubility of β -carotene does not change in the presence of capsaicin. Oppositely, the solubility of capsaicin is lower in the presence of β -carotene. The solubility at 25 °C is even independent of pressure.

For the binary system capsaicin–CO₂ (Knez and Steiner, 1992) phase behavior where a slight inflection of the 60 °C solubility isotherm at approximately 260 bar could be observed (Figure 2). The melting point of capsaicin at ambient conditions is 65 °C. In present work it was observed that in presence of CO₂ the melting point of capsaicin decreases with increasing pressure to the temperature minimum of approximately 40 °C at 100 bar.

For the 40 °C solubility isotherm of capsaicin when in mixture with β -carotene a similar trend as for the 60 °C solubility isotherm of pure capsaicin can be observed. From previously reported data about the

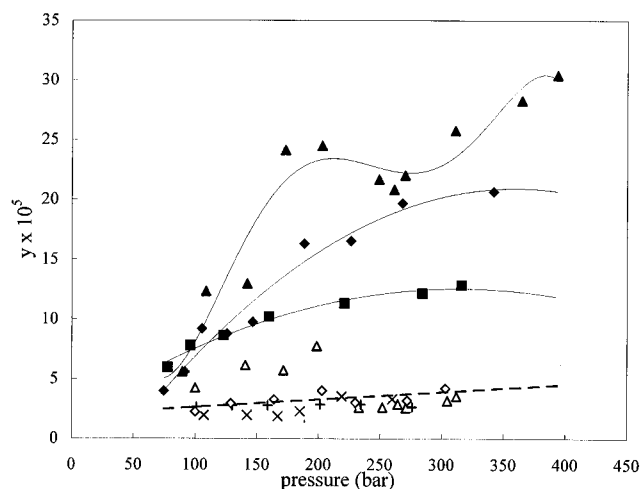


Figure 2. Solubility of capsaicin (C2) in dense CO₂ in binary system and in ternary system with β -carotene (C1) at different mass ratios (w) of both solid components: (x) 25 °C, $w_{C1}:w_{C2} = 1:1$; (Δ) 40 °C, $w_{C1}:w_{C2} = 1:1$; (+) 25 °C, $w_{C1}:w_{C2} = 2:1$; (\diamond) 40 °C, $w_{C1}:w_{C2} = 2:1$; (\blacksquare) 25 °C, pure C2 (Knez and Steiner, 1992); (\blacklozenge) 40 °C, pure C2 (Knez and Steiner, 1992); (\blacktriangle) 60 °C, pure C2 (Knez and Steiner, 1992); (- - -) best fit for C1–C2 mixture isotherms; (-) best fit for pure C2 isotherms.

Table 1. Physicochemical Properties of β -Carotene and Capsaicin

property	estimated value	method of estimation
Capsaicin		
molecular weight	M_w (g/mol)	305.42
normal boiling point	T_b (K)	853.7
critical temperature	T_c (K)	1062.11
critical pressure	P_c (Pa)	17.125×10^5
critical volume	V_c (m ³ /kmol)	0.95
critical compressibility	z_c	0.1842
acentric factor	ω	1.1851
vapor pressure	P^s (Pa)	
	C_1	154.4
	C_2	-25995.0
	C_3	-16.683
	C_4	0.47359×10^{-18}
β -Carotene		
molecular weight	M_w (g/mol)	536.88
normal boiling point	T_b (K)	1209.38
critical temperature	T_c (K)	1485.57
critical pressure	P_c (Pa)	7.993×10^5
critical volume	V_c (m ³ /kmol)	1.846
critical compressibility	z_c	0.1195
acentric factor	ω	0.6927
vapor pressure	P^s (Pa)	
	C_1	105.97
	C_2	-25171.0
	C_3	-10.393
	C_4	0.43787×10^{-18}

$${}^a \ln P^s \text{ (Pa)} = C_1 + \frac{C_2}{T} + C_3 \ln T + C_4 T^6.$$

presence of a second solid increasing the freezing point depression significantly, regardless of whether its triple point is higher or lower than that of the first solid (Zhang et al., 1992), in the ternary system β -carotene–capsaicin–CO₂ an even greater decrease of the capsaicin melting point can be proposed.

An attempt was made to correlate phase equilibrium of the systems capsaicin–CO₂ and β -carotene–CO₂ with the Peng–Robinson equation of state (McHugh and Krukoniš, 1986; Prausnitz et al., 1986; Van Ness and Abbott, 1982). The required critical properties of both solid components (Table 1) were estimated with the

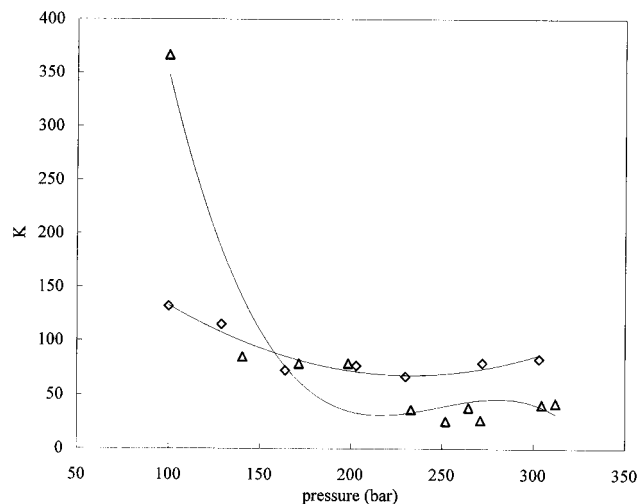


Figure 3. Extraction ratios K of β -carotene and capsaicin at 40 °C as function of pressure: (Δ) 40 °C, $w_{C1}:w_{C2} = 1:1$; (\diamond) 40 °C, $w_{C1}:w_{C2} = 2:1$; (—) best fit.

Lydersen group contribution method (Lydersen, 1955; Klincewicz and Reid, 1984; Somayajulu, 1989). The interpolated sublimation pressure (Table 1) was estimated by the Riedel method (Van Ness and Abbott, 1982). Solid molar volume was obtained with the regression of experimental data. The agreement of the model with the data was bad, so no further correlation of the binary solid mixture solubility data in CO_2 was carried out because the deviation would probably be further enhanced. Peng Robinson equation of state is obviously not an appropriate model for predicting equilibrium of the system capsaicin- CO_2 (and also β -carotene- CO_2). Beside the fact that all physical properties of solid components are predicted with models, the model used does not consider the solubilization of CO_2 in the capsaicin, which occurs due to observed melting point depression.

The extraction ratio K , defined as

$$K = \frac{[y_{C2}/y_{C1}]_{\text{SCF phase}}}{[y_{C2}/y_{C1}]_{\text{solid phase}}}$$

was calculated and is presented in Figure 3. It can be observed that the extraction ratio decreases with increasing the pressure at 40 °C independently of mass ratio of both components in the mixture. The same phenomenon can be observed also at 25 °C at a mass ratio of both components 2:1.

The dependency of extraction ratio on the pressure confirms the results of paprika extraction experiments. It was found (Knez et al., 1991; Knez and Škerget, 1994) that the best quality of paprika extract was obtained when extraction was performed in two steps:

- step 1: extraction of aromatic components at 40 °C and 90 bar. Obtained extract was orange-yellow in color and had an extreme pungent taste.
- step 2: extraction of coloring components at 40 °C and 400 bar. Obtained extract was dark-red (CU value, 80 000–190 000) and contained capsaicin in traces.

The extraction data for three experiments at different conditions are summarized on Figure 4. With higher pressure or/and temperature the amount of extractable substances in the first step was increased due to lower selectivity of CO_2 . Similar data can be also found in

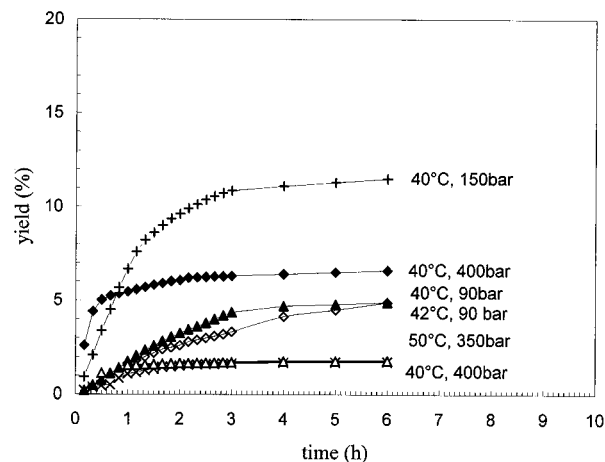


Figure 4. Kinetics of extraction of paprika [yield = (mass of extract) \times 100/(mass of paprika)]: (Δ) experiment 1 aromatic components; (\diamond) experiment 1 coloring components; (+) experiment 2 aromatic components; (\times) experiment 2 coloring components; (\circ) experiment 3 aromatic components; (\square) experiment 3 coloring components.

literature (Coenen et al., 1982; Coenen and Kriegel, 1983; Coenen and Hagen, 1983).

From the obtained solubility data it can be concluded that at lower pressures a higher separation of both components can be achieved. This confirms the fact that the quality of paprika extract of coloring component is better, when the aromatic components are extracted at moderate pressure (90 bar) and moderate temperature (40 °C).

ABBREVIATIONS USED

C1, β -carotene; C2, capsaicin; C_i ($i = 1-4$), constants; CU, color units; K , extraction ratio; M_w , molecular weight (g/mol); P^s saturated vapor pressure (Pa); P_c , critical pressure (Pa); SCF, supercritical fluid; T_b , normal boiling point (K); T_c , critical temperature (K); V_c , critical volume (m^3/kmol); y , mole fraction; w , mass ratio; z_c , critical compressibility; ω , acentric factor.

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