

Solubilities of Dodecanoic and Tetradecanoic Acids in Supercritical CO₂ with and without Entrainers

Chandrasekhar Garlapati and Giridhar Madras*

Department of Chemical Engineering, Indian Institute of Science, Bangalore 560012, India

The solubilities of dodecanoic acid (lauric acid) and tetradecanoic acid (myristic acid) in supercritical carbon dioxide without entrainers and with two entrainers, namely, ethanol and isoamyl alcohol (3-methyl-1-butanol), were determined at (308 and 318) K from (9.9 to 22.6) MPa. The solubility data were correlated with a thermodynamic model based on the Peng–Robinson equation of state with one binary interaction parameter.

Introduction

Supercritical fluids (SCFs) are fluids above its critical temperature and critical pressure. They have several attractive properties such as gaslike diffusivity, liquid-like densities, high compressibility, and negligible surface tension. These unique properties make them attractive solvents for many industrial separation processes. Supercritical carbon dioxide (SCCO₂) is commonly used because of its abundant availability, near-ambient critical temperature, and nontoxicity. However, polar substances are poorly soluble in SCCO₂,^{1,2} but these solubilities can be enhanced by adding (1 to 5) mol % of a polar entrainer.^{3,4}

The solubilities of saturated fatty acids in SCCO₂ are of considerable industrial importance. Dodecanoic acid is naturally present in cinnamon oil [(80 to 90) %] and in coconut oil [(40 to 60) %]. The major industrial uses of dodecanoic acid are in the manufacture of soaps, shampoos, and other surface-active agents including special lubricants. Tetradecanoic acid is another naturally available saturated fatty acid that is found in whale oil (15 %), dairy fats [(8 to 12) %], and palm kernel oil. It is largely used as a flavoring agent in the food industry and in the manufacture of emulsifiers. These saturated fatty acids have a large alkyl and strong polar head. The chemical formulas of dodecanoic and tetradecanoic acid are CH₃(CH₂)₁₀COOH and CH₃(CH₂)₁₂COOH, respectively. Isoamyl myristate and isoamyl laurate are used as flavors in foods.^{5,6} The solubilities of these natural products in supercritical fluids are critical in the design of supercritical extraction processes as well as supercritical reaction processes. The solubility of dodecanoic and tetradecanoic acid in pure SCCO₂ is available at 13.9 MPa in the pressure range considered.⁷ In this work, we have investigated the solubilities of dodecanoic acid and tetradecanoic acid at (308 and 318) K at various pressures without entrainers as well as in the presence of two entrainers.

Experimental Section

Materials. CO₂ (CAS No. 124-38-9, 99 %) purchased from Vinayaka Gases (India) was purified to 99.9 %, by passing the gas through a bed of silica gel. Ethanol (CAS No. 64-17-5, 99.9 %), dodecanoic acid (CAS No. 143-07-7, 99 %) and tetradecanoic acid (CAS No. 44-63-8, 98 %), and 3-methyl-1-butanol (CAS No. 123-51-3, 98 %) were purchased from Merck, Inc. (India).

* Corresponding author. Tel.: +91 80 22932321. Fax: +91 80 23600683. E-mail: giridhar@chemeng.iisc.ernet.in.

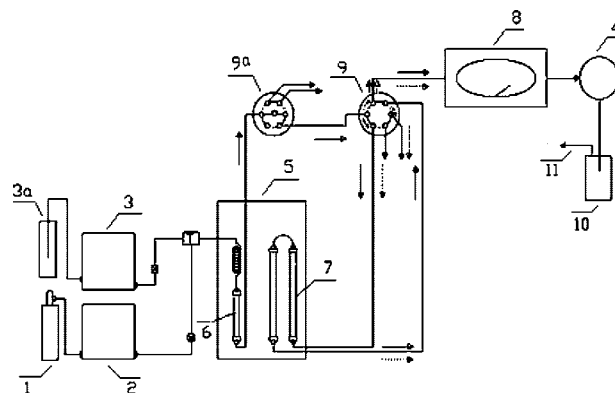


Figure 1. Schematic diagram of the experimental apparatus. 1, Carbon dioxide cylinder; 2, Carbon dioxide pump; 3, Entrainer pump; 3a, Entrainer reservoir; 4, Back pressure regulator; 5, Thermostat; 6, Accumulator; 7, Packed column; 8, UV detector; 9, Switching valve; 9a, Injector port; 10, Collector; 11, Gas vent. The dotted and solid arrows indicate when the packed column containing the solute is offline and online, respectively.

Equipment and Procedure. Figure 1 shows the schematic diagram of the apparatus used for the solubility studies. A flow system, also known as saturation (or transpiration) method, was used to measure the solubility of pure solid components and SCCO₂ + entrainers. The saturation method is often used to study the entrainer effects. More details regarding the principles and characteristics of the saturation method are found elsewhere.^{8,9} Carbon dioxide supplied from a gas cylinder (1) was liquefied and then directed to a CO₂ pump (Jasco model PU-1580-CO₂) (2), where the temperature was maintained at 263 K (factory set). This pump works on the SSQD (slow suction quick delivery) method and was operated in a constant flow mode. The entrainer was compressed using an HPLC pump (3) (Jasco model PU-2080, intelligent HPLC pump) and supplied to a T-joint and mixed with liquefied CO₂. A back pressure regulator (Jasco model BP-1580-81) (4) was used to maintain a constant pressure within the system. The mixed stream was then fed to a column thermostat (5), which maintains the desired temperature. The SCCO₂ and the entrainer were thoroughly mixed in an accumulator (6) and then sent through the solid packed column (7) in the upward direction. Initially, the packed columns (saturation column or equilibrium cells) were bypassed to obtain a baseline at the UV detector (8). A Rheodyne switching valve (9) was then used to direct the supercritical mixed stream

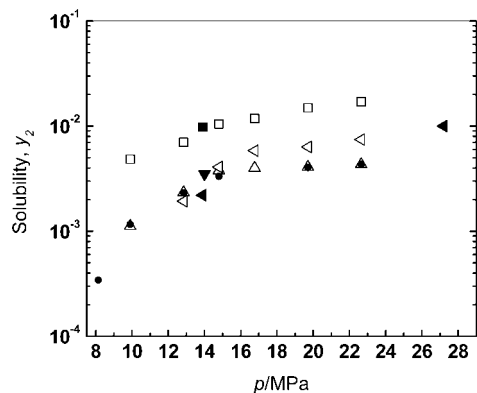


Figure 2. Solubility of saturated fatty acids, y_2 , in SCCO_2 . Dodecanoic acid at 308 K: \square , this work; \blacksquare , ref 7. Tetradecanoic acid at 308 K: Δ , this work; \blacktriangledown , ref 7; \bullet , ref 20. Tetradecanoic acid at 318 K: open arrow pointing left, this work; solid arrow pointing left, ref 7.

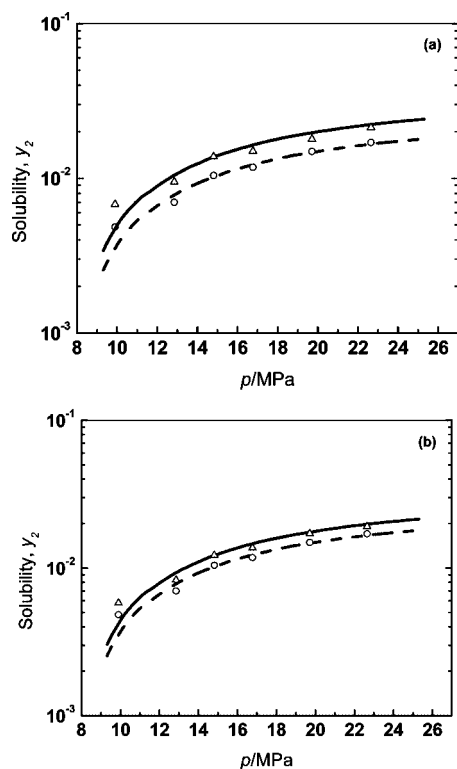


Figure 3. Solubility of dodecanoic acid y_2 , at 308 K, with (a) \circ , 0 mol % ethanol; Δ , 0.5 mol % ethanol and (b) \circ , 0 mol % 3-methyl-1-butanol; Δ , 0.5 mol % 3-methyl-1-butanol. The lines are model predictions based on the interaction parameters given in Table 3.

Table 1. Solubility of Dodecanoic Acid ($y_2 \cdot 10^3$) at $T = 308$ K

p/MPa	$T/\text{K} = 308$		
	0 mol % entrainer	0.5 mol % 3-methyl-1-butanol	0.5 mol % ethanol
9.90	4.84	5.81	6.78
12.85	7.00	8.26	9.45
14.81	10.44	12.01	13.78
16.77	11.78	13.43	14.96
19.71	14.90	16.84	17.88
22.65	17.06	19.11	21.33

through the packed column. In all our experiments, two packed columns (300 mm \times 14 mm) in series were used. In each packed column, the solute was packed in layers alternatively with dry glass wool, and each column has two $2 \mu\text{m}$ filters, one at inlet

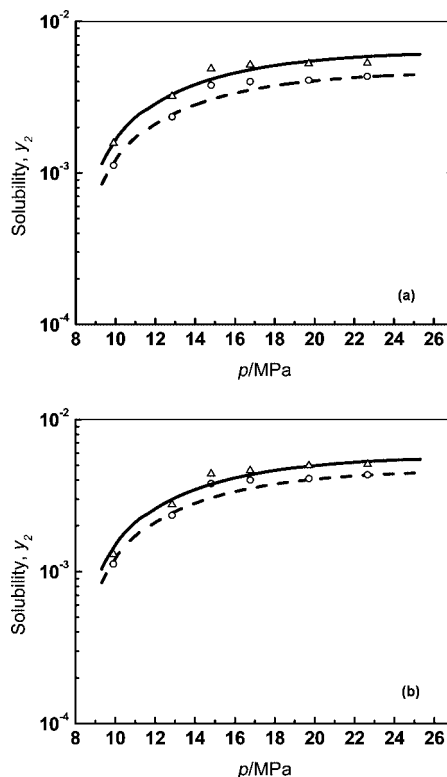


Figure 4. Solubility of tetradecanoic acid y_2 , at 308 K, with (a) \circ , 0 mol % ethanol; Δ , 0.73 mol % ethanol and (b) \circ , 0 mol % 3-methyl-1-butanol; Δ , 0.73 mol % 3-methyl-1-butanol. The lines are model predictions based on the interaction parameters given in Table 3.

and the other at the outlet and also packed with glass wool. A continuous stream of supercritical fluid was passed through the two columns packed with the solute. By ensuring an adequate contact time, the exiting stream was saturated with the solute. The exiting solute was then captured in a trap and measured gravimetrically. On the basis of the total flow of the supercritical fluid, the solubility of the solute was determined. The primary criterion for measuring the solubilities accurately is that the exiting stream is saturated. Therefore, experiments were conducted by varying the flow rate from (0.05 to 0.5) $\text{mL} \cdot \text{min}^{-1}$. No change in solubilities was observed when the flow rates were less than $0.3 \text{ mL} \cdot \text{min}^{-1}$. Therefore, all experiments were conducted with $0.2 \text{ mL} \cdot \text{min}^{-1}$.

Ternary System. The presence of an entrainer increases both the critical temperature and pressure of the resulting mixture. The critical locus of supercritical carbon dioxide–ethanol and equilibrium data for the CO_2 –3-methyl-1-butanol mixture were readily available.^{10,11} In SCFs–entrainer studies, it is necessary to ensure the existence of a single homogeneous fluid phase,¹² and all experiments were conducted above the critical temperature and pressure of mixtures.

Preparation of CO_2 –Enrainer Binary Mixtures. The binary mixtures of CO_2 with ethanol or 3-methyl-1-butanol were prepared by adjusting the flow rates of CO_2 and alcohols. The volumetric flow of the entrainer, Q_e , required to achieve a composition of X mol % of the entrainer (i.e., solute free basis) in the binary mixture at a given density of CO_2 (at given temperature and pressure) can be readily determined from

$$Q_e = \frac{Q_{\text{CO}_2} \rho_{\text{CO}_2} \text{MW}_e X}{\rho_e \text{MW}_{\text{CO}_2} (1 - X)} \quad (1)$$

In eq 1, MW_{CO_2} and MW_e are the molecular weights of CO_2 and entrainer, respectively. The carbon dioxide and entrainer

densities are denoted by ρ_{CO_2} and ρ_e , respectively. The density of carbon dioxide was calculated using a 27-parameter equation of state.¹³ The uncertainty in the composition estimation was within $\pm 2\%$ (relative). To ensure the reliability of the experimental data, each measurement was carried out at least three times, and the relative uncertainty (deviation) was less than $\pm 3\%$.

Thermodynamic Model for Solubility of Solids in Supercritical Fluids. The equation of state approach (EOS) is often used in modeling SCF phase equilibria.⁴ The fugacity of a pure solid solute f_2^s at a given temperature and pressure is^{1,14}

$$f_2^s = p_2^{\text{sub}} \phi_2^{\text{sat}} \exp\left(\frac{(p - p_2^{\text{sub}})V_2^s}{RT}\right) \quad (2)$$

where p_2^{sub} is the sublimation vapor pressure of the pure solid solute at system temperature T ; p is the system pressure; and R is the universal gas constant. ϕ_2^{sat} is the fugacity coefficient of the solid at saturation and is assumed to be unity. The exponential is the Poynting factor, which involves the molar volume of the solid solute, V_2^s . The fugacity of the solute in the supercritical phase f_2^{scf} is^{1,14}

$$f_2^{\text{scf}} = y_2 p \hat{\phi}_2^{\text{scf}} \quad (3)$$

$\hat{\phi}_2^{\text{scf}}$ represents the fugacity coefficient of the solute in the supercritical phase. Equating the fugacities of the solute in the two phases, the molar solubility of the solid solute in the supercritical fluid, y_2 , is^{1,14}

$$y_2 = \frac{p_2^{\text{sub}} \phi_2^{\text{sat}}}{p \hat{\phi}_2^{\text{scf}}} \exp\left(\frac{(p - p_2^{\text{sub}})V_2^s}{RT}\right) \quad (4)$$

In this work, the Peng–Robinson equation of state with the one-parameter mixing rule¹⁵ (see Supporting Information) was used to determine $\hat{\phi}_2^{\text{scf}}$. This is used in eq 4 to determine the solubility by the model and compared with the experimental data. The critical properties of carbon dioxide, tetradecanoic acid, ethanol, and 3-methyl-1-butanol were taken from the literature.^{11,16} The sublimation pressure of the solid solutes was obtained from Huang et al.¹⁶ The optimization procedure reduces the averaged absolute relative deviation percentage, AARD (%).

It is defined as $100/N_i \sum_{i=1}^{N_i} |y_2^{\text{cal}} - y_2^{\text{exp}}|/y_2^{\text{exp}}$ where N_i is number of data points; y_2 represents the molar solubility of the solute; and the superscripts cal and exp denote the calculated and experimental values, respectively. Correlation of the experimental solubility data requires an optimization process where

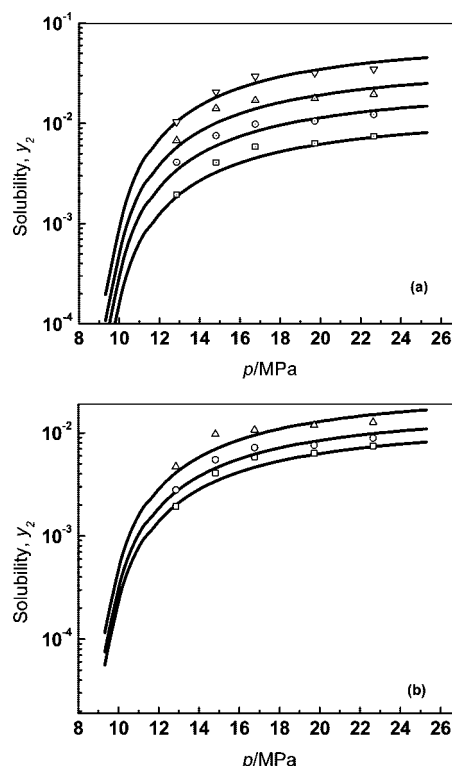


Figure 5. Solubility of tetradecanoic acid y_2 , at 318 K, with (a) \square , 0 mol % ethanol; \circ , 0.73 mol % ethanol; \triangle , 1.98 mol % ethanol; ∇ , 4.16 mol % ethanol and (b) \square , 0 mol % 3-methyl-1-butanol; \circ , 0.73 mol % 3-methyl-1-butanol; \triangle , 1.98 mol % 3-methyl-1-butanol. The lines are model predictions based on the interaction parameters given in Table 3.

k_{ij} is obtained for each binary pair. The three-component system of SCCO₂, entrainer, and solute requires three binary interaction parameters, k_{12} , k_{13} , and k_{23} , where subscripts 1, 2, and 3 represent CO₂, solid solute (fatty acid), and entrainer (alcohol), respectively. The parameter k_{12} is determined based on the experimental data of the solubility of fatty acid in SCCO₂ in the absence of an entrainer. The parameter k_{13} is obtained independently from the VLE data of CO₂–ethanol¹⁷ and CO₂–3-methyl-1-butanol.¹¹

Results and Discussion

The reliability of the apparatus was tested with solubility of naphthalene¹⁸ in supercritical carbon dioxide and the

Table 2. Solubility of Tetradecanoic Acid ($y_2 \cdot 10^3$) at (a) $T = 308$ K and (b) $T = 318$ K

(a)		$T/K = 308$				
p/MPa	0 mol % entrainer	0.73 mol % 3-methyl-1-butanol	0.73 mol % ethanol			
9.90	1.12	1.34	1.57			
12.85	2.34	2.76	3.21			
14.81	3.79	4.39	4.87			
16.77	4.00	4.62	5.16			
19.71	4.09	4.98	5.25			
22.65	4.33	5.08	5.31			
(b)		$T/K = 318$				
p/MPa	0 mol % entrainer	0.73 mol % 3-methyl-1-butanol	1.98 mol % 3-methyl-1-butanol	0.73 mol % ethanol	1.98 mol % ethanol	4.16 mol % ethanol
12.85	1.93	2.85	4.75	4.09	6.75	10.33
14.81	4.08	5.54	7.72	7.56	14.14	20.64
16.77	5.84	7.25	10.72	9.84	16.98	29.43
19.71	6.33	7.65	11.54	10.54	17.79	31.84
22.65	7.45	8.88	12.69	12.27	19.54	34.75

Table 3. Adjustable Binary Interaction Parameters, k_{13} and k_{23} , for the SCCO_2 –Entrainer–Fatty Acid Ternary System Obtained Using the PR EOS

ternary system	T/K	k_{12}	$k_{13}^{11,17}$	k_{23}	N_i	AARD (%)
dodecanoic acid– SCCO_2 –ethanol	308	0.024	0.086	0.952	6	8.48
dodecanoic acid– SCCO_2 –3-methyl-1-butanol	308	0.024	0.088	0.790	6	7.77
tetradecanoic acid– SCCO_2 –ethanol	308	0.040	0.086	0.200	6	12.60
tetradecanoic acid– SCCO_2 –3-methyl-1-butanol	308	0.040	0.088	0.180	6	8.70
tetradecanoic acid– SCCO_2 –ethanol	318	0.020	0.086	–0.044	15	16.55
tetradecanoic acid– SCCO_2 –3-methyl-1-butanol	318	0.020	0.088	0.124	10	14.64

Table 4. Average Entrainer Effect (E) for the Fatty Acids

entrainer	E				
	$T/K = 308$		$T/K = 318$		
	dodecanoic acid	tetradecanoic acid	tetradecanoic acid		
	entrainer mol % (solute free percentage basis)				
	0.5 mol %	0.73 mol %	0.73 mol %	1.98 mol %	4.16 mol %
ethanol	1.29	1.32	1.79	3.05	5.10
3-methyl-1-butanol	1.15	1.18	1.29	1.94	

solubility of salicylic acid¹⁹ in supercritical carbon dioxide with ethanol. Good agreement was obtained with the literature data within $\pm 6\%$. Similarly, the experimental data of tetradecanoic acid obtained in this study are in agreement with the results of Iwai et al.²⁰ (Figure 2). We have determined the solubilities of dodecanoic at 308 K and tetradecanoic acids at (308 and 318) K. The solubility of dodecanoic acid at 318 K was not investigated because dodecanoic acid melts at 316 K.

Pure Component Solubility. The solubilities of dodecanoic acid and tetradecanoic acid obtained in this study are shown in Table 1, Table 2a and b, and Figure 3a and b.

Correlation Results. All correlations results are reported in Table 3 along with AARD (%). The solubilities of dodecanoic acid in SCCO_2 and SCCO_2 + ethanol and SCCO_2 + 3-methyl-1-butanol ternary systems are shown in Figures 3a and b. The solubilities of tetradecanoic acid in SCCO_2 and SCCO_2 + ethanol and SCCO_2 + 3-methyl-1-butanol ternary systems at (308 and 318) K along with the model predictions are shown in Figures 4a and b and Figures 5a and b.

Entrainer Effect. An enhancement in solubility is observed as a result of the entrainer. The solubility enhancement effect can be quantified by E , which is defined as the ratio of the solubility obtained with entrainer to that obtained without entrainer. The average entrainer enhancement factors (over all pressures) are listed in Table 4. From E values, it is apparent that the entrainer effect of ethanol is much greater than that of 3-methyl-1-butanol. This may be due to the hydrogen bonding of ethanol compared to that of 3-methyl-1-butanol.¹² The solubilities of the saturated fatty acids are increased to higher values by the presence of a high concentration of entrainer rather than by increasing the pressure. For example, the solubility enhancement of tetradecanoic acid at 318 K by adding entrainer is 5.1 for 4.16% ethanol, as shown in Figure 5a. In comparison, an increase in the pressure from (12.8 to 22.6) MPa increases the solubility only by a factor 3.86 at 318 K.

Conclusion

The solubilities of dodecanoic acid and tetradecanoic acid in SCCO_2 and in SCCO_2 + ethanol and SCCO_2 + 3-methyl-1-butanol at (308 and 318) K, (9.9 to 22.6) MPa, were determined. The results obtained indicate that the solubilities of dodecanoic acid and tetradecanoic acid are higher in the SCCO_2 + ethanol system compared with that of SCCO_2 + 3-methyl-1-butanol.

The solubility data were correlated with the PR EOS with a single binary interaction parameter.

Supporting Information Available:

Supporting Information discusses the Peng–Robinson equation of state with mixing rules. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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