Solubility of Small-Chain Carboxylic Acids in Supercritical Carbon Dioxide

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The solubility of heptanoic acid and octanoic acid in supercritical carbon dioxide has been determined at temperatures of (313.15, 323.15, and 333.15) K over a pressure range of (8.5 to 30.0) MPa, depending upon the solute. The solubility of heptanoic acid ranged from a solute concentration of (0.08 ± 0.03) $\text{kg}\cdot\text{m}^{-3}$ ($T = 323.15$ K, $p = 8.5$ MPa) to (147 ± 0.2) $\text{kg}\cdot\text{m}^{-3}$ ($T = 323.15$ K, $p = 20.0$ MPa). The lowest octanoic acid solubility obtained was a solute concentration of (0.40 ± 0.1) $\text{kg}\cdot\text{m}^{-3}$ ($T = 333.15$ K, $p = 10.0$ MPa), while the highest solute concentration was (151 ± 2) $\text{kg}\cdot\text{m}^{-3}$ ($T = 333.15$ K, $p = 26.7$ MPa). Additionally, solubility experiments were performed for nonanoic acid in supercritical carbon dioxide at 323.15 K and pressures of (10.0 to 30.0) MPa to add to the solubility data previously published by the authors. In general, carboxylic acid solubility increased with increasing solvent density. The results also showed that the solubility of the solutes decreased with increasing molar mass at constant supercritical-fluid density. Additionally, the efficacy of Chrastil's equation and other density-based models was evaluated for each fatty acid.

Introduction

One of the keys to reducing dependence upon petroleum is the efficient use of renewable feedstocks for production of chemicals. A large portion of these chemicals could be produced using lipids from renewable feedstocks such as vegetable oils, animal fats, and bacterial lipids. In fact, oils and fats have been considered one of the most important renewable raw materials for the chemical industry.[1] Uses for lipid-based chemicals include lubricants, pharmaceuticals, cosmetics, surfactants, cleaning agents, solvents, and intermediates for the synthesis of plastics and coatings.[2,3] Christie (2003) defined lipids as fatty acids, fatty acid derivatives, and substances related either functionally or biosynthetically to fatty acids and their derivatives;[4] hence, the wide range of applications for lipids is due to the chemical transformations that can be applied to the fatty acids. Fatty acid can exist in several forms including saturated, mono- and polyunsaturated, and branched-chain. Chemical reactions involving fatty acids are typically centered on the terminal carboxyl group and any C−C double bonds that may be present.[1]

One of the most well-known reactions utilizing lipids is the oxidation of unsaturated fatty acids. Table 1 lists some of the most common unsaturated fatty acids found in nature. Depending upon the degree of oxidation, a variety of products can be obtained from fatty acid oxidation, such as aldehydes, epoxides, diols, and carboxylic acids. If enough oxidant is present, unsaturated fatty acids can be converted to a mixture of mono- and dicarboxylic acids. For example, *cis*-9-octadecenoic acid (CAS No. 112-80-1) can be converted to nonanoic acid (CAS No. 112-05-0) and nonanedioic acid (CAS No. 123-99-9) using hydrogen peroxide in the presence of a catalyst, as shown in eq 1.[5]

$$\begin{aligned} &H_3C(CH_2)_7CH = CH(CH_2)_7COOH + \\ &\qquad 4H_2O_2 \xrightarrow{\text{Catalyst}} H_3C(CH_2)_7COOH + \\ &\qquad\qquad HOOC(CH_2)_7COOH + 4H_2O \qquad (1) \end{aligned}$$

Other oxidizers such as potassium permanganate and ozone can be used as well to yield a similar acid product mixture.[6,7] Essentially, the oxidation results in the complete cleavage of double bonds. As can be seen from Table 1, depending upon the starting unsaturated fatty acid(s), possible carboxylic acid reaction products include small-chain mono- and dicarboxylic acids ranging from C3 to C9. These reaction products have uses in many applications. The monocarboxylic acids are used in the manufacturing of dyes, antimicrobial agents, food flavoring, plasticizers, lubricants, emulsifiers, adhesives, alkyd resins, and soaps and as intermediates for food flavor and perfume manufacturing.[8−10] Dicarboxylic acids such as hexanedioic acid (CAS No. 124-04-9) and nonanedioic acid can be used in the manufacturing of polymers, resins, lubricants, baking powders, and pharmaceutical products.[9,11−13]

Several studies have been conducted to explore the feasibility of oxidizing lipids in a supercritical fluid medium, which has the potential advantage of removing mass-transfer limitations between organic and oxidant phases.[14−16] Another advantage of using a supercritical-fluid medium is the possibility of product fractionation postreaction, eliminating the need for other separation processes such as distillation and crystallization.[6] Therefore, knowledge of the solubilities of the resulting products in the supercritical fluid is necessary in designing a process that can fractionate the product mixture. Other than solubility data for hexanoic acid (142-62-1) in supercritical carbon dioxide,[17,18] most solubility data for carboxylic acids exist primarily for

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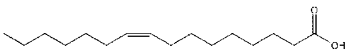
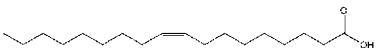
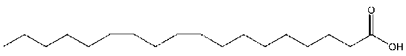
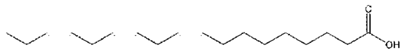
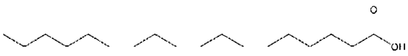
Table 1. Structures of Common Unsaturated Fatty Acids[36]

Common Name	Systematic Name	CAS No.	Structure
Palmitoleic Acid	*cis*-9-Palmitoleic Acid	373-49-9	
Oleic Acid	*cis*-9-Octadecenoic acid	112-80-1	
Linoleic Acid	*cis*-9, *cis*-12-Octadecadienoic Acid	60-33-3	
α-Linolenic Acid	*cis*-9, *cis*-12, *cis*-15-Octadecatrienoic Acid	463-40-1	
γ-Linolenic Acid	*cis*-6, *cis*-9, *cis*-12-Octadecatrienoic Acid	506-26-3	

longer-chain fatty acids (C12 to C22).[18−24] Previously, this research group has studied the solubility of nonanoic acid and nonanedioic acid at (313.15 and 333.15) K and at pressures of (10.0 to 30.0) MPa.[25,26] The goal of this work was to determine the solubility of heptanoic acid (CAS No. 111-14-8) and octanoic acid (124-07-2) at temperatures of (313.15, 323.15, and 333.15) K and, depending upon the solute, at pressures ranging from (8.5 to 30.0) MPa. Nonanoic acid solubility at 323.15 K at pressures of (10.0 to 30.0) MPa was also evaluated. Additionally, various forms of density-based, Chrastil-type models were evaluated for their efficacy at correlating fatty-acid solubility in supercritical carbon dioxide.

Experimental Methods

Materials. Octanoic acid ($CH_3(CH_2)_6COOH$, minimum mass fraction of 0.99) and nonanoic acid ($CH_3(CH_2)_7COOH$, minimum mass fraction of 0.96) were supplied by Sigma-Aldrich. Heptanoic acid ($CH_3(CH_2)_5COOH$, mass fraction of 0.98) and hexane (Optima grade) were purchased from Fisher Scientific. Nitrogen (ultrahigh purity mass fraction > 0.999) and carbon dioxide (mass fraction of 0.995) were obtained from NexAir (Memphis, TN). Carbon dioxide was provided as a liquid in cylinders equipped with a diptube, and it was further purified by passing it through a 2 μm filter (Valco Instrument Company, Inc.; Houston, TX). Additional purification of all other chemicals was not carried out.

Procedure. Heptanoic acid and octanoic acid solubility experiments were performed at temperatures of (313.15, 323.15, and 333.15) K in triplicate. For heptanoic acid, experiments were conducted at pressures of (8.5 to 20.0) MPa, while pressures of (10.0 to 30.0) MPa were utilized for studies with octanoic acid. Since experimental solubility data at (313.15 and 333.15) K have been published by the authors,[26] additional nonanoic acid experiments were only conducted at 323.15 K and at pressures of (10.0 to 30.0) MPa. All experiments utilized a dynamic, flow-through technique to determine lipid solubility in supercritical carbon dioxide (SC-CO_2). The basis of the dynamic approach is that the solute−solvent system achieves equilibrium as the solvent passes through the sample vessel.[27] Then, the (equilibrium) concentration of the exit stream is determined. The primary experimental apparatus consisted of a supercritical fluid extractor manufactured by TharSFC (model SFE-100; Pittsburgh, PA) and equipped with a dual-piston solvent pump, backpressure regulator, cyclone separator, and mass-flow meter for monitoring solvent usage. The uncertainty of the mass flow rate measurements was 0.2 %. The uncertainties of the temperature and pressure measurements were 1 K and 0.2 MPa, respectively. A typical experiment would begin with a measured portion of fatty acid suspended in the 100 mL stainless-steel sample vessel using alternating layers of glass wool (Fisher Scientific) and 2 mm diameter glass beads (Chemglass; Vineland, NJ). The packing material serves to hold the sample in place and to prevent channeling of the solvent.[27,28] The sample vessel, which was equipped with a resistive heating jacket, was allowed to reach the desired operating temperature of the experiment. The carbon dioxide was delivered to the system by the dual-piston pump at a flow rate of $0.25\ g\cdot s^{-1}$. To ensure that equilibrium had been achieved at this flow rate, preliminary experiments were conducted at flow rates from (0.167 to 0.33) $g\cdot s^{-1}$ at constant temperature and pressure, and the solubility was found to be independent of solvent flow rate. Before entering the sample vessel, the solvent passed through an electric heat exchanger, which raised the temperature of the solvent to the experimental set point. The system was maintained at the desired pressure via the backpressure regulator. As the solvent passed through the sample vessel, part of the fatty acid dissolved in the supercritical carbon dioxide, and the fatty acid + solvent solution passed through the backpressure regulator to the cyclone separator where the solvent was separated from the solute. The 500 cm^3 cyclone vessel was rinsed with 25 cm^3 of hexane to dissolve fatty acid. The fatty acid + hexane mixture was collected in a tared, 60 cm^3 glass vial, and then the hexane was removed using a TurboVap model LV (Caliper Life Sciences; Hopkinton, MA) at $T = 323.15$ K and $p = 0.07$ MPa. The tared vial was then reweighed to determine the mass of fatty acid that had dissolved in the supercritical carbon dioxide. Gravimetric analysis was performed using a Mettler Toledo model AB265-S/FACT (Columbus, OH; uncertainty: 0.01 mg).

Results and Discussion

Solubility Results. The solubility results of heptanoic acid, octanoic acid, and nonanoic acid in SC-CO_2 are summarized in Tables 2 through 4. Heptanoic acid solubility ranged from a solute concentration of (0.08 ± 0.03) $kg\cdot m^{-3}$ ($T = 323.15$ K, $p = 8.5$ MPa) to (147 ± 0.2) $kg\cdot m^{-3}$ ($T = 323.15$ K, $p = 20.0$

Table 2. Solubility of Heptanoic Acid in Supercritical Carbon Dioxide[a,b]

T / K	P / MPa	ρ_1 / $\text{kg}\cdot\text{m}^{-3}$	average concentration c_2 / $\text{kg}\cdot\text{m}^{-3}$	average mole fraction $10^3\ y_2$
313.15	10.0	628.61	33.4 ± 0.2	17.7 ± 0.08
	11.5	702.17	54.5 ± 0.7	25.6 ± 0.3
	15	780.23	76.9 ± 2	32.3 ± 0.7
	17.5	813.83	96.6 ± 2	38.6 ± 0.9
	20.0	839.81	119 ± 8	45.6 ± 3
323.15	8.5	248.95	0.08 ± 0.03	0.10 ± 0.05
	10.0	384.33	1.23 ± 0.1	1.08 ± 0.1
	11.5	548.84	27.6 ± 3	16.7 ± 2
	15.0	699.75	71.7 ± 8	33.5 ± 3
	17.5	749.27	108 ± 0.8	46.3 ± 0.3
	20.0	784.29	147 ± 0.2	59.8 ± 0.07
333.15	8.5	212.37	0.10 ± 0.01	0.16 ± 0.01
	10.0	289.95	0.35 ± 0.03	0.41 ± 0.03
	11.5	395.79	1.41 ± 0.1	1.20 ± 0.09
	15.0	604.09	25.8 ± 3	14.2 ± 2
	17.5	676.38	99.6 ± 1	47.4 ± 0.5
	20.0	723.68	118 ± 5	52.2 ± 2

[a] Average values for solute concentration (c_2) and mole fraction (y_2) taken from triplicate runs. [b] ± uncertainties refer to one standard deviation (σ).

Table 3. Solubility of Octanoic Acid in Supercritical Carbon Dioxide[a,b]

T / K	P / MPa	ρ_1 / $\text{kg}\cdot\text{m}^{-3}$	average concentration c_2 / $\text{kg}\cdot\text{m}^{-3}$	average mole fraction 10^3 y_2
313.15	10.0	628.61	30.4 ± 2	14.6 ± 0.9
	13.3	750.23	40.4 ± 0.3	16.2 ± 0.1
	16.7	803.71	42.3 ± 3	15.8 ± 1
	20.0	839.81	45.6 ± 0.7	16.3 ± 0.2
	23.3	867.59	51.9 ± 7	17.9 ± 3
	26.7	890.40	61.8 ± 0.9	20.7 ± 0.3
	30.0	909.89	76.6 ± 0.2	25.0 ± 0.06
323.15	10.0	384.33	0.69 ± 0.3	0.55 ± 0.2
	13.3	648.12	36.8 ± 4	17.0 ± 2
	16.7	735.55	50.4 ± 5	20.5 ± 2
	20.0	784.29	84.5 ± 6	31.8 ± 2
	23.3	819.28	92.9 ± 5	33.4 ± 2
	26.7	847.61	101 ± 4	35 ± 1
333.15	10.0	289.95	0.40 ± 0.1	0.43 ± 0.10
	13.3	395.79	1.39 ± 0.1	1.07 ± 0.09
	16.7	525.73	7.32 ± 0.2	4.23 ± 0.1
	20.0	657.00	75.7 ± 2	34 ± 0.9
	23.3	723.68	106 ± 6	42.6 ± 2
	26.7	802.74	151 ± 2	54.5 ± 0.6

[a] Average values for solute concentration (c_2) and mole fraction (y_2) taken from triplicate runs. [b] ± uncertainties refer to one standard deviation (σ).

Table 4. Solubility of Nonanoic Acid in Supercritical Carbon Dioxide[a,b]

T / K	P / MPa	ρ_1 / $\text{kg}\cdot\text{m}^{-3}$	average concentration c_2 / $\text{kg}\cdot\text{m}^{-3}$	average mole fraction $10^3\ y_2$
313.15[c]	10.0	628.61	16.1 ± 0.4	7.07 ± 0.2
	13.3	750.23	21.3 ± 0.7	7.82 ± 0.3
	16.7	803.71	21.8 ± 1	7.50 ± 0.4
	20.0	839.81	23.2 ± 1	7.63 ± 0.4
	23.3	867.59	24.0 ± 0.7	7.64 ± 0.2
	26.7	890.40	24.7 ± 1	7.64 ± 0.3
	30.0	909.89	25.4 ± 0.6	7.70 ± 0.2
323.15	10.0	384.33	0.23 ± 0.1	0.16 ± 0.09
	13.3	648.12	16.5 ± 0.4	7.03 ± 0.2
	16.7	735.55	18.8 ± 0.3	7.07 ± 0.1
	20.0	784.29	19.3 ± 0.8	6.79 ± 0.3
	23.3	819.28	21.1 ± 0.3	7.10 ± 0.1
	26.7	847.61	21.7 ± 0.4	7.07 ± 0.1
	30.0	870.43	23.3 ± 1	7.4 ± 0.4
333.15[c]	10.0	289.95	0.14 ± 0.07	0.13 ± 0.07
	13.3	525.73	4.68 ± 0.7	2.47 ± 0.4
	16.7	657.00	16.1 ± 2	6.75 ± 1
	20.0	723.68	19.7 ± 0.7	7.52 ± 0.3
	23.3	768.62	21.3 ± 1	7.65 ± 0.4
	26.7	802.74	21.1 ± 1	7.24 ± 0.4
	30.0	829.71	21.3 ± 2	7.09 ± 0.6

[a] Average values for solute concentration (c_2) and mole fraction (y_2) taken from triplicate runs. [b] ± uncertainties refer to one standard deviation (σ). [c] Ref 26.

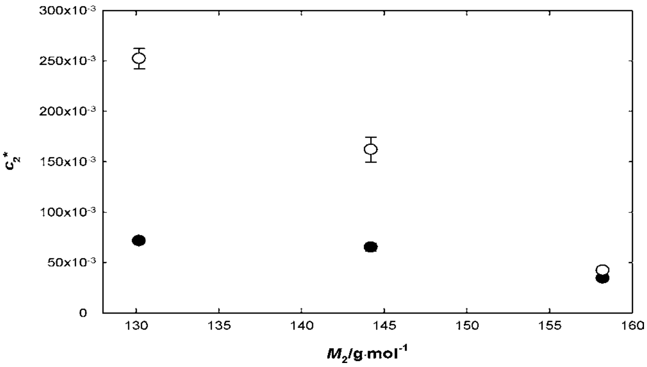


Figure 1. Plot of fatty acid solubility (c_2^*) in SC-CO_2 vs solute molar mass (M_2): ●, P = 10.0 MPa and T = 313.15 K; ○, P = 20.0 MPa and T = 333.15 K. Error bars correspond to uncertainties of one standard deviation (σ) taken from triplicate runs.

MPa). Octanoic acid solubility varied from a solute concentration of (0.40 ± 0.1) $\text{kg}\cdot\text{m}^{-3}$ (T = 333.15 K, p = 10.0 MPa) to a concentration of (151 ± 2) $\text{kg}\cdot\text{m}^{-3}$ (T = 333.15 K, p = 26.7 MPa). In terms of the new nonanoic acid data obtained in this study, solute concentration ranged from (0.23 ± 0.1) $\text{kg}\cdot\text{m}^{-3}$ (T = 323.15 K, p = 10.0 MPa) to (23.3 ± 1) $\text{kg}\cdot\text{m}^{-3}$ (T = 323.15 K, p = 30.0 MPa). In general, the solubility increased as pressure increased (and hence as supercritical-solvent density increased) with constant temperature for each fatty acid in supercritical carbon dioxide. The density of supercritical carbon dioxide was obtained from the NIST *Thermophysical Properties of Fluid Systems* database.[29] Since density increases as pressures increases at constant temperature, a good correlation of density with solubility is expected. The results show that as temperature increased, the effect of temperature on the solubility tended to be more pronounced at lower pressures. For example, at a pressure of 10.0 MPa, heptanoic acid solubility was (33.4 ± 0.2) $\text{kg}\cdot\text{m}^{-3}$ at 313.15 K but was only (1.23 ± 0.1) $\text{kg}\cdot\text{m}^{-3}$ at 323.15 K. However, at a pressure of 17.5 MPa, the solubility of heptanoic acid was (96.6 ± 2) $\text{kg}\cdot\text{m}^{-3}$ at 313.15 K and was (108 ± 0.8) $\text{kg}\cdot\text{m}^{-3}$ at 323.15 K. This example emphasizes the effect of density on solubility. As temperature increased from (313.15 to 323.15) K, SC-CO_2 density at 10.0 MPa went from (628.61 to 248.95) $\text{kg}\cdot\text{m}^{-3}$. However, under the same increase in temperature, SC-CO_2 density at 17.5 MPa only changed from (813.83 to 749.27) $\text{kg}\cdot\text{m}^{-3}$. Based upon the solubility results, the relationship between carboxylic acid solubility and molar mass was determined. Component molar masses were 130.19 $\text{g}\cdot\text{mol}^{-1}$ for heptanoic acid, 144.21 $\text{g}\cdot\text{mol}^{-1}$ for octanoic acid, and 158.23 $\text{g}\cdot\text{mol}^{-1}$ for nonanoic acid.[30] Figure 1 shows normalized solute concentration (c_2^*) plotted against solute molar mass (M_2). This graph indicates that normalized solute solubility tends to decrease as molar mass increases at constant solvent density (since temperature and pressure are held constant). This behavior has been reported for higher molecular weight fatty acids as well.[31]

Modeling. One of the earliest semiempirical solubility models applied to lipid + supercritical fluid systems is Chrastil's equation, which is based upon the theory that a solvato complex forms between molecules of the solute and solvent.[32] According to Chrastil's equation (eq 2), a log−log plot of normalized solute solubility (c_2^*) versus reduced solvent density ($\rho_{r,1}$) should result in a linear relationship.

$$c_2^* = \rho_{r,1}^k \exp\left(\alpha + \frac{\beta}{T_r}\right) \tag{2}$$

where c_2^* is the normalized solubility of solute, $\rho_{r,1}$ is the supercritical fluid reduced density, k is the association number, α is a function of the association number and molar masses of the solute and solvent, β is a function of the heat of solvation and heat of vaporization, and T_r is reduced solvent temperature. The association constant k shows the dependence of the solubility on density, and parameter β reflects the dependence of the solubility on temperature.[24] Equation 2 is a modified version of the original Chrastil equation that normalizes the equation to create dimension consistency.[26,33] For all equations, solute concentration, solvent density, and temperature have been normalized according to the following relationships:

$$c_2^* = \frac{c_2}{\rho_{c,1}}; \quad \rho_{r,1} = \frac{\rho_1}{\rho_{c,1}}; \quad T_r = \frac{T}{T_{c,1}} \tag{3}$$

where $\rho_{c,1}$ and $T_{c,1}$ are the critical density[29] (467.6 $\text{kg}\cdot\text{m}^{-3}$) and critical temperature[30] (304.2 K) of carbon dioxide.

Several variations of Chrastil's model have been developed to better account for effects of different parameters on solubility. del Valle and Aguilera (1988) proposed the following model to help compensate for the change in the heat of vaporization with temperature:[34]

$$c_2^* = \rho_{r,1}^k \exp\left(\alpha + \frac{\beta}{T_r} + \frac{\gamma}{T_r^{\,2}}\right) \tag{4}$$

Another modified form of Chrastil's equation that has been used to model lipid solubility is the Adachi−Lu equation:[35]

$$c_2^* = \rho_{r,1}^{(e_0 + e_1\rho_{r,1} + e_2\rho_{r,1}^{\,2})} \exp\left(\alpha + \frac{\beta}{T_r}\right) \tag{5}$$

As can be seen from eq 5, Adachi and Lu treated the association number k as a quadratic function of density such that

$$k = e_0 + e_1\rho_{r,1} + e_2\rho_{r,1}^{\,2} \tag{6}$$

However, expression of the association number as a linear function of density has been found to be adequate in some situations.[26,33] Hence, the association number would be expressed as

$$k = e_0 + e_1\rho_{r,1} \tag{7}$$

Incorporation of eq 7 with the del Valle-Aguilera equation (eq 4) results in the following expression:

$$c_2^* = \rho_{r,1}^{(e_0 + e_1\rho_{r,1})} \exp\left(\alpha + \frac{\beta}{T_r} + \frac{\gamma}{T_r^{\,2}}\right) \tag{8}$$

A previous study[31] on the solubility of solids in supercritical carbon dioxide showed eq 8 provided excellent correlation because it combined the strengths of the Adachi−Lu and del Valle-Aguilera models.

To evaluate the effectiveness of each model, the percent average absolute deviation ($|\Delta y_2\ \%|$) was determined with each compound. The percent average absolute deviation can be written as:

$$|\Delta y_2| = \frac{100}{N}\sum_{i=1}^{N}\frac{|y_{i,\text{calc}} - y_{i,\text{exp}}|}{y_{i,\text{exp}}} \tag{9}$$

where N is the number of data points, $y_{i,\text{exp}}$ is the experimental solubility of the carboxylic acid solute for experimental point i, and $y_{i,\text{calc}}$ is the calculated solubility corresponding to point i. The constants for the semiempirical models were determined by using the Solver tool in Excel (Microsoft; Redmond, WA) by minimizing the following objective function:

$$\text{OF} = \sum_{i=1}^{N}\frac{|y_{i,\text{calc}} - y_{i,\text{exp}}|}{y_{i,\text{exp}}} \tag{10}$$

Tables 5 thru 8 summarize the modeling results for each compound, including percent average absolute deviation and values for regressed constants. For each fatty acid, Chrastil's equation (eq 2) gave the highest deviation. For heptanoic acid, eqs 4 and 8 provided the lowest percent deviation of the models considered, although eq 5 provided a similar deviation. In the case of octanoic acid and nonanoic acid, the models that express the association number as a function of density (eqs 5 and 8) performed better than either Chrastil's model (eq 2) or the del Valle-Aguilera equation (eq 4). These results can be explained when the association number k is calculated using the regressed parameters (Table 7) of the Adachi−Lu equation and plotted against reduced solvent density, as shown in Figure 2. For

Table 5. Chrastil (eq 2) Modeling Results

comp.	k	α	β	$\|\Delta y_2\ \%\|$
heptanoic acid	6.46	10.09	−15.65	22
octanoic acid	6.35	18.58	−25.35	23
nonanoic acid	4.95	−1.52	−4.64	29

Table 6. del Valle-Aguilera (eq 4) Modeling Results

comp.	k	α	β	γ	$\|\Delta y_2\ \%\|$
heptanoic acid	5.45	−125.18	270.96	−151.1	15
octanoic acid	4.51	3.36	6.75	−15.65	17
nonanoic acid	2.41	61.02	−138.45	73.21	17

Table 7. Adachi−Lu (eq 5) Modeling Results

comp.	E_0	e_1	e_2	α	β	$\|\Delta y_2\ \%\|$
heptanoic acid	4.18	4.72	−2.08	7.38	−12.62	16
octanoic acid	48.69	−41.62	10.50	13.77	−21.18	11
nonanoic acid	36.7	−32.36	8.06	−6.68	0.99	4

Table 8. Equation 8 Modeling Results

comp.	e_0	e_1	α	β	γ	$\|\Delta y_2\ \%\|$
heptanoic acid	7.75	−1.07	−112.18	242.81	−136.16	15
octanoic acid	10.76	−2.94	28.22	−50.16	16.05	14
nonanoic acid	8.35	−2.92	64.24	−148.48	79.72	8

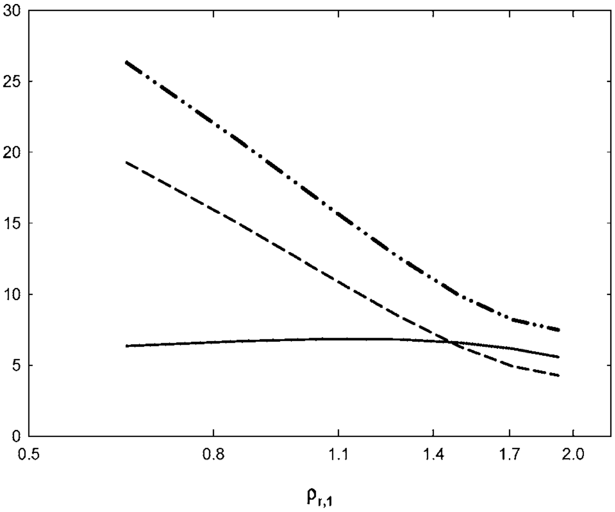


Figure 2. Plot of the association value *k* resulting from the Adachi−Lu equation (eq 5) vs reduced solvent density ($\rho_{r,1}$): —, heptanoic acid; —••—, octanoic acid; −−, nonanoic acid.

octanoic acid and nonanoic acid, a nonlinear relationship exists between the association number and reduced solvent density. Therefore, eq 5 (and eq 8 to a lesser extent) would be expected to provide better correlations compared to eqs 2 and 4. However, the association number for heptanoic acid is more linearly dependent upon density; hence, not much difference is seen in terms of average absolute deviation between eqs 4, 5, and 8 for this solute.

Conclusions

In this work, the solubility of heptanoic acid, octanoic acid, and nonanoic acid in supercritical carbon dioxide has been experimentally evaluated. Heptanoic acid solubility ranged from a solute concentration of (0.08 ± 0.03) $\text{kg}\cdot\text{m}^{-3}$ ($T = 323.15$ K, $p = 8.5$ MPa) to (147 ± 0.2) $\text{kg}\cdot\text{m}^{-3}$ ($T = 323.15$ K, $p = 20.0$ MPa). Solubility of octanoic acid ranged from a solute concentration of (0.40 ± 0.1) $\text{kg}\cdot\text{m}^{-3}$ ($T = 333.15$ K, $p = 10.0$ MPa) to (151 ± 2) $\text{kg}\cdot\text{m}^{-3}$ ($T = 333.15$ K, $p = 26.7$ MPa). Nonanoic acid solubility varied from (0.23 ± 0.1) $\text{kg}\cdot\text{m}^{-3}$ ($T = 323.15$ K, $p = 10.0$ MPa) to (23.3 ± 1) $\text{kg}\cdot\text{m}^{-3}$ ($T = 323.15$ K, $p = 30.0$ MPa). Overall, solute solubility increased with increasing pressure and increasing density at constant temperature. Additionally, carboxylic acid solubility showed an inverse relationship with molar mass. Semiempirical equations of the Chrastil-type were used to model solubility data. Modified forms of Chrastil's equation, such as the del Valle-Aguilera equation and the Adachi−Lu equation, provided lower deviations than the original Chrastil model.

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