

Solubility of Nonanoic (Pelargonic) Acid in Supercritical Carbon Dioxide

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The solubility of nonanoic acid (also known as pelargonic acid) in supercritical carbon dioxide has been determined at (313.15 and 333.15) K over a pressure range of (10 to 30) MPa. The experimental apparatus was of a flow-type, dynamic design, and the solubility was obtained gravimetrically. The solubility ranged from a pelargonic acid concentration of $(0.14 \pm 0.07) \text{ kg} \cdot \text{m}^{-3}$ (333.15 K, 10.0 MPa) to $(25.39 \pm 0.61) \text{ kg} \cdot \text{m}^{-3}$ (313.15 K, 30.0 MPa). The results showed that the solubility of pelargonic acid at 313.15 K was always greater than at 333.15 K at each pressure considered, a common behavior in liquid + SCF phase equilibria. No supercritical fluid solubility data for pelargonic acid were found in the literature. To ensure the validity of the experimental technique, solubility data for oleic acid were measured and compared to literature values. Oleic acid solubilities agreed with literature data within estimated uncertainties. A modified Adachi–Lu model, in terms of dimensionless variables, was used to correlate the solubility of pelargonic acid. Excellent agreement between experimental data and the correlation was found.

Introduction

From an economic point of view, the goal of most chemical processes is to convert low-value materials into more valuable ones. Monounsaturated fatty acids, such as *cis*-13-docosenoic acid (erucic acid, CAS No. 112-86-7) and *cis*-9-octadecenoic acid (oleic acid, CAS No. 112-80-1) can be oxidized to form compounds such as epoxides, aldehydes, monoacids, and diacids. For example, oleic acid can be oxidized to produce an equimolar mixture of nonanoic acid (pelargonic acid, CAS No. 112-05-0) and nonanedioic acid (azelaic acid, CAS No. 123-99-9). Pelargonic acid forms esters with alcohols that can be used as plasticizers and lubricating oils. Azelaic acid can be used to formulate polymers and pharmaceutical products.^{1–4} Pelargonic acid is also used as a chemical intermediate for synthetic flavors, cosmetics, pharmaceuticals, and corrosion inhibitors.⁵ Additionally, it is used in modifying alkyd resins to prevent discoloring and to keep flexibility and resistance to aging since saturated pelargonic acid is resistant to oxidation. C8–C12 straight- and saturated-chain fatty acids such as pelargonic acid are capable of removing the waxy cuticle of broad-leaved, grassy weeds, thus causing tissue death. Therefore, they are used as active ingredients of environment-friendly and fast-acting herbicides.⁵

Due to the increase in the demand for dibasic acids, such as azelaic acid, more uses for the coproduct pelargonic acid are being researched.⁶ A recent study has shown that pelargonic acid is an excellent solvent for extracting ethanol from water.⁷ Due to the value of the oxidation products, there is a strong economic incentive to carry out this oxidation reaction industrially.

Oxidation via ozonolysis is the most well-known method of producing azelaic and pelargonic acids from oleic acid.⁸ This reaction takes place in the liquid phase; therefore, the ozone

and the oxygen have to be transferred to the liquid phase. Typically, the limiting step in the process is the mass transfer of these reactants into the liquid. By having the reactants in a single phase, the mass-transfer limitations are removed, and this can be accomplished by carrying out the reaction in a supercritical fluid medium, such as supercritical carbon dioxide.⁹ Knowledge of the solubilities of the reactants and products in the supercritical fluid is crucial in determining reactor operating conditions and the feasibility of separating the products via supercritical fluid fractionation. In a recent publication, this research group reported the solubility of azelaic acid in supercritical carbon dioxide at (313.15 and 333.15) K over a pressure range of (10 to 30) MPa.¹⁰ In this work, the solubility of pelargonic acid in supercritical carbon dioxide was determined at the same conditions.

Experimental Methods

Materials. Nonanoic or pelargonic acid ($\text{CH}_3(\text{CH}_2)_7\text{COOH}$, minimum 96 % purity) and oleic acid ($\text{CH}_3(\text{CH}_2)_7(\text{CH})_2(\text{CH}_2)_7\text{COOH}$; ≈ 99 % purity) were supplied by Sigma-Aldrich, and hexane (Optima grade) was purchased from Fisher Scientific. Nitrogen (ultrahigh purity) and carbon dioxide (99.5 % purity) 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. Solubility of pelargonic acid, a liquid at room temperature, in supercritical carbon dioxide (SC-CO₂) was determined using a dynamic technique. The dynamic method is based on the assumption that the solute–solvent system reaches equilibrium as the solvent flows over the solute.¹¹ The solubility experiments used a supercritical fluid extractor manufactured by Thar Technologies (model SFE-100; Pittsburgh, PA). Figure 1 provides a diagram of the supercritical fluid extraction unit. The system was equipped with a Coriolis mass-flow meter, dual-piston pump, backpressure regulator, and

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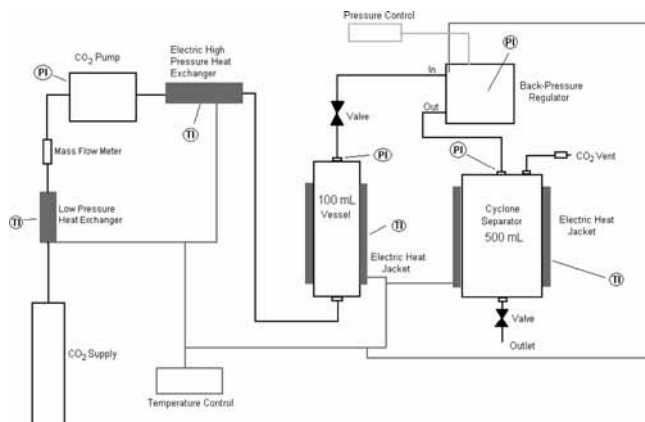


Figure 1. Experimental apparatus.

cyclone separator. 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 quantity of about 10 g of pelargonic acid was placed in a stainless-steel equilibrium vessel (volume of 100 mL) packed with alternating layers of 2 mm diameter borosilicate glass beads (Chemglass; Vineland, NJ) and glass wool (Fisher Scientific). The packing was necessary to reduce channeling of the SC-CO₂ and prevent pelargonic acid entrainment.^{11,12} The temperature of the equilibrium vessel was increased to the prescribed operating value using a heating jacket. CO₂ was pumped through a heat exchanger to raise its temperature prior to entering the equilibrium cell. Upon entering the equilibrium vessel, the CO₂ was in a supercritical state at the desired pressure, which was maintained by a backpressure regulator.

Pelargonic acid solubility experiments were performed in triplicate at (313.15 and 333.15) K and at pressures ranging from (10 to 30) MPa. Approximately 0.3 kg of SC-CO₂ was allowed to flow over the pelargonic acid in each experiment. A Coriolis mass-flow meter was used to quantify the mass of liquid CO₂ used. The CO₂ was delivered by a dual-piston pump at a flow rate of 0.25 g·s⁻¹. To confirm that equilibrium had been reached, preliminary experiments were conducted at flow rates ranging from (0.167 to 0.33) g·s⁻¹ at constant pressure. These preliminary experiments indicated that solubilities were not a function of SC-CO₂ flow rate. The solute–solvent mixture flowed from the equilibrium vessel to the cyclone separator through a valve and the backpressure regulator undergoing a continuous expansion. Consequently, the pressure was reduced resulting in a phase separation; the gaseous CO₂ exited the system, while the pelargonic acid was deposited on the vessel walls. The cyclone separator was rinsed with 25 mL of hexane to dissolve the pelargonic acid. The pelargonic acid + hexane mixture was collected in a tared, 40 mL amber glass vial, and then the hexane was removed using a TurboVap model LV (Caliper Life Sciences; Hopkinton, MA). This device evaporated the solvent (hexane) using a stream of nitrogen. The vials were then reweighed to measure the mass of pelargonic acid that had dissolved in the SC-CO₂. After each extraction, the system was cleansed with an additional 0.3 kg of SC-CO₂. The balance used to tare and reweigh the vials was Mettler Toledo model AB265-S/FACT (Columbus, OH; uncertainty: 0.01 mg).

Results and Discussion

Solubility Results. The solubility results of pelargonic acid in SC-CO₂ are summarized in Table 1. The density of CO₂ was obtained from the NIST fluid property database.¹³ In general,

Table 1. Solubility of Pelargonic Acid in Supercritical Carbon Dioxide^{a,b}

average solubility	average solubility			
<i>T</i> /K	<i>P</i> /MPa	ρ /kg·m ⁻³	c_2 /kg·m ⁻³	10 ³ <i>y</i> ₂
313.15	10.0	628.61	16.09 ± 0.43	7.07 ± 0.19
	13.3	750.23	21.26 ± 0.68	7.82 ± 0.25
	16.7	803.71	21.84 ± 1.17	7.50 ± 0.4
	20.0	839.81	23.23 ± 1.09	7.63 ± 0.36
	23.3	867.59	24.01 ± 0.65	7.64 ± 0.21
	26.7	890.40	24.66 ± 0.99	7.64 ± 0.30
	30.0	909.89	25.39 ± 0.61	7.70 ± 0.18
333.15	10.0	289.95	0.14 ± 0.07	0.13 ± 0.07
	13.3	525.73	4.68 ± 0.72	2.47 ± 0.38
	16.7	657.00	16.05 ± 2.34	6.75 ± 0.98
	20.0	723.68	19.72 ± 0.68	7.52 ± 0.26
	23.3	768.62	21.3 ± 1.18	7.65 ± 0.42
	26.7	802.74	21.06 ± 1.02	7.24 ± 0.35
	30.0	829.71	21.3 ± 1.86	7.09 ± 0.61

^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).

as pressure increased at constant temperature, the solubility of pelargonic acid in SC-CO₂ increased. The results show that solubility at 333.15 K is greatly dependent upon pressure; in fact, an overall increase in solubility of over 2 orders of magnitude was observed. For the pressure range considered in this study, the solubility at 333.15 K is slightly lower than the solubility at 313.15 K. This is usually the case for liquid + SCF phase equilibria up to pressures close to the mixture critical point; beyond that pressure, the liquid solute becomes completely miscible in the SCF.

As previously mentioned, this research group recently reported on the solubility of azelaic acid in supercritical carbon dioxide.¹⁰ Since the pelargonic acid and azelaic acid solubility experiments were conducted at the same densities and temperatures, the separation factor of the two compounds can be determined. According to Chrastil (1982), the separation factor can be defined as follows

$$\mu_{AB} = \frac{c_A}{c_B} \quad (1)$$

where μ_{AB} is the separation factor and c_A and c_B are the concentrations of the solutes. The separation factor is based upon the assumption that the solute molecules behave independently of each other.¹⁴ Taking pelargonic acid to be c_A and azelaic acid to be c_B , the separation factor ranges from approximately 267 (313.15 K, 10 MPa) to 4073 (333.15 K, 10 MPa). Based upon these values of the separation factor, supercritical fluid fractionation of pelargonic acid and azelaic acid appears feasible.

Modeling. The solubility data did not fit well to Chrastil's semiempirical equation, which is based on the law of mass action applied to the formation of a complex between a molecule of solute and a number of solvent molecules.¹⁴ A log–log plot of solubility versus density produced a slightly curved line rather than a straight line. The Chrastil equation for the solubility c_2 of component 2 (solid or liquid), in component 1 (SCF) is

$$c_2 = \rho_1^k \exp\left(\alpha + \frac{\beta}{T}\right) \quad (2)$$

A modification of the Chrastil equation proposed by Adachi and Lu was used as the basis in the modeling.¹⁵ The Adachi–Lu equation is

$$c_2 = \rho_1^{(e_0 + e_1 \rho_1 + e_2 \rho_1^2)} \exp\left(\alpha + \frac{\beta}{T}\right) \quad (3)$$

In eqs 2 and 3, c_2 is the concentration of the solute in the supercritical fluid expressed as mass per unit volume; ρ_1 is the density of the supercritical fluid; α is a function of the association number and the molecular weights of the solute and supercritical fluid; β is a function of the enthalpy of solvation and enthalpy of vaporization; and T is temperature. The dimensionless association number is the exponent of the density (referred to as k in the original Chrastil equation) and shows the dependence of the solubility on density. In the Adachi–Lu version of the model, k is a function of density. As seen in eq 3, they chose the following function

$$k = e_0 + e_1 \rho_1 + e_2 \rho_1^2 \quad (4)$$

The approach used here is a version of the Adachi–Lu method modified in two ways. The first modification has to do with the form of the function for k used by Adachi–Lu in eq 4. The Chrastil equation has been shown to work fine in many instances. If the fit is not as good as necessary or expected, then a first correction would be to assume that the association number varies linearly with density (rather than being a constant, as Chrastil assumed). Adachi and Lu used a quadratic form for the association number, which might be necessary in extreme cases. The Supporting Information available with this article contains a graph of the association number versus density for three of the compounds analyzed by Adachi and Lu that were liquids. Constants e_0 , e_1 , and e_2 used (and included in the file) were those reported by Adachi and Lu.¹⁵ Only liquid solutes (at experimental conditions) were included since pelargonic acid is a liquid. It is observed that a first-degree polynomial would be enough to describe these systems. The second modification was introduced just to correct a dimensional inconsistency. Both the Chrastil equation and several of its modifications, including that by Adachi and Lu, are dimensionally inconsistent because the units of the left-hand side do not match those of the right-hand side. To overcome this inconsistency, dimensionless variables have been used.

Based on the above analysis, the model chosen to fit the pelargonic solubility data is as follows

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

where

$$c_2^* = \frac{c_2}{\rho_{c,1}}; \quad \rho_{r,1} = \frac{\rho_1}{\rho_{c,1}}; \quad T_r = \frac{T}{T_{c,1}} \quad (6)$$

For calculation purposes, the critical density of carbon dioxide was $467.6 \text{ kg} \cdot \text{m}^{-3}$, and its critical temperature was 304.2 K .^{10,13} The values for model parameters were regressed via Excel (Microsoft; Redmond, WA) by minimizing an objective function based on the relative deviation between the experimental solubility and the predicted solubility and are presented in Table 2 along with the objective function (OF) value. The objective function can be expressed as follows:

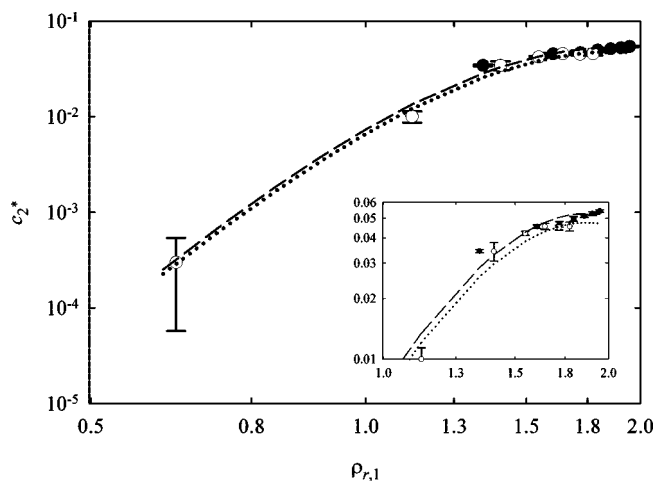


Figure 2. Plot of pelargonic acid solubility (c_2^*) in SC-CO₂ vs solvent density ($\rho_{r,1}$): ●, 313.15 K; ○, 333.15 K; —, 313.15 K model prediction; ---, 333.15 K model prediction. Inset: Enlarged view of top log cycle. Error bars correspond to uncertainties of one standard deviation (σ) taken from triplicate runs.

$$\text{OF} = \sum_{i=1}^{N_p} \left[\frac{c_{2,i} - c_{2,\text{calcd},i}}{c_{2,i}} \right]^2 = \sum_{i=1}^{N_p} \left[\frac{c_{2,i}^* - c_{2,\text{calcd},i}^*}{c_{2,i}^*} \right]^2 \quad (7)$$

where N_p is the total number of experimental points; $c_{2,i}$ is the experimental concentration of the solute (component 2) at the i th experimental point; $c_{2,\text{calcd},i}$ is the calculated solute concentration at the i th point; $c_{2,i}^*$ is the normalized experimental solute concentration at the i th experimental point; and $c_{2,\text{calcd},i}^*$ is the normalized, calculated solute concentration at the i th point. Table 2 also provides the objective function values for the dimensionless forms of the Adachi–Lu equation and Chrastil's equation. The dimensionless Adachi–Lu equation and eq 5 provide considerably better correlation than the dimensionless form of Chrastil's equation. The additional parameter of the dimensionless Adachi–Lu equation provides a slightly better correlation than that of eq 5; however, that slight difference does not justify the complexity of adding a parameter.

Figure 2 illustrates that the concentration of pelargonic acid generally increases as the density of SC-CO₂ increases. The error bars correspond to one standard deviation calculated based on the three measurements done at the corresponding temperature and pressure. As Figure 2 illustrates, the solubilities calculated from eq 5 correlate quite well with the experimental data.

Apparatus Validation. It was imperative for the authors to ensure that the experimental technique was adequate. However, no literature values for nonanoic (pelargonic) acid solubility in SC-CO₂ could be found. The solubility of close acids in the same homologous series (such as octanoic or decanoic acids) in SC-CO₂ could not be found either, which could have served as an indirect way to validate the results. Therefore, oleic acid (also a liquid a room temperature) was used for validation purposes. Solubility data for oleic acid were obtained experimentally and compared to literature values. Experiments were performed at 323.15 K and at pressures of (10 to 25) MPa. The procedure was identical to that used for the pelargonic acid

Table 2. Modeling Results

compound	solubility constants for eq 5				eq 5 OF	Adachi–Lu OF	Chrastil OF
	e_0	e_1	α	β			
pelargonic acid	8.23	-2.71	-6.66	1.8	0.12	0.10	1.31

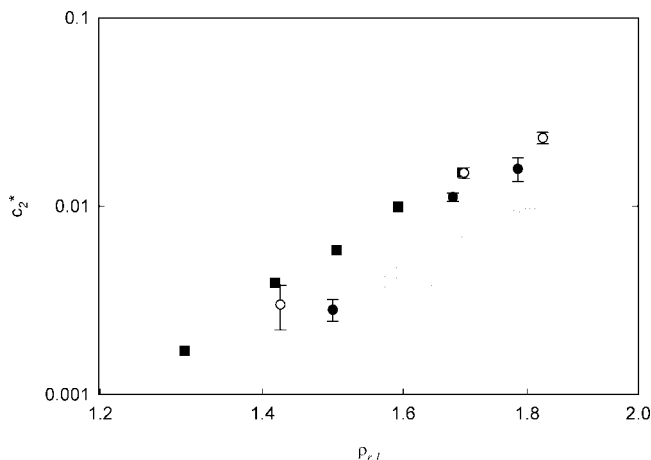


Figure 3. Plot of oleic acid solubility (c^*_2) in SC-CO₂ vs solvent density ($\rho_{r,1}$) at 323.15 K: \square , ref 16; \circ , ref 17; \bullet , this work; \square , ref 18. Error bars correspond to uncertainties of one standard deviation (σ) taken from triplicate runs.

experiments, including equilibrium determination and runs in triplicate. The oleic acid results are presented in Figure 3. The experimental results and the data from the literature at 323.15 K are presented in tabular form in the Supporting Information provided. A log–log graph of c^*_2 versus $\rho_{r,1}$ for the oleic acid data shows a linear relationship for the data produced from this work and for the literature values.^{16–18} Since no standard deviations were provided in the work of Nilsson et al. or Škerget et al., standard deviations are only provided for the experimental values and the study by Maheshwari et al. For this work, the error bars correspond to one standard deviation calculated from experiments done in triplicate. The experimental results show good agreement with the literature values, especially with the data of Nilsson et al. and Maheshwari et al. In both studies, a flow-through technique was used. However, in the work by Škerget et al., a static method was employed. These results validate the experimental method used in this study.

Conclusions

The solubility of pelargonic acid in supercritical carbon dioxide has been determined experimentally. The solubility varied from a concentration of $(0.14 \pm 0.07) \text{ kg} \cdot \text{m}^{-3}$ at 333.15 K and 10.0 MPa to $(25.39 \pm 0.61) \text{ kg} \cdot \text{m}^{-3}$ at 313.15 K and 30.0 MPa. In general, the solubility of pelargonic acid increased with increasing pressure at constant temperature. Overall, the solubility was higher at 313.15 K than at 333.15 K. The solubility data were modeled with a semiempirical equation intermediate to Chrastil's equation and the Adachi–Lu equation. To avoid dimensional inconsistency, the proposed model was expressed in terms of normalized concentration and reduced density and temperature. The model provided a better fit than Chrastil's equation and was comparable to the Adachi–Lu equation. To the authors' knowledge, this is the first reported data of pelargonic acid solubility in SC-CO₂. Therefore, the experimental approach was validated with oleic acid with good results.

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Supporting Information Available:

Graph of k values (Adachi and Lu model) versus solvent density and a summary of literature and experimental solubility values for oleic acid in supercritical carbon dioxide at 323.15 K are included in an Excel file. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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