Solubility of Fatty Acids in Supercritical Carbon Dioxide

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The solubilities of lauric, linoleic, myristic, oleic, palmitic and stearic acid in supercritical carbon dioxide (SC-CO_2) at different pressures and temperatures were measured. The solubility values obtained in this work were compared with previously published data, and possible causes for observed discrepancies were discussed. The solubilities of the six fatty acids were modeled by Chrastil's equation, and estimated model parameters were used to plot the solubility isotherms of fatty acids at 313, 323 and 333°K (40, 50 and 60°C) as a function of SC-CO_2 density. The comparison of solubility isotherms of fatty acids and vegetable oil suggests that separation of fatty acids from triglycerides might be possible by using SC-CO_2 at densities less than 700 kg/m^3. From the effect of temperature on fatty-acid and vegetable-oil solubility, it seems that the extraction yield could be increased without sacrificing the selectivity of SC-CO_2 for fatty acids by choosing a higher operating temperature. The data also suggest that fractionation of certain fatty acids might be possible by manipulating the processing conditions. Given the values of the constants, Chrastil's equation could serve as a guideline for choosing appropriate processing conditions and predicting the effect of pressure and temperature of SC-CO_2 on solute solubility.

KEY WORDS: Fatty acids, modeling, solubility, supercritical carbon dioxide.

Various economic, environmental and social factors have motivated government agencies and industry to search for cheaper and safer extraction and separation technologies for food processing. The cost of energy was initially the incentive to develop more flexible and energy-efficient processes based on supercritical fluid technology. The more recent interest in supercritical fluid separations stems from the increased scrutiny of traditional solvents, increased government regulations regarding solvent residues and fugitive hydrocarbons in the environment, increased performance demands on the product, and increased food-safety awareness (1,2). During the last ten years, supercritical carbon dioxide (SC-CO_2) has emerged as an ideal solvent for a variety of separation applications in food and bioprocessing. Although the fractionation of glycerides and fatty acids by using SC-CO_2 has been demonstrated, such as in the separation of alkyl esters derived from fish oil (2,3), in the removal of mono- and diglycerides from triglycerides (4) and in deacidification of palm (5) and olive oil (6,7), the feasibility of a particular separation still requires a separate evaluation (2). SC-CO_2 technology is currently being evaluated for deacidification of soybean oil and for fractionation and modification of butter oil. One factor that limits the application of SC-CO_2 technology for fats and oils is reliable data on solubilities of fatty acids and triglycerides. Relatively few data on fatty acid solubility in SC-CO_2 are available, and those reported often are contradictory.

A collaborative study between Iowa State University (ISU) and the University of Wisconsin-Madison (UW) was undertaken to measure the solubilities of six fatty acids in SC-CO_2. These data were compared with previously published data, and possible causes for observed discrepancies were discussed. In addition, a model proposed by Chrastil (8) was used to correlate the experimental data for fatty acids and the predicted solubility isotherms of fatty acids, compared with the solubility isotherm of vegetable oil (9).

EXPERIMENTAL PROCEDURES

Materials. Solubilities of lauric, myristic, palmitic, stearic, oleic and linoleic acid were determined. All fatty acids were purchased from Sigma Chemical Co. (St. Louis, MO) (99–100% pure) and were used as received. Carbon dioxide of greater than 99.9% purity was used.

Extraction equipment. Custom-assembled supercritical-fluid-extraction systems were used at ISU and UW. A schematic diagram of the flow-through apparatus is shown in Figure 1. An air-driven gas booster compressor (Haskel Inc., Burbank, CA) was used to compress carbon dioxide.

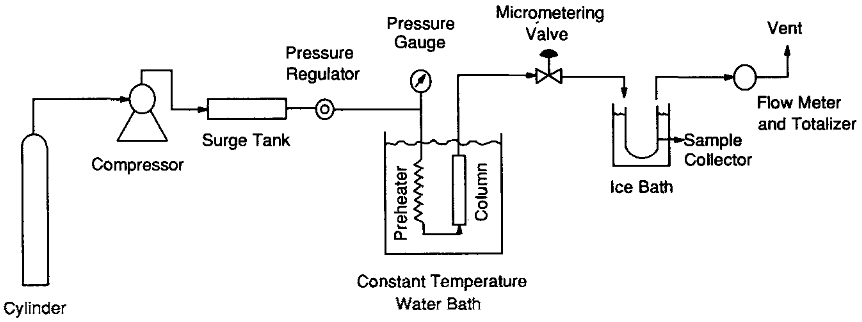

FIG. 1. Schematic diagram of supercritical fluid extraction system.

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To obtain a pulse-free flow of SC-CO_2 to the extractor, CO_2 was compressed beyond the operating pressure in a stainless-steel surge tank. Downstream from the surge tank, the CO_2 pressure was controlled by a pressure regulator. Before entering the extraction vessel, carbon dioxide was preheated to the operating temperature by passing it through a stainless-steel coil immersed in a constant-temperature water bath.

The ISU extraction vessel was a 20-cm long 316 stainless-steel column with an internal diameter (i.d.) of 1 cm. At UW, two 50-mL stainless-steel vessels were connected in series. A third 8-mL column containing glass beads was added for all fatty acids except stearic acid to eliminate possible liquid phase entrainment. The 8-mL column was not needed for stearic acid because this acid was not liquified under the operating conditions. The SC-CO_2 carrying dissolved fatty acids was passed through a heated, flow-regulating, micrometering valve and expanded to ambient pressure. At ISU, fatty acids that precipitated during the pressure-reduction step were separated from the CO_2-gas in U-tube collectors immersed in a sub-zero ethylene glycol-water bath. At UW, a 25-mL plastic syringe immersed in an ice bath was used as a sample collector. The amount of CO_2 consumed during the process was measured by a mass flow controller and totalizer (Omega Engineering, Stamford, CT) at both labs. The connecting lines downstream from the surge tank were made of 0.64-cm (1/4 in.) outer diameter (o.d.) stainless-steel tubing at UW, and of 0.32-cm (1/8 in.) o.d. at ISU. For more detailed information on either equipment setup, refer to White (10) and Maheshwari (11), respectively.

Procedures. The solubilities of myristic, stearic, oleic and linoleic acid were measured at ISU at pressures ranging from 13.7 to 27.6 MPa and temperatures from 313 to 333°K (40 to 60°C). The UW group determined the solubilities of lauric, myristic, palmitic and stearic acid at pressures from 13.8 to 41.5 MPa and temperatures from 308 to 328°K (35 to 55°C). Solid fatty-acid samples (lauric, myristic, palmitic and stearic) were packed in the extractor in alternating layers of glass wool and solid sample to minimize channeling of SC-CO_2. For liquid fatty-acid samples (oleic and linoleic acids), glass wool was soaked with the fatty acid and was packed in alternating layers with dry glass wool. The system was then pressurized and left to equilibrate for at least half an hour before the micrometering valve was opened to start the flow of SC-CO_2.

SC-CO_2 mass flow rate was kept sufficiently low (less than 0.4 g/min) at all pressures and temperatures to ensure that the SC-CO_2 was saturated with fatty acid before leaving the extractor (12). The extraction of fatty-acid samples was performed with various amounts of CO_2, depending on the solubility of the fatty acid; amounts of CO_2 used ranged between 4.5 and 70 g. Whenever the operating pressure or temperature was changed between measurements, the first sample was discarded. The amount of extract collected in the sample tubes was weighed to ±0.1 mg. The residual fatty acid that precipitated in the valves and lines was solubilized and rinsed with 15–20 mL of hexane. Hexane was evaporated in a water bath at 323°K, and the weight of the residue was determined. Solubilities of the various fatty acids were expressed as weight percentage, based on the total mass of carbon dioxide used in the extraction. The total mass of CO_2 consumed was calculated from the normal (101.3 kPa, 298°K) volume of CO_2 measured by the flow totalizer.

Model equation. The model developed by Chrastil (8) was used to correlate the experimental data. Chrastil assumed formation of a solvato complex between solute and solvent molecules (CO_2 molecules in our tests) in the dense gas phase. At equilibrium, Chrastil's model gives a linear relationship between the logarithm of solubility and the logarithm of SC-CO_2 density as shown in Eq. [1]:

$$\ln y = (k - 1) \cdot \ln \varrho + (a/T + b) \qquad [1]$$

where y is the solubility of fatty acid (kg/kg CO_2), ϱ is the density of SC-CO_2 in (kg/m^3), and T is the temperature (°K). The constant k is an association number and represents the average number of CO_2 molecules in the solvato complex, the constant a depends on the heats of vaporization and solvation of the solute, and constant b depends on molecular weights of the solute and CO_2, as well as on the value of k. Model constants were estimated by using a multivariable linear-regression analysis (SAS Institute Inc., Cary, NC).

RESULTS AND DISCUSSION

The average solubility values of the six fatty acids measured are given in Tables 1, 2 and 3. In Figure 2, these data are plotted as function of SC-CO_2 pressure and temperature. Literature data for each fatty acid also are included in Figure 2 for comparison.

For lauric acid, results of Bamberger *et al.* (13) are in agreement with our observations (Fig. 2a). Increasing the pressure at constant temperature increased the solubility of lauric acid. Lauric acid was substantially solubilized at pressures in excess of 20 MPa. Further increases in pressures to 34.2 MPa at 318°K and to 40.6 MPa at 308°K, corresponding to SC-CO_2 densities of 980 kg/m^3 and 910 kg/m^3, respectively, gave solubilities greater than 1 kg/kg CO_2 (data not shown). These unrealistically large numbers suggest that either the upper critical end point (UCEP) of the lauric acid-CO_2 system was reached, where the two phases are completely miscible, or density inversion occurred and liquified lauric acid ($\varrho < 900$ kg/m^3) was pushed out by the denser SC-CO_2 ($\varrho > 900$ kg/m^3) (14).

Solubilities of myristic acid agreed well with previous data, except for the solubility value (0.62 kg/kg CO_2) at 41.9 MPa and 318°K (Fig. 2b). This relatively large solubility value may imply that the system approached the UCEP, although density inversion cannot be ruled out. Myristic acid showed an increase of solubility with an increase in pressure at constant temperature, as well as an increase in solubility with temperature at constant pressure. A substantial increase of myristic acid solubility at constant pressure occurred at temperatures between 308 and 313°K (Table 1), which probably reflects the change of myristic acid phase from a solid at 308°K to a liquid at 313°K (13).

The effects of pressure and temperature on solubility of palmitic acid (Fig. 2c) and stearic acid (Fig. 2d) followed the trend observed for lauric and myristic acids. The palmitic acid solubility data of Brunetti *et al.* (6) were consistently greater than ours and that of Ohgaki *et al.* (15). The values of stearic acid solubility measured at temperatures up to 318°K are fairly comparable among different

TABLE 1

Average Solubility Values of Lauric and Myristic Acids at Different Temperatures and Pressures

Fatty acid	Pressure (MPa)	Temperature (°K)	Measured solubility (kg/kg CO_2) × 10^2	University
Lauric[a]	13.9	308	4.2 ± 0.53[b]	UW[d]
	26.9	308	34 ± 11	UW
	14.2	318	3.0 ± 0.94	UW
	20.7	318	45 ± 4.9	UW
Myristic[c]	14.0	308	1.4 ± 0.41	UW
	27.2	308	2.6 ± 0.88	UW
	39.6	308	2.5 ± 0.49	UW
	15.2	313	3.2 ± 0.25	ISU[e]
	20.7	313	4.4 ± 0.35	ISU
	27.6	313	8.7 ± 0.84	ISU
	13.9	318	0.87 ± 0.25	UW
	27.2	318	7.3 ± 0.92	UW
	41.9	318	62 ± 19	UW
	15.2	323	3.0 ± 1.7	ISU
	20.7	323	4.9 ± 0.49	ISU
	27.6	323	7.4 ± 1.2	ISU
	14.4	328	0.50 ± 0.22	UW
	26.6	328	7.0 ± 0.90	UW
	15.2	333	2.1 ± 0.89	ISU
	20.7	333	4.1 ± 0.96	ISU
	27.6	333	12 ± 0.50	ISU

[a] $n \geqslant 3$. [b] Standard error. [c] $n_{ISU} = 3$; $n_{UW} \geqslant 3$. [d] University of Wisconsin. [e] Iowa State University.

TABLE 2

Average Solubility Values of Palmitic and Stearic Acids at Different Temperatures and Pressures

Fatty acid	Pressure (MPa)	Temperature (°K)	Measured solubility (kg/kg CO_2) × 10^3	University
Palmitic[a]	13.8	308	1.9 ± 1.7[b]	UW[c]
	27.5	308	3.2 ± 1.8	UW
	41.4	308	3.6 ± 4.0	UW
	13.8	318	5.2 ± 3.0	UW
	27.5	318	23 ± 4.2	UW
	41.4	318	23 ± 4.8	UW
	13.8	328	4.0 ± 0.65	UW
	27.5	328	47 ± 6.2	UW
	34.5	328	76 ± 8.8	UW
Stearic[d]	14.1	308	0.90 ± 0.36	UW
	27.3	308	0.93 ± 0.45	UW
	40.5	308	0.55 ± 0.070	UW
	13.8	313	0.28 ± 0.020	ISU[e]
	20.7	313	1.4 ± 0.20	ISU
	27.6	313	0.90 ± 0.40	ISU
	14.0	318	1.2 ± 1.1	UW
	27.5	318	4.1 ± 0.49	UW
	41.2	318	4.0 ± 1.5	UW
	13.8	323	0.96 ± 0.40	ISU
	20.7	323	1.5 ± 0.30	ISU
	27.6	323	5.1 ± 2.3	ISU
	13.9	328	7.1 ± 0.40	UW
	27.5	328	22 ± 5.5	UW
	40.0	328	33 ± 4.6	UW

[a] $n \geqslant 3$. [b] Standard error. [c] University of Wisconsin. [d] $n_{ISU} = 2$; $n_{UW} \geqslant 2$. [e] Iowa State University.

TABLE 3

Average Solubility Values of Oleic and Linoleic Acids at Different Temperatures and Pressures

Fatty acid	Pressure (MPa)	Temperature (°K)	Measured solubility (kg/kg CO_2) × 10^2	University
Oleic[a]	13.8	313	0.57 ± 0.20[b]	ISU[c]
	20.7	313	1.5 ± 0.15	ISU
	27.6	313	2.1 ± 0.77	ISU
	13.8	323	0.30 ± 0.080	ISU
	20.7	323	1.5 ± 0.10	ISU
	27.6	323	2.3 ± 0.16	ISU
	13.8	333	0.048 ± 0.010	ISU
	20.6	333	0.76 ± 0.10	ISU
	27.6	333	2.0 ± 0.28	ISU
Linoleic[d]	13.8	313	0.45 ± 0.040	ISU
	20.7	313	2.2 ± 0.36	ISU
	27.6	313	2.6 ± 0.52	ISU
	13.8	323	0.27 ± 0.040	ISU
	20.7	323	1.6 ± 0.28	ISU
	27.6	323	2.7 ± 0.22	ISU
	13.8	333	0.11 ± 0.010	ISU
	20.6	333	1.8 ± 0.080	ISU
	27.6	333	1.9 ± 0.86	ISU

[a]n = 4. [b]Standard error. [c]Iowa State University. [d]n = 2.

investigators, but significant discrepancies were observed at higher temperatures (Fig. 2d). These differences are probably caused by experimental difficulties in measuring stearic acid solubility at higher temperatures. For example, greater solubility of stearic acid at 333°K caused occasional clogging of the tubing (0.32 cm i.d.) between the extractor and micrometering valve at ISU, which precluded obtaining reliable solubility values at 333°K. Stearic acid solubilities measured at UW agreed well with those of Kramer and Thodos (16), as shown in Figure 2d. Brunetti *et al.* (6) reported greater solubilities for stearic acid than other researchers have reported; the greater solubilities for both palmitic and stearic acid are probably caused by the lower purity of the fatty acid samples used in their work.

Figure 2e shows solubility data of oleic acid. The ISU data agree well with most of the reported values (4,8,17, 18), although Chrastil (8) measured greater solubility of oleic acid at 25.3 MPa and 333°K, which may be attributed to impurities present in the sample (4). Significantly greater solubilities were obtained by Brunetti *et al.* (6) at all pressures and temperatures; those findings also may be explained by the impurity (68% pure) of their oleic acid sample. On the other hand, the solubilities of 99% pure oleic acid measured by Zou *et al.* (19) at pressures less than 15 MPa were an order of magnitude greater than those obtained by us and others; at pressures above 15 MPa, Zou *et al.* (19) obtained values two or three times greater than data reported here (Fig. 2e).

Figure 2f compares our values for linoleic acid with those of Zou *et al.* (19). Again, their reported solubilities of linoleic acid were notably greater than ours, especially at lesser operating pressures. Much greater oleic and linoleic acid solubilities measured by Zou *et al.* (19) could be attributed to solute entrainment during the sampling of the SC-CO_2 phase (17).

In summary, the variability in solubility data obtained by different research groups underscores the importance of sample purity. Impurities may act as entrainer molecules and could either increase or decrease the solubility of the molecule of interest (13,20). Other potential sources of error include build-up and clogging of lines and valves with heavy solid or liquid, density inversion, failure to achieve equilibrium in the system, and entrainment of the solute in the supercritical phase (14).

The solubility data of the six fatty acids in SC-CO_2 were modeled by using Equation 1. The constants *k*, *a* and *b* (Table 4) were estimated from the data presented in Figure 2. Fatty acid solubilities greater than 0.1 kg/kg CO_2 were not included in the regression analysis because Chrastil's model is not valid for solute concentrations greater than 0.1 kg/kg CO_2 (8,9). The oleic and linoleic acid data of Zou *et al.* (19) were not included in estimating model constants because their solubilities deviated significantly from the values of other researchers. The multivariable linear-regression analysis of lauric acid solubilities gave statistically insignificant ($P > 0.05$) values for *a* and *b* because only one solubility value, less than 0.1 kg/kg CO_2, was available at 308 and 318°K, and five were available at 313°K. Therefore, a linear regression was employed to estimate the association number of lauric acid by using the data at 313°K. It should be noted that the inability to obtain an estimate of constant *a* because of insufficient data at temperatures other than 313°K does not imply that there is not a temperature effect on lauric acid solubility.

Experimental fatty acid solubilities were a linear function of SC-CO_2 density, as predicted by Equation 1 (Fig. 3). The variation of model constants that were obtained by model fitting arose from the scatter of experimental data (Fig. 2), and standard errors of the constants given in Table 4 reflect those variations. The *k*

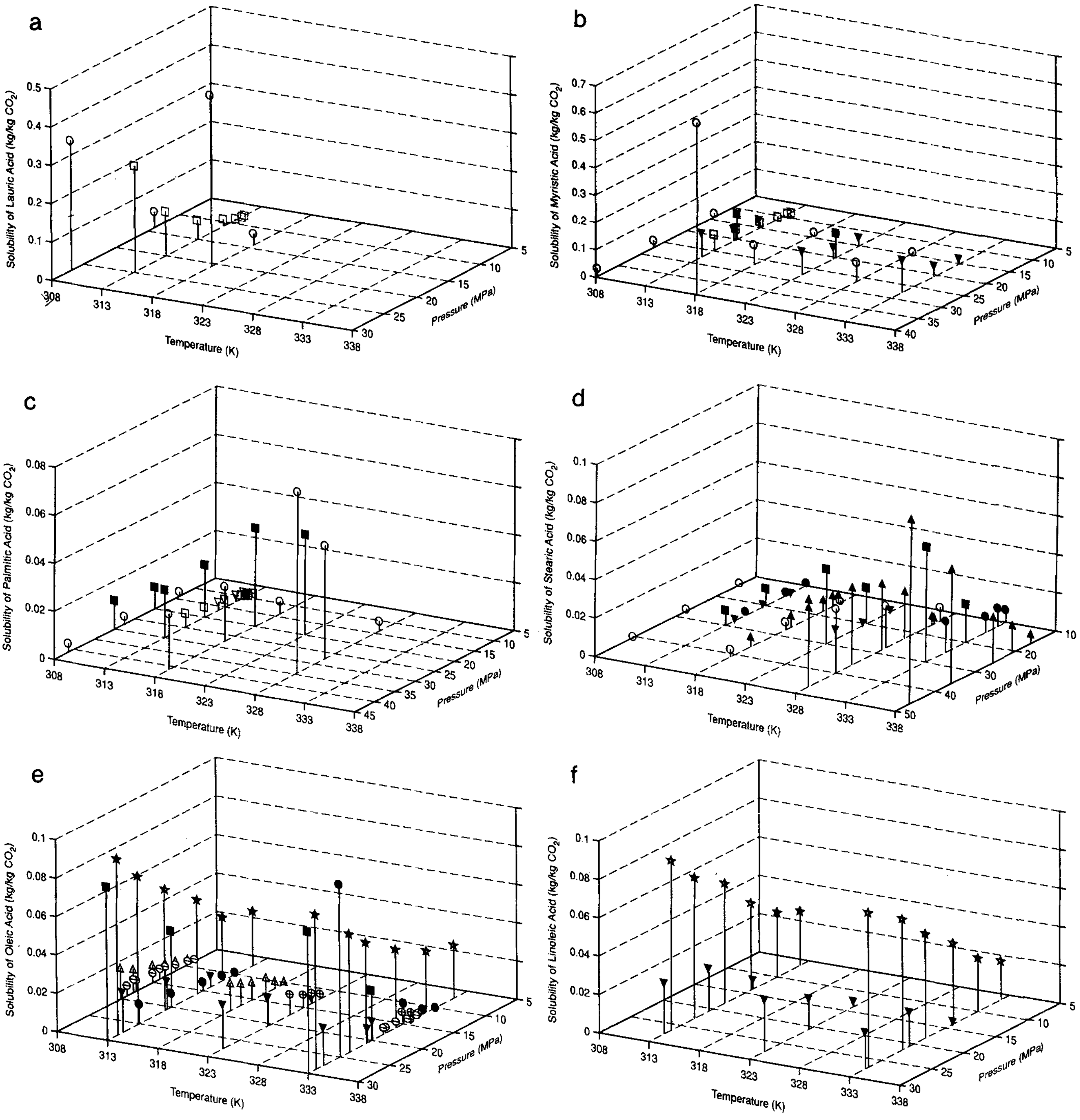

FIG. 2. Solubility of fatty acids as function of supercritical carbon dioxide pressure and temperature: a, lauric; b, myristic; c, palmitic; d, stearic; e, oleic; and f, linoleic acid. Symbols refer either to references or to Iowa State University (ISU) or University of Wisconsin/Madison (UW). Key: ○, UW; □, Bamberger *et al.* (13); ■, Brunetti *et al.* (6); ▼, ISU; ▽, Ohgaki *et al.* (15); ●, Chrastil (8); ▲, Kramer and Thodos (16); △, Foster *et al.* (17); ⊕, Nilsson *et al.* (4); ⊖, King *et al.* (18); and ☆, Zou *et al.* (19).

values in Table 4 are similar to those found by individual authors who used Chrastil's equation to fit experimental solubilities of various fatty acids, but the other two constants, *a* and *b*, differ considerably (8,10,11,17).

Based on the physical meaning of the association number in Chrastil's model (number of solvent molecules in the solvato complex), little or no difference in *k* values was expected for these fatty acids. In addition, any differences should have been proportional to the carbon number or molecular weight of the fatty acids. This was not true, and for the three C_{18} fatty acids of similar molecular size (linoleic, oleic and stearic) the association number ranged from 3.7 to 9.4 (Table 4). In addition, the values of constants *a* and *b* for the six fatty acids did not exhibit any clear trend anticipated from their melting points.

TABLE 4

Model Constants and Physical Properties of Different Fatty Acids

Fatty acid	MW	m.p.[a] (°K)	*k*	*a*	*b*	N[b]
Lauric, $C_{12:0}$	200.3	317.2	9.5 ± 1.1[c]	—[d]	—[d]	5
Myristic, $C_{14:0}$	228.4	327.6	7.2 ± 0.5	−6161 ± 1525	17.4 ± 4.8	23
Palmitic, $C_{16:0}$	256.4	335.9	7.3 ± 0.5	−13531 ± 2544	39.4 ± 8.1	29
Linoleic, $C_{18:2}$	280.4	268.2	9.4 ± 0.9	−5011 ± 1683	13.2 ± 5.4	9
Oleic, $C_{18:1}$	282.5	286.5	6.8 ± 0.5	−4694 ± 1041	11.5 ± 3.3	70
Stearic, $C_{18:0}$	284.5	342.8	3.7 ± 0.6	−13993 ± 1538	40.0 ± 4.8	45

[a]Melting point. [b]Number of observations. [c]Standard error. [d]Statistically insignificant.

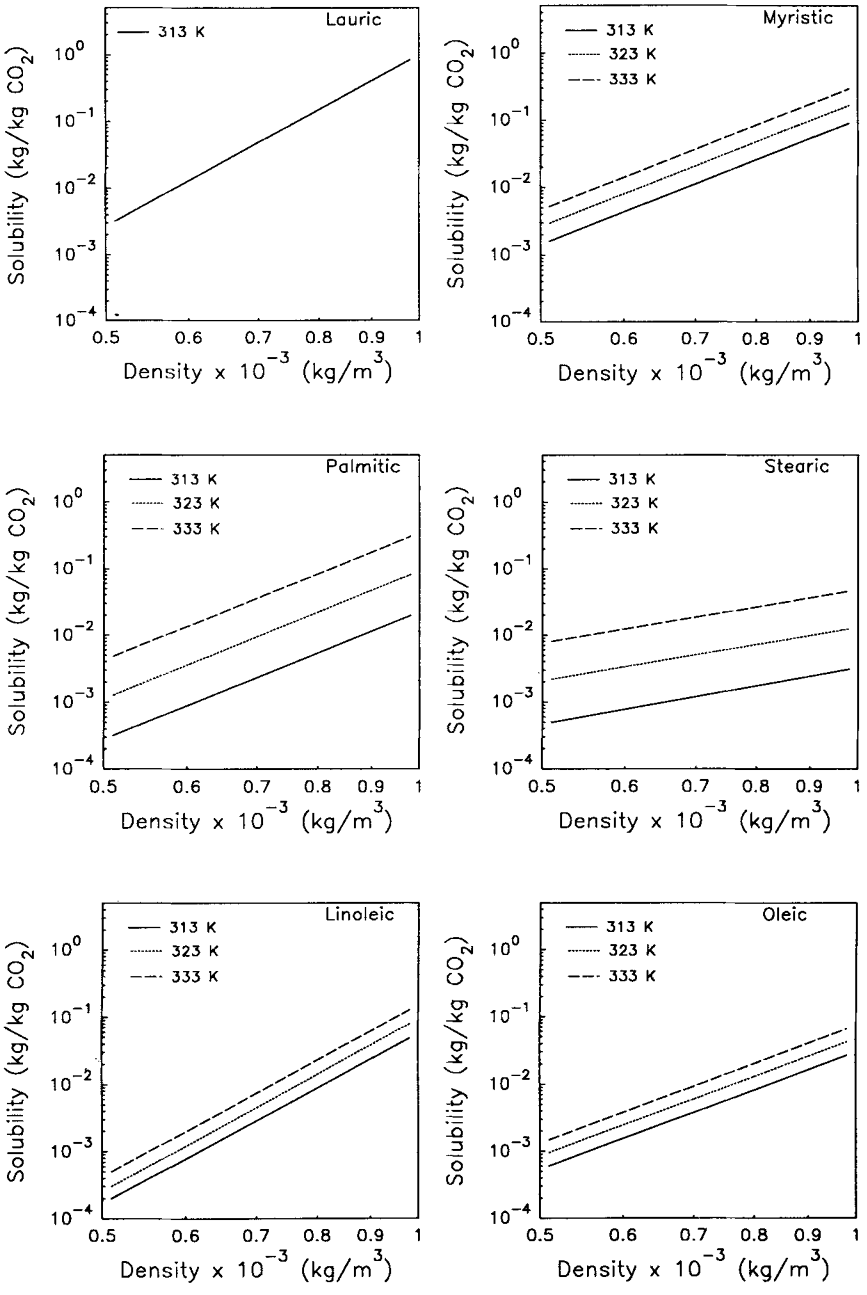

FIG. 3. Predicted solubilities of fatty acids as a function of temperature and density of supercritical carbon dioxide.

One can rationalize that, because of the variability of the data, variation of association number between 6.8 and 9.5 is acceptably close. But the *k* value for stearic acid is much lower than that of the other fatty acids. This significant discrepancy in the association number suggests that Chrastil's model (Eq. 1), based on the solute-solvent interaction in the supercritical fluid phase, cannot completely predict the solubilization of fatty acids by SC-CO_2. Nevertheless, this model is simple and has been used successfully to describe the effect of temperature and pressure on the solubility of various nonpolar compounds (8,17). In our opinion, Chrastil's model can be used, within the limits of its validity, to predict the relationship between the solute solubility and the density of the supercritical fluid without assigning a particular physical meaning to the constants *k, a* and *b*.

The value of the association number (*k*) shows the effect of SC-CO_2 density on solubility of fatty acids. The solubility of stearic acid increases with density about five times over the studied range, whereas the solubility of the other five fatty acids increases more than two orders of magnitude (Fig. 3). The effect of temperature on the fatty acid solubility, which depends on the values of parameter *a*, seems to be related to the melting point of fatty acids; the higher the melting point, the more pronounced is the temperature effect on solubility (Fig. 3). Palmitic and stearic acids, which have the two highest melting points (Table 4), also have considerably larger *a* values, and their solubilities at constant density increased the most as temperature increased (Fig. 3). Solubility of linoleic and oleic acid, having the lowest melting points among the six fatty acids, increased the least as the temperature increased from 313 to 333°K.

In Figure 4, solubility isotherms of vegetable oil (triglycerides) are plotted for comparison with fatty acid isotherms. The solubilities of vegetable oil at 313, 323 and 333°K were calculated from the model proposed by del Valle and Aguilera (9). Their model is similar to that of Chrastil and correlates triglyceride solubilities with process temperature and SC-CO_2 density. The model constants were determined by fitting the experimental solubilities of three different vegetable oils to the proposed model (9). The comparison of solubility isotherms of fatty acids and vegetable oil suggests that separation of fatty acids from triglycerides might be possible by using SC-CO_2 at densities below 700 kg/m^3 (Fig. 4). From the effect of temperature on fatty acid and oil solubility, as shown in Figure 4, it seems that choosing a higher operating temperature would increase the extraction yield without sacrificing the selectivity of SC-CO_2 for fatty acids. The data in Figure 4 suggest that fractionation of certain fatty acids might be possible by manipulating the processing conditions. The fractionation of a mixture containing oleic and linoleic acid does not seem possible under any operating conditions, nor does fractionation of myristic and palmitic acids at 333°K. Other fatty acids, depending on the complexity of the mixture, could probably be fractionated by choosing a proper combination of pressure and temperature. Therefore, operating conditions should be optimized according to the main objective of the SC-CO_2 separation process.

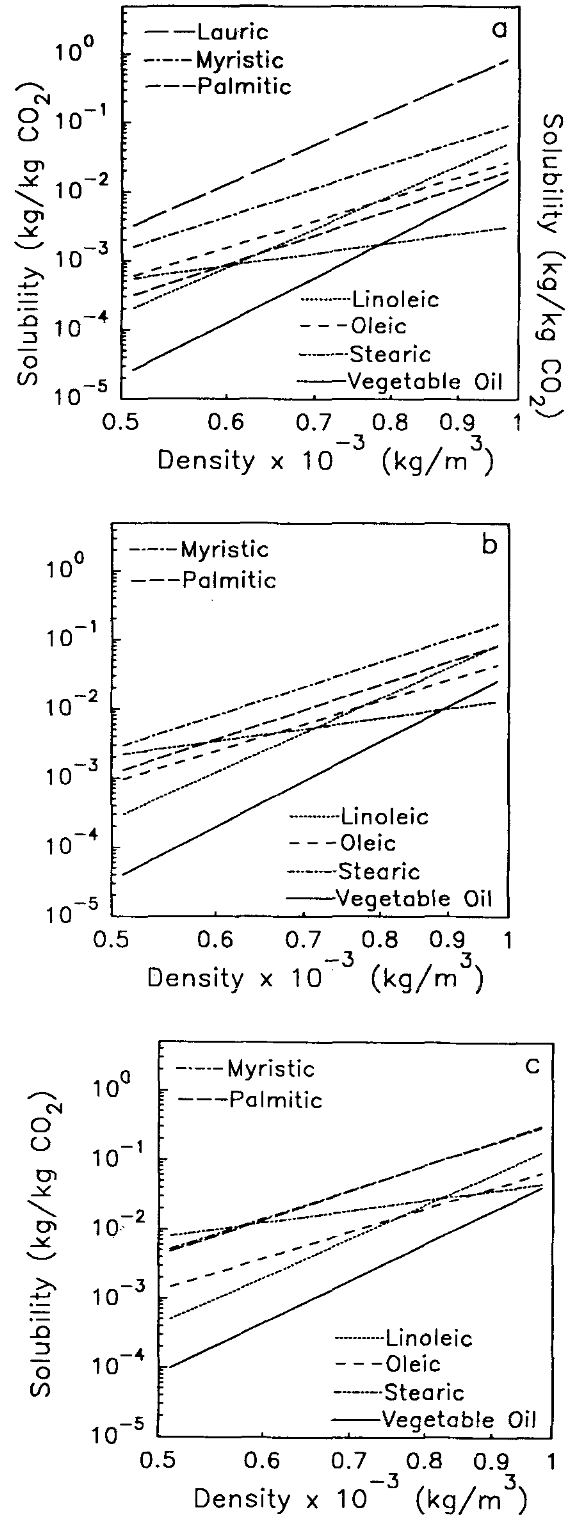

FIG. 4. Predicted solubility isotherms of fatty acids and vegetable oil as a function of temperature and density of supercritical carbon dioxide at: a, 313°K; b, 323°K; and c, 333°K. Vegetable oil isotherms are based on the equation of del Valle and Aguilera (ref. 9).

It should be noted that our conclusions are based on the pure component solubilities. Chrastil's model does not take into account intermolecular interactions in the liquid phase between the components of the system, including dissolved SC-CO_2, which will exist in the liquid mixture of a fatty acid and triglycerides. The previous studies with mixtures of oleic acid and olive oil revealed that the presence of triglycerides affected the oleic acid as well as overall mixture solubility in the SC-CO_2 phase (6,12). Entrainer effects in the mixture of pure triglycerides and fatty acids have been measured and discussed before by Bamberger *et al.* (13).

In conclusion, studies with pure compounds provide useful information regarding the effect of pressure and temperature on their solubility. Given the values of the constants, simple models, such as those of Chrastil (8) and del Valle and Aguilera (9) could serve well as a guideline for choosing the appropriate operating conditions or predicting the effect of pressure and temperature of SC-CO_2 on the component solubility and extraction yields. In light of the presented data and the possible pitfalls discussed in this paper, we recommend that one should test a synthetic mixture containing the compounds of interest before making a final conclusion about whether or not a particular mixture can be fractionated.

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