Correlating the Solubility Behavior of Fatty Acids, Mono-, Di-, and Triglycerides, and Fatty Acid Esters in Supercritical Carbon Dioxide

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The knowledge of the solubility behavior of different lipid classes in supercritical carbon dioxide ($SCCO_2$) is of great importance in the design of $SCCO_2$ fractionation, extraction, and reaction processes. Solubility data from the literature for binary mixtures of $SCCO_2$ and pure lipids (fatty acids, mono-, di-, and triglycerides, and fatty acid esters) were correlated using Chrastil's equation to determine the effect of compound properties (molecular weight and polarity) and operating conditions (density of CO_2, pressure, and temperature) on the solubility behavior. The physical state of the lipid solute had a significant effect on model parameters and, hence, the solubility behavior. An isothermal increase in the pressure and a temperature increase at constant CO_2 density led to an increase in solubility for all the compounds studied. Retrograde solubility behavior was observed for liquid solutes, whereas the solid solutes were in the nonretrograde region under the examined conditions. In a homologous series, solubility decreased with an increase in the molecular weight and polarity. The effect of solute properties on solubility was observed to be dependent on operating conditions. The solubility behaviors of pure lipid classes outlined in this study are intended to provide the basis for further study of complex multicomponent lipid mixtures in supercritical processes.

Introduction

Potential applications of supercritical fluid (SCF) technology in fats and oils processing have been extensively studied over the last 2 decades. While earlier research focused mainly on the extraction of oil from oil seeds,[1−4] fractionation of fats and oil mixtures[5−8] and reactions in SCF media[9−13] have been the subject of more recent investigations. Although SCFs such as ethane[14−16] and propane[17] have been reported to be better solvents for lipids, the majority of the studies were carried out using supercritical carbon dioxide ($SCCO_2$), because it is a nonflammable and nontoxic solvent, which is inexpensive and readily available in high purity.

Knowledge of phase behavior is essential for the design of any SCF process. The lack of reliable phase equilibrium data has been one of the major impediments to the wider commercialization of SCF technology. The applicability of the existing database for lipids is further limited by the discrepancies between the literature data and the lack of phase behavior information, which is essential for accurate interpretation of the data.

Complete phase diagrams of binary systems of $SCCO_2$ and pure lipids are not available. Information on the melting behavior of lipids when in contact with $SCCO_2$ is quite limited. Most of the available information is based on the visual observation of the phases during phase equilibria studies and the indirect observation of a substantial increase in solubility in a certain temperature range due to the effect of phase change on solubility behavior. The physical properties of a substance are expected to have a substantial influence on the extraction process only in the narrow temperature range where the equilibrium shifts from solid−SCF to liquid−SCF.[18]

Increasing the hydrostatic pressure increases the melting point of the pure solid.[19] The phase behaviors of natural fats and oils, triolein, and trilaurin from atmospheric pressure to 150 MPa[20] and of binary mixtures of *cis*-unsaturated fatty acids under various pressures up to 200 MPa[21] have been investigated to determine the effect of pressure on the phase behavior of lipid systems. However, when a solid is compressed in the presence of a SCF, the melting point of the solid decreases with increasing pressure because of the solubility of the supercritical solvent in the heavy liquid phase.[22]

Bamberger et al.[23] studied the melting point depression of pure fatty acids, triglycerides, and mixtures of triglycerides in CO_2 at 15 MPa and 313 K. They reported that lauric acid (L), myristic acid (M), LLL and MMM, LLL−MMM, and LLL−MMM−PPP mixtures melted, while palmitic acid (P), PPP, LLL−PPP, and MMM−PPP did not melt. Nilsson and Hudson[24] observed a melting point depression for tripalmitin to 57 °C at 17.2 MPa and concluded that at 40 °C tripalmitin would occur as a solid up to 31 MPa but as a liquid at 60 °C. In their study on the phase behavior of pure lipids, Hammam and Sivik[25] determined the phase boundary curves for laurin glycerides, trimyristin, tripalmitin, and tristearin.

Fats and oils are complex mixtures of various components that belong to different lipid classes including fatty acids, mono-, di-, and triglycerides, and fatty acid esters. In such multicomponent mixtures, complex intermolecular interactions lead to significant deviations from pure-component solubilities. Binary systems of various pure lipids and $SCCO_2$ have been studied by

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various researchers; however, multicomponent data are relatively scarce. An exhaustive literature survey of binary and multicomponent data of fish oil components was carried out by Staby and Mollerup.[26] Although limited, the information obtained by studying the extensive literature database for much simpler binary systems would be useful in the study of real mixtures. The general solubility trends of binary mixtures would contribute to our understanding of the fundamentals of lipid solubility in SCFs and, hence, provide a sound basis on which the solubility behavior of complex multicomponent mixtures can be evaluated. However, such a systematic study comparing the solubility behavior of the different lipid classes has not been carried out.

Therefore, the objectives of this study were (a) to compile a database of literature solubility data for pure components of fatty acids, fatty acid esters, and mono-, di-, and triglycerides in $SCCO_2$, (b) to correlate the lipid component solubility data using Chrastil's equation, and (c) to establish the general trends in the solubility behavior of pure lipids of various classes in $SCCO_2$ as affected by operating conditions and solute properties. Chrastil's equation was used to extract maximum information from the available data. This is a simple empirical model used quite commonly, and its parameters can be used to interpret the effect of operating conditions on solubility. No attempt was made to apply in-depth thermodynamic models to describe solubility data.

Solubility Data and Correlation

Solubility Data. The compilation of studies reporting the solubility of pure lipid components in $SCCO_2$ is presented in Table 1. As has been noted by others previously, there is discrepancy between the solubility data reported by various researchers, which limits the applicability of the existing database. Major factors contributing to such a discrepancy in the database are the purity of the samples used in the solubility measurements and the limitations of the experimental techniques used. The comparison of the literature data is further complicated by the necessity to use pure CO_2 density to convert the solubilities reported in different units such as mole fraction, weight fraction, and weight percent to the same basis.

The solute purity is a critical factor because impurities present in the samples may affect the solubility. The solute solubility can be enhanced substantially in a multicomponent system because of the presence of other solutes, which act as entrainers.[23,27,28] On the other hand, the solubility of an individual component may decrease with the addition of a second solute if the solute mixture is liquid under extraction conditions.[29] The solubilities of samples with different purities have been compared in order to demonstrate the effect of the sample purity on the solubility.[23,30] Bamberger et al.[23] compared the solubility of 90% tripalmitin with that of 99% pure tripalmitin under the same conditions and reported more than 1 order of magnitude higher solubility for the lower purity sample. As well, Nilsson et al.[30] reported that the solubility of 65% triolein was nearly twice that of the 99% purity sample. The overall effect of impurities on the solubility of a sample will depend on the nature of the solute and impurities as well as the level of impurities.

Experimental Techniques. The experimental techniques used in the investigation of high-pressure phase equilibria have been described and reviewed by various authors.[31−35] Analytical techniques involve compositional analysis by sampling once equilibrium is attained. In synthetic methods, a premixed sample of known composition is charged to the equilibrium cell for determination of phase equilibria without sampling. Analytical methods are subdivided into three types: static, dynamic, and recirculation depending on how the equilibrium is attained. Static techniques involve loading the solute and solvent into a high-pressure cell and allowing them to reach equilibrium. A thorough agitation is applied by stirring or rocking to ensure a rapid approach to equilibrium. Dynamic methods are characterized by the passage of a gas through a layer of liquid to achieve the saturation of the exit gas phase with the liquid-phase components. In recirculation methods, one or both of the phases are recirculated to achieve equilibrium conditions faster.

A major limitation of the experimental apparatus used for solubility measurements in many studies is the lack of a visual observation window on the high-pressure cell due to its high cost, which may lead to an error in solubility measurements. At high pressures, the density of the SCF-rich phase can become greater than that of the solute-rich phase. This phenomenon is referred to as density inversion and results in the liquid phase being pushed out of the cell, leading to erroneous solubility information.[19] If the experimental system used does not allow the visual observation of a potential density inversion, the solubility data cannot be interpreted accurately. For example, Maheshwari et al.[36] observed very high solubilities for lauric acid at 34.2 MPa/318 K and 40.6 MPa/308 K as well as for myristic acid at 41.9 MPa/318 K; however, they could not ascertain whether these results were due to the proximity of experimental conditions to the upper critical end point or density inversion. Another aspect that cannot be observed without a window on the cell is the phase equilibria, and it is not possible to ascertain the physical state of the solute from the shape of the solubility isotherms. Therefore, it is essential to have information on the melting behavior of the solid solutes in order to interpret the solubility data accurately.[22]

Other factors that have been cited by various authors to explain the discrepancy between literature data are the entrainment of a liquid solute while sampling and failure to achieve equilibrium in the system. Moreover, greater solubility of solutes at higher temperatures, which results from the nonretrograde solubility behavior, can result erroneously low data because of solute hold-up or in complete clogging of the tubing between the extractor and metering valve.[24,36]

Correlation. Chrastil's equation[37] was used to describe the solubility data compiled for various pure lipid components of different classes. This model is based on the formation of a solvato complex upon association of the solute and solvent molecules. Chrastil's equation establishes a linear relationship between ln(solubility) and ln(density), which was first observed by Stahl et al.,[38] as follows:

$$\ln c = k \ln d + a/T + b \qquad (1)$$

where c is the solubility of the solute in the supercritical solvent (g/L), d is the density of the pure solvent (g/L), and k (association number) is the number of molecules in the solvato complex. Parameter a is dependent on the total heat of the reaction, and b is dependent on the

Table 1. Literature Solubility Data for Binary Systems of Pure Lipids and $SCCO_2$

component	no. of data[a] liquid	no. of data[a] vapor	data presented as[b]	temp (K)	pressure (MPa)	purity[c] (%)	experimental method[d]	ref
				Fatty Acids				
caproic acid	10	8	mf	313, 353	2.72−15.88	>95	R	60
lauric acid		4	w/w	308, 318	13.9−26.9	99−100	D	36
		10	mf	313	7.7−24.8	99	D	23
	16	14	mf	333, 353	2.57−27.65	>95	R	60
myristic acid		17	w/w	308−333	13.9−41.9	99−100	D	36
		7	mf	313	8.2−24.9	99.5	D	23
		6	mf	308	8.1−22.8	>99	D	61
		2	w/w	313,323	20	≥90	D	41
			qs	323	10−50	nr	Syn	62
palmitic acid		9	w/w	308−328	13.9−41.4	99−100	D	36
		9	mf	313	8.0−24.8	99−100	D	23
		6	mf	308	9.9−23.0	>99	D	61
		22	mf + w/v	298, 313	7.98−18.7	>99	St	63
		6	w/w	308−323	20, 30	≥96	D	41
		19	mf	318−338	14.21−57.48	95	D	64
	7	5	mf	353, 373	13.60−30.52	>90	R	60
stearic acid		15	w/w	308−328	13.8−41.2	99−100	D	36
		8	mf	308	9.0−23.7	99[e]	D	65
		6	w/w	313−333	20,30	≥95	D	41
		7	w/v	313, 333	10.1−25.3	nr	St	37
		18	mf	310, 320	11.35−36.40	≥99.5	D	66
		17	mf	318−338	14.54−46.75	≥97	D	54
		g	dr + rs	313	27.4−192.5	nr[f]	D	53
		9	mf	318	9.6−16.2	nr[f]	R	67
		11	mf	318	9.6−16.5	nr[f]	R	68
		6	mf	308	8−16	nr[f]	R	69
		9	mf	308	8−16	nr[f]	R	70
oleic acid		9	w/w	313−333	13.8−27.6	99−100	D	36
		12	mf + w/v	308, 318	9.6−20.09	>99	D	46
		4	w/w	313, 333	20, 30	≥68	D	41
	12	12	mf + w/w	313, 333	7.1−28.81	99	R	45
		9	w/v	313, 333	10.1−25.3	nr	St	37
		20	w/v	303−323	10.55−27.90	nr	St	47
	15	12	wf	313−353	10.17−30.02	>90	R	71
	g	g	wf	313−353	2−20	70	St	72
			qs	323	10−50	nr	Syn	62
		15	mf	308, 333	8.51−19.13	>90	R	73
		10	w%	323, 333	12.4−20.6	≥99	D	30
	17	17	mf	313, 333	3.36−31.12	99	R	74
	16		mf	313, 323	0.94−8.01	90	R	75
linoleic acid		9	w/w	313−333	13.8−27.6	99−100	D	36
	12	12	mf + w/w	313, 333	6.34−27.14	99	R	45
behenic acid		9	w/v	313, 333	8.1−25.3	nr	St	37
		12	mf	308, 318	8−16	nr[f]	R	76
				Monoglycerides				
monolaurin		6	mf	313, 338	15−40	99	D	59
		g	w/v	313	15−35	99	D	77
			qs	323	10−50	nr	Syn	62
monostearate			qs	323	10−50	nr	Syn	62
monoolein		12	mf	308, 333	10.37−18.92	97	R	73
		11	w%	323, 333	15.1−30.9	≥99	D	30
				Diglycerides				
dilaurin		9	mf	313, 338	15−40	99	D	59
		g	w/v	313	15−35	99	D	77
			qs	323	10−50	nr	Syn	62
diolein		11	w%	323, 333	15.1−30.9	≥99	D	30
				Triglycerides				
tributyrin		8	w/v	313, 333	10.1−25.3	nr	St	37
		g	w/v	313	8−35	99	D	77
tricaproin		g	w/v	313	15−35	99	D	77
tricaprylin	10	10	mf	333, 353	5.33−25.00	>90	R	60
	42	29	w%	313−393	5.0−32.15	99	St	78
		g	w/v	313	10−35	99	D	77
tricaprin		g	w/v	313	15−35	99	D	77
trilaurin		6	mf	313	9.1−25.3	99	D	23
	5	4	mf	353	10.28−31.80	>90	R	60
		16	mf	308−333	15−40	99	D	59
		g	w/v	308−333	15−35	99	D	77
		g	mf	308−328	8.52−36.1528	nr	D	79

Table 1. Continued

component	no. of data[a] liquid	no. of data[a] vapor	data presented as[b]	temp (K)	pressure (MPa)	purity[c] (%)	experimental method[d]	ref
			Triglycerides					
trimyristin		8	mf	313	9.5−30.4	99[e]	D	23
		g	mf	308−328	8.52−36.1528	nr	D	79
tripalmitin		7	mf	313	12.2−29.7	99[e]	D	23
		18	w/v	313−353	8.1−25.3	nr	St	37
	5	5	mf	353	5.55−24.31	>90	R	60
		16	mf + w/v	298, 313	8.60−18.2	>96.5	St	63
		9	w/w	313, 333	17.2−31.0	nr	D	24
		g	mf	308−328	8.52−36.1528	nr	D	79
tristearin		6	w/w	313−333	20, 30	≥65	D	41
		11	w/v	313, 333	8.1−25.3	nr	St	37
		g	w% vs vol	313, 333	9.8−27.0	nr	D	80
		g	mf	308−328		nr	D	79
triolein		4	w/w	313, 333	20, 30	≥65	D	41
		20	w/v	313−353	8.1−25.3	nr	St	37
	8	8	wf	313, 333	15.34−31.00	>70[e]	R	71
		10	w/v	308	9.6−22.0	99	St	81
		11	w%	323, 333	17.2−30.9	≥99	D	30
		5	w/w	313	17.2−31.0	nr	D	24
		113	w/w	308−328	8.0−21.0	99	St	43
		g	w% vs vol	313	19.6	nr	D	80
		g	wf	298−333	7−20	98	R	82
trilinolein		8	w/v	313, 333	8.1−25.3	nr	St	37
			Methyl Esters					
lauric acid	25	12	mf	313−333	2−12	98	R	83
		g	mf	313, 333	6.5−20	nr	D	56
myristic acid	43	14	mf	313−333	0.88−12	>99	R	75
	24	16	mf	313−343	1.16−15.97	95	R	84
		g	mf	313, 333	6.5−20	nr	D	56
palmitic acid	38	16	mf	313−333	0.98−13	95	R	75
	38	19	mf	313−343	1.01−18.29	95	R	84
stearic acid	27	24	mf	313−343	2.15−20.42	98	R	84
		g	mf	313, 333	6.5−20	nr	D	56
oleic acid		8	w%	323, 333	11.0−15.1	≥99	D	30
	13	13	mf + w/w	313, 333	4.05−18.96	99	R	45
	38	29	mf	313−343	1.80−20.00	72	R	84
	8	8	mf	313, 333	2.91−13.69	99	R	74
		g	mf	313, 333	6.5−20	nr	D	56
	19	22	mf	313, 343	2.02−19.68	98−99	R	42
linoleic acid	13	13	mf + w/w	313, 333	3.81−20.29	99	R	45
	8	9	mf	313, 343	4.138−21.305	99	R	85
		g	mf	313, 333	6.5−20	nr	D	56
	7	7	mf	343	2.13−14.03	99	R	44
			Ethyl Esters					
lauric acid		2	qs	298, 305	17.24	nr	St	18
palmitic acid		g	w/v	298−328	6.89−17.24	>99	D	48
stearic acid	29	37	mf	313−333	1.47−18.26	>90	R	55
oleic acid	38	40	mf	313−333	1.14−18.62	>90	R	55
		g	mf	313−373	9−25	99	D	49
		g	w/v	298−328	6.89−17.24	>99	D	48
linoleic acid	33	35	mf	313−333	1.97−16.97	>90	R	55
eicosatrienoic acid		g	mf	313−373	9−25	99	D	49
arachidonic acid		g	mf	313−373	9−25	99	D	49
EPA	36	26	mf	313−333	2.01−20.00	>90	R	55
		g	w/v	298−328	6.89−17.24	90.9	D	48
DHA	28	27	mf	313−333	1.87−21.07	>90	R	55
		g	mf	313−373	9−25	99	D	49
		g	w/v	298−328	6.89−17.24	90.3	D	48

[a] No of data: g, data presented only in graphs. [b] Data presented as: mf, mole fraction; wf, weight fraction; qs, quantitative solubility; dr, detector response; rs, relative solubility; w% vs vol, graph of w% extracted versus volume of CO_2 consumed. [c] Purity: nr, not reported. [d] Experimental method: R, recirculation; D, dynamic; St, static; Syn, synthetic. [e] Purified further by supercritical fluid extraction. [f] Purified further by recrystallization.

molecular weights of the solute and solvent and the association constant. Parameter k, which is the slope of the solubility isotherm, reflects the density dependence of solubility. Parameter a, which is the slope of the ln(solubility) versus $1/T$ plot, is a measure of the temperature dependence of solubility at constant density.

The concentration and temperature range of the model is determined by the validity range of its approximations. Deviation from the linear relation is expected at high solute concentrations as the solvent density starts to deviate from the density of the pure supercritical solvent.[37] The solute polarity has also been reported to affect the accuracy of the model. The model was not accurate for highly polar solid solutes up to a reduced density of 1.5, indicating density dependence of the association number.[39]

In this study, model parameters a, b, and k were

estimated from the lipid solubility data using multivariate regression analysis of the SAS statistical software package.[40] To improve the goodness of fit of the model, solubilities higher than 0.1 kg/kg[36] and data for solutes with unknown purities or with purities <95% were excluded from the analysis. Data that consistently deviated from the rest of the database[41−45] were also excluded. CO_2 density data used in the model as well as for the conversion of solubility data to the required units (g/L) were obtained using the pressure/density calculator in Dionex SFC/GC Control Software (version 3.32, Mississauga, ON).

The expected linear relationship between ln(solubility) and ln(density) has been observed for fatty acids,[37,46,47] triglycerides,[37,43] and fatty acid ethyl esters[48,49] by others; however, the temperature dependence of k has not been well established. Both parallel and nonparallel isotherms have been reported for pure lipids. Some researchers correlated experimental data at only one temperature[50] or did not provide a comparison of the k values at different temperatures.[36] In this study, both the overall k values (using eq 1) valid for the whole temperature range studied and the individual k values at each temperature (using eq 2) were estimated in order to determine the temperature dependence of k and any associated trend. At constant temperature, eq 1 simplifies to

$$\ln c = k' \ln d + b' \qquad (2)$$

Results and Discussion

Model Parameters. Regression Analysis Using Equation 2. The model parameters estimated using eq 2 at each temperature are presented in Table 2. Only temperatures at which significant parameters ($p < 0.05$) could be estimated by the regression analysis were reported. When data from two studies were included in the analysis, the discrepancies between some studies were reflected in low R^2 values. The results of the analysis of individual and combined data sets for palmitic acid at 313 K, stearic acid at 328 K, monoolein at 333 K, and tripalmitin at 313 K are given in Table 3 to illustrate the extent of variation between studies. Because of the low R^2 values, these temperatures were not taken into consideration while interpreting the results because it was not possible to ascertain the source of the discrepancy.

Preliminary analyses of the solubility data using Chrastil's equation showed a deviation from linearity at low solvent densities (280−400 g/L) for lauric acid at 313−353 K and oleic acid at 333 K. The exclusion of low-density data improved the R^2 values considerably (from 0.7361 to 1.000 for lauric acid at 353 K) but did not improve the correlation for the other fatty acids. Therefore, a low-density limit could not be determined and low-density data were only excluded for lauric and oleic acids.

The slopes of the solubility isotherms (k' values) were observed to be dependent on the physical state of the solute. At 308 K, myristic, palmitic, and stearic acids are solid and have similar k' values in the range of 4.9−5.3 (Table 2). An increase in the k' value was observed from 308 to 313 K for myristic acid, from 308 to 318 K for palmitic acid, and from 320 to 338 K for stearic acid. This increase is most probably caused by the melting of these solutes in this temperature range due to the solvent effect of $SCCO_2$. The low k' values for solid fatty

Table 2. Model Parameters for Pure Lipids Estimated Using Equation 2 ($\ln c = k' \ln d + b'$)

solute	temp (K)	$k' \pm$ standard error	$b' \pm$ standard error	R^2	ref
Fatty Acids					
caproic acid	353	4.64 ± 0.60	−25.0 ± 3.4	0.967	60
lauric acid	313	7.78 ± 0.17	−48.2 ± 1.1	0.999	23
lauric acid	333	9.72 ± 0.40	−60.4 ± 2.6	0.997	60
lauric acid	353	9.10 ± 0.05	−55.5 ± 0.3	1.000	60
myristic acid	308	4.87 ± 0.30	−30.2 ± 2.0	0.974	36, 61
myristic acid	313	7.23 ± 0.31	−45.1 ± 2.0	0.987	23, 36
myristic acid	323	5.52 ± 0.35	−33.1 ± 2.4	0.996	36
palmitic acid	308	5.34 ± 0.49	−35.3 ± 3.3	0.944	36, 61
palmitic acid	313	6.75 ± 0.67	−43.8 ± 4.3	0.873	23, 63
palmitic acid	318	7.29 ± 1.20	46.3 ± 8.1	0.859	36, 64
palmitic acid	328	9.47 ± 0.91	−60.1 ± 6.1	0.947	36, 64
palmitic acid	338	7.97 ± 0.70	−49.5 ± 4.5	0.985	64
stearic acid	308	5.02 ± 0.93	−34.5 ± 5.0	0.762	36,65
stearic acid	310	2.32 ± 0.53	−15.5 ± 3.6	0.834	66
stearic acid	320	4.71 ± 0.41	−30.1 ± 2.7	0.956	66
stearic acid	328	6.98 ± 0.88	−44.0 ± 5.9	0.900	36, 54
stearic acid	338	8.24 ± 0.33	−51.7 ± 2.2	0.995	54
oleic acid	308	8.78 ± 0.33	−56.9 ± 2.2	0.995	46
oleic acid	313	8.75 ± 0.64	−56.3 ± 4.3	0.959	36, 74
oleic acid	318	6.76 ± 0.37	−42.7 ± 2.4	0.988	46
oleic acid	323	9.06 ± 0.45	−58.1 ± 3.0	0.985	36, 30
oleic acid	333	7.92 ± 0.76	−50.0 ± 4.9	0.900	36, 74
Monoglycerides					
monolaurin	313	5.26 ± 0.43	−34.2 ± 2.9	0.981	59
monoolein	308	8.06 ± 1.23	−54.2 ± 8.2	0.896	73
monoolein	323	7.66 ± 0.37	−49.8 ± 2.4	0.993	30
monoolein	333	10.43 ± 1.59	−68.1 ± 10.4	0.827	30, 73
Diglycerides					
dilaurin	313	7.41 ± 0.51	−46.6 ± 3.5	0.981	59
diolein	323	10.71 ± 0.36	−70.1 ± 2.4	0.997	30
diolein	333	10.39 ± 0.35	−67.6 ± 2.3	0.995	30
Triglycerides					
tricaprylin	313	4.13 ± 0.40	−23.9 ± 2.5	0.923	78
tricaprylin	353	10.17 ± 0.59	−62.0 ± 3.8	0.980	78
tricaprylin	393	7.81 ± 0.56	−46.2 ± 3.5	0.984	78
trilaurin	313	11.33 ± 0.86	−73.1 ± 5.7	0.966	23, 59
trimyristin	313	9.27 ± 0.37	−61.0 ± 2.5	0.991	23
tripalmitin	313	5.50 ± 1.22	−32.1 ± 8.1	0.601	23, 63
triolein	308	8.36 ± 0.82	−55.4 ± 5.5	0.928	81
triolein	323	12.89 ± 0.62	−85.4 ± 4.1	0.993	30
triolein	333	13.14 ± 0.47	−88.6 ± 3.1	0.995	30
Methyl Esters					
lauric acid	333[a]	4.70 ± 0.35	−26.3 ± 2.0	0.983	83
myristic acid	313[a]	1.97 ± 0.38	−10.6 ± 2.2	0.897	75, 84
myristic acid	333[a]	2.10 ± 0.28	−11.2 ± 1.6	0.919	75, 84
palmitic acid	333[a]	2.61 ± 0.47	−14.4 ± 2.7	0.910	75, 84
palmitic acid	333	7.77 ± 1.15	−46.2 ± 7.3	0.958	75, 84
stearic acid	313	7.50 ± 0.34	−45.4 ± 2.2	0.992	84
stearic acid	343	11.35 ± 0.37	−69.6 ± 2.4	0.998	84
oleic acid	323	7.69 ± 0.03	−46.5 ± 0.2	1.000	30, 74
linoleic acid	343	10.94 ± 0.53	−66.9 ± 3.4	0.998	85
Ethyl Esters					
stearic acid	313	6.08 ± 1.10	−36.4 ± 7.1	0.938	55
stearic acid	323	5.34 ± 0.78	−31.3 ± 5.0	0.940	55
stearic acid	333	5.86 ± 1.21	−34.5 ± 7.7	0.887	55
oleic acid	313	7.63 ± 0.69	−46.2 ± 4.4	0.984	55
oleic acid	323	8.36 ± 0.28	−50.8 ± 1.8	0.997	55
oleic acid	333	7.30 ± 0.77	−43.6 ± 4.9	0.968	55
linoleic acid	313	7.14 ± 0.67	−43.0 ± 4.3	0.974	55
linoleic acid	323	6.84 ± 0.96	−41.0 ± 6.2	0.962	55
linoleic acid	333	7.50 ± 2.23	−44.9 ± 14.3[b]	0.791	55
EPA	313	8.51 ± 0.24	−52.4 ± 1.6	0.997	55
EPA	323	9.73 ± 0.48	−60.1 ± 3.1	0.993	55
EPA	333	8.54 ± 0.18	−52.1 ± 1.2	0.998	55
DHA	313	6.80 ± 0.54	−41.5 ± 3.5	0.969	55
DHA	323	8.19 ± 0.51	−50.4 ± 3.3	0.977	55
DHA	333	8.64 ± 0.40	−53.1 ± 2.6	0.985	55

[a] Parameters estimated for $d < 470$ g/L. [b] Nonsignificant ($p < 0.05$).

Table 3. Discrepancies in the Results of Different Studies Used in Modeling (Equation 2)

solute	temp (K)	k' (R^2)	ref	k' (R^2)	ref	combined dataset k' (R^2)
palmitic acid	313	3.66 (0.985)	63	7.84 (0.997)	23	6.75 (0.873)
stearic acid	328	4.99 (0.998)	36	8.69 (0.955)	54	6.98 (0.900)
monoolein	333	7.52 (0.997)	30	3.66 (0.808)	73	10.43 (0.827)
tripalmitin	313	1.37 (0.969)	63	11.10 (0.991)	23	5.50 (0.601)

acids were accompanied by relatively low R^2 values due to deviation from linearity at high densities as the solubility approached a maximum. The density dependence of solubility decreased for these compounds at high solvent densities. No clear trend with temperature could be observed in the k' values of liquid fatty acids. The k' values for triglycerides, all of which were liquid over the studied temperature range, were in the range of 4.13−13.14. In general, the association constants for triglycerides appeared to be higher than those for the corresponding fatty acids, indicating greater association between CO_2 and nonpolar triglycerides than between CO_2 and polar fatty acids.

When the ln(c) vs ln(d) plots of fatty acid esters were analyzed, there appeared to be a break in the solubility isotherms of all of the esters around the critical density. Because it was not possible to determine the density limit accurately, the critical density of CO_2 (470 g/L) was used as the density limit for the model for consistency in analysis. The high-density and low-density data were analyzed separately, and two sets of model parameters were reported whenever there were enough data for the analysis. The k' values for methyl esters were in the range of 1.97−4.70 for the low-density range (d < 470 g/L) and 7.50−11.35 for the high-density (d > 470 g/L) range (Table 2). Although deviation around critical conditions has been noted for highly polar solid solutes in $SCCO_2$,[39] such a deviation has not been reported for pure lipids. On the contrary, Liong et al.[49] reported excellent correlation for ethyl esters ($R^2 \geq 0.994$) at 313−373 K and 9−25 MPa. This break in the isotherms might be due to model limitations or due to the relatively low solubility of esters in this density range (d < 470 g/L), resulting in higher variation within the experimental data. Lower R^2 values of some esters could be due to the dependence of the limit density on solute properties among esters. The k' values for methyl esters could only be compared at 343 K for methyl stearate and methyl linoleate and were found to be similar. No trend could be observed in the k' values of ethyl esters with temperature, which were in the range of 5.34−9.73. The k' values for stearic acid ethyl ester were lower than those for the other ethyl esters.

The k' values and, hence, the density dependence of the solubility, were observed to be strongly dependent on the physical state of the solute. Therefore, regression analysis using eq 2 should be carried out at each temperature for solutes for which a phase transition is anticipated over the experimental range to correlate experimental solubility data. For the liquid solutes, no general trend could be observed in the k' values with temperature. It is necessary to carry out the regression analysis at each temperature (eq 2) to ascertain the parallel nature of the isotherms before estimating common slopes using eq 1 for these compounds. Because deviations from linearity were observed to be density dependent, experimental data over similar density ranges should be used in the analysis. The model parameters listed in Table 2 can be used to provide preliminary information on the solubility of pure lipids in $SCCO_2$ at constant temperature.

Table 4. Model Parameters for Pure Lipids Estimated Using Equation 1 ($\ln c = k \ln d + a/T + b$)

solute	$k \pm$ standard error	$a \pm$ standard error	$b \pm$ standard error	R^2
		Fatty Acids		
lauric acid	8.03 ± 0.27	−2853 ± 507	−40.7 ± 2.3	0.991
myristic acid	6.42 ± 0.33	−9300 ± 1727	−10.2 ± 5.9[a]	0.958
palmitic acid	7.00 ± 0.39	−12029 ± 1043	−7.0 ± 4.1[a]	0.909
stearic acid	5.81 ± 0.54	−15890 ± 741	12.0 ± 3.7	0.933
oleic acid	7.92 ± 0.37	−3982 ± 691	−38.1 ± 2.3	0.922
linoleic acid	9.71 ± 0.90	−5211 ± 1626	−46.3 ± 5.3	0.954
		Monoglycerides		
monoolein	10.68 ± 1.093	−7925 ± 1360	−45.8 ± 6.1	0.828
		Diglycerides		
diolein	10.48 ± 0.25	−4601 ± 533	−54.3 ± 1.9	0.996
		Triglycerides		
tricaprylin	5.32 ± 0.50	−355 ± 634[a]	−30.3 ± 3.2	0.848
triolein	10.28 ± 0.66	−2057 ± 480	−61.5 ± 4.6	0.934
		Ethyl Esters		
stearic acid	5.80 ± 0.50	−2446 ± 857	−26.7 ± 3.9	0.926
oleic acid	7.78 ± 0.34	−1947 ± 503	−40.9 ± 2.7	0.980
linoleic acid	7.17 ± 0.63	−2193 ± 896	−36.2 ± 4.4	0.921
EPA	8.62 ± 0.17	2473 ± 262	−45.2 ± 1.2	0.994
DHA	7.76 ± 0.32	−1784 ± 529	−42.1 ± 2.5	0.966
		Methyl Esters		
stearic acid	7.99 ± 0.55	−2099 ± 479	−41.93 ± 3.46	0.968

[a] Nonsignificant (p < 0.05).

Regression Analysis Using Equation 1. Table 4 gives the model parameters estimated using eq 1. The a values for all of the lipids studied had negative values (Table 4), indicating an inverse relationship between ln (c) and 1/T or an increase in the solubility with temperature at constant density. Therefore, the absolute values were considered while comparing the a values.

The a values for fatty acids increased with an increase in the melting point. The highest melting fatty acid, stearic acid, had the highest a value, indicating the highest temperature dependence at constant density. Fatty acid esters and triolein had the lowest a values (−2473 to −1784), indicating a decreasing temperature dependence with increasing volatility. Increasing temperature at constant density results in an increase in the solubility of the solute due to an increase in its vapor pressure. Thus, the a value is indicative of the relative effect of temperature on the vapor pressure of solutes. No trend could be observed for the b values, which were in the range of (−61.5 to +12.0). The estimated model parameters (Table 4) can be used to calculate the lipid solubility for those solutes that have been shown to have a common slope over the range of interest.

Solubility Behavior. The literature data were reviewed in order to establish the general trends of the solubility behavior of pure lipids in $SCCO_2$. To observe the effect of operating conditions and solute properties on the solubility, the data were analyzed in solubility versus pressure and solubility versus density plots. The model parameters were used to compare the solubility isotherms for analogous glyceride series.

The differences in solute properties such as molecular weight, polarity, and vapor pressure should be considered while comparing the solubility behavior of lipid

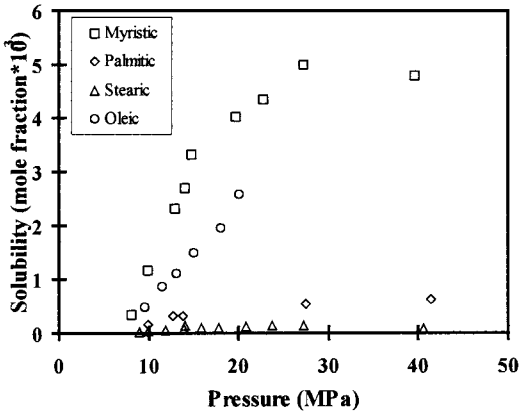

Figure 1. Solubility isotherms of myristic, palmitic, stearic, and oleic acids in $SCCO_2$ at 308 K.

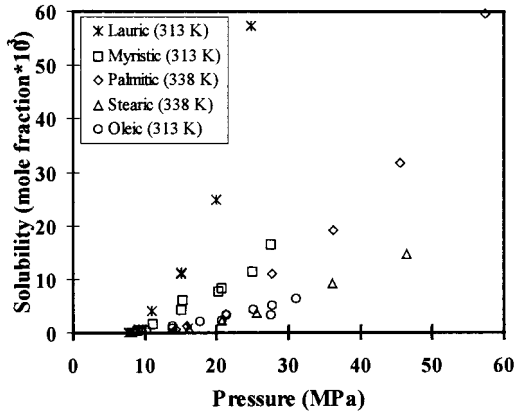

Figure 2. Solubility isotherms of lauric, myristic, palmitic, and oleic acids at 313 K and stearic and palmitic acids at 338 K in $SCCO_2$.

classes. Among the compounds studied, fatty acid esters have the highest vapor pressure followed by fatty acids. Vapor pressures of monoglycerides are appreciably higher than those of triglycerides, which have extremely low vapor pressures.[51] The vapor pressures of diglycerides are intermediate between those of mono- and triglycerides.[52] Esterification enhances the solubility of fatty acids in $SCCO_2$ because of the conversion of polar acid groups into less polar ester groups.[18]

As expected, an isothermal increase in the pressure increased the solubility because of an increase in the solvent density and, hence, the solvation power. The pressure effect was considerable in the vicinity of the critical density because the solvent density is very sensitive to changes in the pressure in this region. A comparison of the solubility isotherms for several fatty acids at 308 K is given in Figure 1. At this temperature myristic, palmitic, and stearic acids are solid, whereas oleic acid is liquid over the entire pressure range. Figure 2 is a plot of the fatty acid solubility isotherms under experimental conditions where all of the solutes are liquid. Because fatty acid solubility data at 338 K were not available for all of the fatty acids, 313 K data were used for myristic, lauric, and oleic acids, which were liquid at that temperature.

The differences in the pressure dependence of lipid solubility reflect the changes in phase behavior due to phase transition of a solute or differences between the phase behavior of different solutes. The pressure dependence of the lipid solubility isotherms increased with increasing volatility of the solute. Fatty acid esters, which were the most volatile of the compounds studied, had the highest pressure dependence. While liquid or liquefied solutes showed increasing solubility with pressure over the entire experimental range (Figure 2), a solubility maximum was approached in the isotherms of solid solutes (Figure 1). The solubility of stearic acid was observed to decrease with pressure at pressures ≥ 30 MPa and temperatures up to 318 K. A solubility maximum was first observed for stearic acid by Czubryt et al.,[53] around 30 MPa at 313 K. Kramer and Thodos[54] also observed maximum solubility for stearic acid at pressures of around 28−30 MPa at 318 K.

In a homologous series, the solubility decreased with increasing carbon number or molecular weight (Figures 1 and 2). Oleic acid was more soluble than stearic acid at 308 K (Figure 1). This solubility enhancement was due to the presence of a double bond in the oleic acid structure, which decreased the melting point considerably. However, such a solubility increase could not be observed in the unsaturated acid or ester series, where the introduction of a double bond changed the solubility only slightly. Therefore, the effect of the presence of a double bond on solubility seems to be mainly due to the difference in the physical state of the solutes. When both solutes are liquid (Figure 2), the solubilities of stearic and oleic acids were fairly similar. The solubilities of fatty acid esters with a higher degree of unsaturation were reported to be both higher[55] and lower[49,56] than those with less unsaturation by different researchers. For the esters, which were the most soluble lipid class, the effect of molecular weight or carbon number was more pronounced than the effect of unsaturation. Methyl esters had higher solubilities than the corresponding ethyl esters because of their higher vapor pressures.

Increasing the temperature at constant CO_2 density increases the solubility because of an exponential increase in the solute vapor pressure. Temperature effect at constant CO_2 density was observed for all compounds, although the magnitude of the effect varied. Contrary to the pressure effect, the temperature effect on the solubility was negatively dependent on volatility, such that the solubility of fatty acid esters increased the least with an increase in the temperature at constant density. This trend was also reflected in the estimated *a* values (Table 4).

An isobaric increase in the temperature decreases the solvent density and increases the vapor pressure of the solute. The overall impact of these two competing effects is dependent on the pressure. Below the crossover pressure, the density effect predominates and the solubility decreases with increasing temperature, which is referred to as retrograde behavior. Above this crossover point, the solubility increases with temperature because of the vapor pressure effect.[28] The existence of a crossover pressure in solid−SCF systems has been suggested as an indication of the reliability and consistency of experimental solubility data.[57] For solid lipid−SCF systems where one of the operating temperatures exceeded the melting point of the solid lipid, solid- and liquid-phase isotherms were analyzed separately because a common crossover pressure could not be observed for such systems.[57] However, the interpretation of the data was hindered by the lack of reliable phase behavior information for these systems and the variability between literature data. Although distinct crossover pressures could not be observed for all fatty acids, some general trends could be reached in this study.

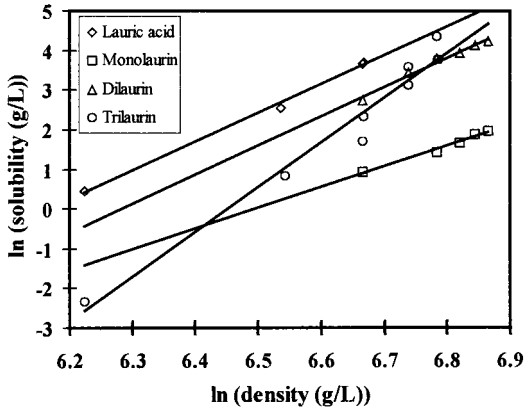

Figure 3. Solubility isotherms for laurin glycerides in $SCCO_2$ at 313 K.

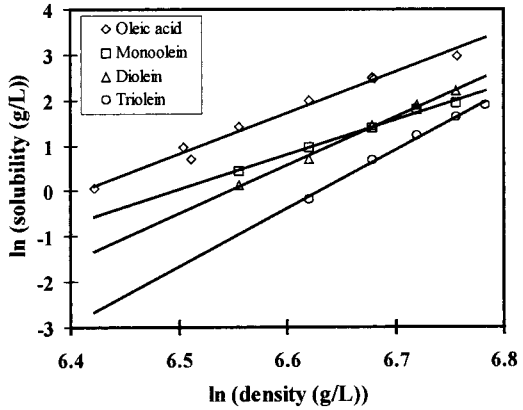

Figure 4. Solubility isotherms for olein glycerides in $SCCO_2$ at 323 K.

The crossover of isotherms shifted to higher pressures with the decreasing temperature dependence of solutes. For solutes whose vapor pressures and solubilities are only slightly affected by temperature, the density effect is compensated at relatively high pressures, whereas for solutes with a higher temperature dependence, this occurs at lower pressures.[58] The solubility of lauric acid and fatty acid esters showed retrograde solubility behavior over the entire experimental range. Solid fatty acids were in the nonretrograde region over the entire experimental range, indicating that the crossover pressures were lower than or close to the minimum pressure used. There appeared to be a second crossover pressure in the region where these solutes liquefy, which was considerably higher than the value for the solid solutes. The crossover pressures for palmitic and stearic acids under experimental conditions where they were liquid were around 20−25 MPa. Crossover pressures around 25 MPa were observed for dilaurin and trilaurin.[59] There appeared to be a crossover around 28 MPa for mono- and diolein, which was slightly lower than the crossover pressure reported for triolein[24] (31 MPa).

When the solubilities in a glyceride series (mono-, di-, and triglycerides) are compared, differences in the polarity of the solutes as well as their molecular weight should be taken into account. In both olein and laurin glycerides, fatty acids were the most soluble compounds over the entire experimental range. Different k' values of the laurin glycerides led to crossover of the solubility isotherms of tri- and dilaurin and mono- and trilaurin at two different points (Figure 3). For di- and trilaurin, the crossover density was calculated to be 870 g/L. At densities > 870 g/L, trilaurin, which has a higher molecular weight, was more soluble than the more polar dilaurin. However, below this pressure, dilaurin was more soluble than trilaurin because of its lower molecular weight. The crossover density for mono- and trilaurin was determined to be 611 g/L (Figure 3). Upon interpretation of the laurin glycerides plot, it must be noted that lauric acid, dilaurin, and trilaurin were liquid, whereas monolaurin was solid at 313 K. The low solubility of monolaurin was in part due to the physical state of the solute.

For the olein glycerides (Figure 4), where all of the solutes were liquid under the experimental range, the least soluble compound was triolein. A crossover of the solubility isotherms of di- and monoolein was observed at a density of 794 g/L. At densities > 794 g/L, the less polar diolein was more soluble. In general, the solubilities of fatty acids were always higher than those of the remaining glycerides for all of the systems studied. However, there can be a crossover between fatty acids and glycerides of different series because of the competing effects of polarity and molecular weight on the solubility isotherms as noted by Bamberger[23] for trilaurin and palmitic acid at 313 K.

Upon comparison of the solubility of lipids, the physical state of the solutes and the effect of an isobaric temperature change on solubility under the conditions of interest should be considered to make informed decisions. For example, solid tripalmitin was less soluble than triolein at 40 °C, whereas at 60 °C, the solubility of liquid tripalmitin was higher than that of triolein because of the difference in their temperature dependence in this region.[24]

Summary and Implications

Development and potential commercialization of $SCCO_2$ technology in fats and oils processing requires reliable and sufficient design data and a good understanding of the solubility behavior of the compounds of interest. The success of the models used to correlate experimental data is largely limited by the reliability of the data. However, there are wide variations in both the levels and trends of solubility data of even the most studied compounds, which limits the applicability of the existing database. These discrepancies are mainly due to differences in the purity of samples and limitations of the experimental techniques used. Extreme caution should be exercised while measuring lipid solubilities to eliminate the potential sources of error.

The problem is further complicated by the lack of phase behavior information, such as phase transitions, which is essential for the accurate interpretation of the data. Although the physical state of the solute seems to be the main factor affecting the solubility behavior, information on the melting behavior of pure lipids in $SCCO_2$ media is lacking in the literature.

Most of the studies on binary mixtures of lipid classes in $SCCO_2$ only involve the sampling of the supercritical phase. The composition of the liquid phase is also necessary in order to determine the complete phase behavior. Mono- and diglycerides are the least studied classes of lipids, although information on their phase behavior is essential for the design of processes such as fractionation of glyceride mixtures or refining of vegetable oils which are of great commercial importance. Although mixed triglycerides are the main components in many fats and oils products, there are no studies on

the binary solubilities of such compounds in $SCCO_2$, which is mainly because of the high cost of pure samples.

The knowledge of the effect of operating conditions and solute properties on the solubility behavior is essential for the design of fractionation processes. The existence of a crossover region in multicomponent systems between the crossover pressures of two compounds, where an isobaric change in the temperature affects the solubilities of the two compounds in opposite directions, can be used to achieve separation of a mixture into its components.[28]

The effect of solute properties on the solubility is largely dependent on the operating conditions. In an analogous glyceride series, the net effect of the factors, molecular weight, and polarity on solubility is dependent on the density of the solvent. At low densities, the effect of the molecular weight dominates, whereas at higher densities, the polarity effect becomes more dominant. The crossover behavior is significant in terms of fractionation of these compounds and, therefore, merits further consideration. Fractionation of these compounds should be carried out at pressures as far away from the crossover pressures as practically possible.

The parameters of the Chrastil equation estimated in this study can be used to obtain preliminary information on the solubility characteristics of pure lipids. However, it should be noted that these results can only be used as guidelines for real systems because various factors such as solute entrainment and component interactions will affect the phase behavior of multicomponent mixtures. Future emphasis, therefore, should be on the solubility behavior of multicomponent mixtures to enhance our understanding of the behavior of fats and oils products in $SCCO_2$.

Acknowledgment

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