

Solubilities of Methyl Oleate, Oleic Acid, Oleyl Glycerols, and Oleyl Glycerol Mixtures in Supercritical Carbon Dioxide

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Solubility isotherms for oleic acid and methyl oleate as well as mono-, di-, and trioleylglycerol (MO, DO, and TO) in supercritical fluid CO₂ at 50 and 60°C are reported. Partition coefficients for quaternary (MO-DO-TO-CO₂) mixtures were obtained at 60°C at pressures ranging from 172 to 309 bar. Data indicate that diolein, and especially monoolein, exhibit positive deviation from ideal behavior, possibly due to intermolecular hydrogen bonding. Supercritical fluid CO₂ appears to be a good media for removal of mono- and diacylglycerol by-products from synthetic triglyceride reaction mixtures at moderate temperatures.

KEY WORDS: Carbon dioxide, dioleylglycerol, methyl oleate, monooleylglycerol, oleic acid, partition coefficients, solubility, supercritical fluid, trioleylglycerol.

Supercritical fluids (SCFs) continue to receive widespread attention as media in a variety of extraction and processing applications (1). A significant body of work has focused on SCF CO₂ extraction and fractionation of various classes of lipids. Supercritical fluid CO₂ has been shown to be effective in extraction of oils from materials ranging from soybeans (2) to algae (3). Work at this laboratory (4-7) and elsewhere (8-10) has demonstrated the utility of SCF CO₂ in fractionating alkyl esters derived from fish oils, thus concentrating the valuable ω 3 fatty acids which are present. A summary of work on this subject has been published recently (11).

Another potential application of supercritical fluid extraction is the fractionation of mixtures of mono-, di-, and triacylglycerols (we will also use the more common terminology of mono-, di-, and triglycerides). Mono- and diacylglycerols are, of course, widely utilized as emulsifiers in the food industry (12). Molecular distillation has long been recognized as a useful technique for isolation of monoacylglycerols of high purity (13); however, this technique exposes process materials to temperatures of up to 200°C or higher. While process temperatures of that magnitude present no major drawback for acylglycerol mixtures containing fatty acids with low levels of unsaturation, elevated temperatures are detrimental to highly unsaturated acylglycerol mixtures. An example of such a material is a reaction mixture obtained in the chemical synthesis of triecosapentaenoyl glycerol starting with the ethyl ester of all *cis*-5,8,11,14,17-eicosapentaenoic acid (20:5 ω 3) (14). There is an embryonic but growing interest in synthesis of such "designer" triacylglycerols, whether by chemical or enzymatic (15) processes. Both approaches necessarily yield mono- and diacylglycerol by-products along with the desired triacylglycerols. Fractionation using SCF CO₂ of-

fers a means of purifying such mixtures to isolate the desired product, usually the triacylglycerol.

Peter and Brunner (16) and Brunner and Peter (17) demonstrated that CO₂ both with and without an acetone cosolvent is useful in separating monoacylglycerols from a mixture of acylglycerols using a single column countercurrent process. These workers reported isolation of a 99% monoacylglycerol product from the top of the column starting with a feed containing 40% diacylglycerols using an unspecified CO₂-acetone mixture at 130 bar and 70°C. Using a similar approach, Panzner (18) reported isolation of ca. 98% triacylglycerols from a mixture initially containing 10% of these compounds using SCF CO₂ and hexane, the latter present as a cosolvent. Quite recently, Ender and Peter (19) reported on the fractionation of oleic acid-containing triacylglycerols using a mixed solvent of 55% propane/45% CO₂ (w/w) under conditions at which the mixed solvent was supercritical. As an aside, these researchers found that at low propane levels (e.g., less than 5%), the mixed solvent selectively extracts mono-, rather than diglycerides. On the other hand, at higher propane concentrations, diglycerides are extracted preferentially with the isolation of monoglycerides as the "bottoms" or residual product.

Fundamental data on solubilities of various classes of lipids in SCF CO₂ do exist. Chrastil (20) measured the solubilities of several fatty acids and their corresponding triglycerides in SCF CO₂ at a number of pressures and temperatures. Bamberger *et al.* (21) measured the solubilities of 99% pure trilaurin, trimyristin, and tripalmitin as well as the corresponding acids in SCF CO₂. These workers also measured partition coefficients of these components in triglyceride mixtures. Brunetti *et al.* (22) reported on the removal of free fatty acids from crude olive oil. As part of their work, the solubilities of triolein and oleic acid as well as other triglycerides and fatty acids were determined. Inomata *et al.* (23) and, more recently, Zou *et al.* (24), have reported vapor-liquid equilibria data for methyl oleate. The latter work also includes data for methyl linoleate as well as oleic and linoleic acids.

Data on the solubility of mono- and diglycerides in SCFs, on the other hand, have not been reported. Our interest in such information derives from a need to remove mono- and diglyceride by-products from synthetic triglyceride reaction mixtures (14). In this report, we present results of a study of the solubilities of various oleic acid-containing lipids in CO₂ as well as partition (or distribution) coefficients for mono-, di-, and triolein in oleylglycerol mixtures.

EXPERIMENTAL PROCEDURES

Materials. Solubilities were determined for the following compounds: triolein and oleic acid, both 99% min purchased from Sigma Chemical Company (St. Louis,

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MO); methyl oleate, diolein, and monoolein, all 99% min purchased from NuChek Prep (Elysian, MN). (Use of trade names in this publication does not imply endorsement by National Marine Fisheries Service.) The supplier of the monoolein indicated that it was primarily composed of 1-monoolein. The diolein was primarily the 1,3-isomer also containing ca. 5% of the 1,2-isomer. A few solubility tests were also performed on practical grade triolein (65%), also from Sigma. Several tests were performed on materials obtained by mixing the 99% pure acylglycerols in the desired proportions.

Extraction equipment and procedures. All solubility measurements were obtained using the flow-through apparatus which has been fully described elsewhere (6). Briefly, the heart of the system is a double-ended, diaphragm-type compressor capable of pressures up to 10,000 psi (Newport Scientific, Inc., Jessup, MD). A 10" stainless steel pipe nipple with an ID of 11/16" and OD of 1" (Autoclave Engineers, Inc., Erie, PA) served as the extraction vessel. Extraction pressure is maintained using a back pressure regulator (Tescom Corp., Inc., Elk River, MN) and measured using a pressure transducer (Validyne Engineering, Inc., Northridge, CA). Surge vessels help dampen pressure pulsations to ± 1.0 bar at the lowest pressure and ± 2.7 bar at the highest pressure. Extraction temperature is maintained using internal iron-constantan thermocouple probes (Newport Scientific) wired to on/off type temperature controllers (Syscon International, Inc., South Bend, IN) which, in turn, supply current to silicon rubber heating tapes wrapped around the extractor and preheater.

In a typical experiment, the test material is suspended on glass wool in the extractor, the remaining volume of which is loaded with 0.16" Propak, a stainless steel packing material (Scientific Development Co., State College, PA). After the extractor is purged and equilibrated at the desired pressure and temperature, sequential fractions are collected in glass U-tubes immersed in an ice bath, and the gas volume is measured using a dry test meter (American Meter Co., Philadelphia, PA). This information, along with the gravimetric determination of the weight of material collected, allows straightforward determination of solubilities.

All solubility tests were performed using a CO₂ flow rate of three standard liters per min (SLM). A series of experiments was performed to show this to be a sufficiently low flow to ensure saturation of fluid with the test material. The experimental solubility of triolein obtained at a flow of 10 SLM was lower than that found at 3 SLM by only about 2%.

Analytical procedures. The lipid mixtures were analyzed by high performance liquid chromatography (HPLC) according to the method of Singleton and Pattee (25). These mixtures were separated on a Zorbax[®] 3 μ ODS column (8 cm \times 6.2 mm, Mac-Mod Analytical, Inc., Chaddes Ford, PA) at 34°C using a Shimadzu LC-6A system with a UV detector at 212 nm. A 5 μ L sample dissolved in isopropanol was injected onto the column using acetonitrile/absolute ethanol (40:60) as the mobile phase. Starting material purities were confirmed by HPLC. Further confirmation of material purity was obtained by methylation (where necessary) followed by determination of the fatty acid profile by gas chromatography using procedures which we have described previously (6).

RESULTS AND DISCUSSION

Solubility of oleic acid-containing lipids in CO₂. Solubility isotherms for triolein (TO), diolein (DO), monoolein (MO), oleic acid (OA), and methyl oleate (MeO) in CO₂ were determined at 50 and 60°C. Pressures ranged from 110 bar for relatively soluble MeO to 309 bar for the less soluble MO, DO, and TO. Results of all solubility measurements for these five binary systems are given in Table 1.

In general, the data display features consistent with previous work. For example, at a given set of conditions, the ester of oleic acid is more soluble than the free acid (26) which, in turn, is more soluble than triolein (22); trends, incidentally which are observed for these compounds in organic solvents, such as acetone, at atmospheric pressure (27).

From the data in Table 1, it is seen that MO, DO, and TO are more soluble at 50°C than at 60°C, i.e., display

TABLE 1

Solubility of Methyl Oleate (MeO), Oleic Acid (OA), Monoolein (MO), Diolein (DO), and Triolein (TO) in CO₂ at Selected Pressures at 50 and 60°C in Units of wt%

P (bar)	T = 50°C					T = 60°C				
	MeO	OA	MO	DO	TO	MeO	OA	MO	DO	TO
110	0.77	—	—	—	—	0.16	—	—	—	—
124	2.91	0.17	—	—	—	0.61	0.04	—	—	—
131	4.00	—	—	—	—	1.10	0.17	—	—	—
137	—	0.39	—	—	—	1.77	0.31	—	—	—
151	—	0.58	0.22	0.16	—	3.63	0.54	0.13	0.07	—
172	—	0.98	0.35	0.27	0.11	—	—	0.26	0.15	0.06
199	—	—	—	—	—	—	0.96	—	—	0.12
206	—	1.49	0.50	0.53	0.25	—	—	0.44	0.35	0.14
241	—	—	0.72	0.79	0.41	—	—	0.69	0.67	0.31
275	—	—	0.80	1.05	0.60	—	—	0.79	0.99	0.53
309	—	—	—	—	0.75	—	—	1.09	1.31	0.76

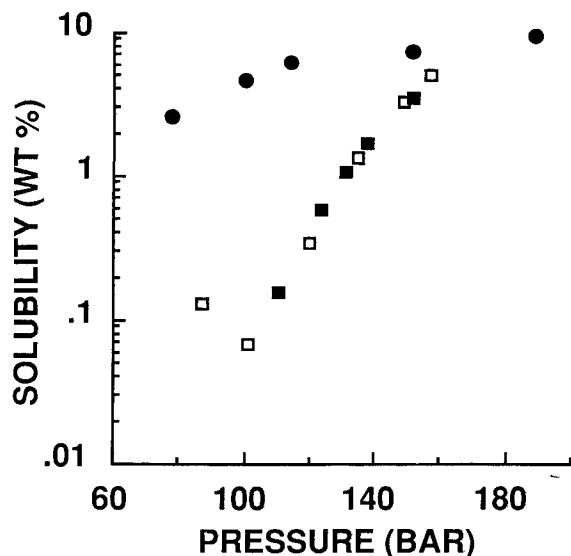
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FIG. 1. Literature values for the solubility of methyl oleate in supercritical fluid CO₂ at 60°C: □, Inomata *et al.* (23); ●, Zou *et al.* (24); and ■, this work.

retrograde behavior, at all pressures investigated in this work. This is also the case for MeO and OA (Table 1). Careful examination of the trend of values for triolein, however, suggests that at some pressure above 309 bar, a crossover to non-retrograde behavior can be expected. This observation is consistent with data on soybean oil solubility reported by Friedrich (2). Data for MO and DO display an interesting feature. At lower pressures, MO solubility is greater than that of DO, whereas at higher pressures DO solubility is greater. The pressure at which the crossover occurs appears to be somewhat lower at the lower temperature.

A review of the literature presents some opportunities to compare the values in Table 1 with previous work. Inomata *et al.* (23) and, more recently, Zou *et al.* (24) have reported vapor-liquid equilibria (VLE) data for methyl oleate. Figure 1 summarizes the solubilities computed from the VLE data of both groups as well as data from Table 1, all at 60°C. Data reported here agree well with those reported by Inomata *et al.*, but at pressures below 140 bar are uniformly much lower than those given by Zou *et al.* (24). Both groups used recirculating static-type systems which are generally recognized to yield more accurate information than the dynamic flow-type system used in our work. Thus, the discrepancy in values given in the two previous reports cannot be readily explained. Oleic acid solubilities shown in Table 1 are also significantly lower than those reported by Zou *et al.* (24). Parenthetically, this group reported the solubility of methyl oleate to be nearly eight times that of methyl linoleate at ca. 100 bar and 60°C. On the basis of similar molecular weight and structural characteristics, one would not expect to find the solubility of these two compounds to differ so greatly.

The solubilities of several lipids, including TO and OA at 60°C, were reported by Chrastil (20). Values reported for OA at 149 bar and TO at 198 bar are significantly higher than those in Table 1 at similar pressures. Bamberger *et al.* (21) also found that their values for

tripalmitin were lower than those of Chrastil by a full order of magnitude and suggested that higher values reported by Chrastil might be due to the presence of highly soluble impurities. We believe the data of Chrastil may be even more fundamentally flawed. For example, careful inspection of the Chrastil data for TO at 198 bar and temperatures from 40 to 80°C leads to the conclusion that TO exhibits nonretrograde behavior. Results in Table 1, as well as the soybean oil solubility data of Friedrich (2) and Stahl *et al.* (28) clearly contradict this observation.

Brunetti *et al.* (22) have reported solubilities of OA and TO, both stated to be of ca. 65% purity, at 200 bar and 60°C. Values reported are higher than those of Table 1 by a factor of about three. This discrepancy can, in part, be attributed to differences in the purities of test materials. For example, assuming that the 65% figure refers to the percentage of total fatty acids incorporated into the triglycerides, and further assuming statistically random distribution of all fatty acids present among the triglycerides, "65% triolein" is actually expected to contain only about 25% triolein. The remaining triglycerides consist primarily of those containing two oleic acid moieties and another either of higher unsaturation than oleic acid (e.g., 18:2 ω 6) or of shorter chain length (e.g., 16:1 ω 7 or 14:0). The latter species are sure to be more soluble in CO₂ than triolein, thus giving rise to erroneously large values. Additionally, Bamberger *et al.* (21) measured the partition (or distribution) coefficients of the quaternary system containing trilaurin (LLL), trimyristin (MMM), tripalmitin (PPP), and CO₂, as well as the solubilities of the individual pure triglycerides at identical conditions. The data suggested that the partition coefficients of the two less volatile lipid components in the quaternary system (PPP and MMM) are significantly enhanced by the presence of the most volatile triglyceride species in the system (LLL). Such a phenomenon has also been reported for mixtures of polycyclic aromatic hydrocarbon derivatives (29). Similar behavior in the much more complex 65% TO mixture would also result in solubility values larger than those for TO of higher purity. To test these hypotheses, we measured the solubility of "practical grade" 65% TO at 60°C and 199 bar and obtained a value of 0.22%, nearly twice that found with 99% TO.

Partition coefficients for MO, DO, and TO in quaternary mixtures. As mentioned in the opening remarks, our initial interest in the present problem grew out of a wish to use SCF CO₂ to purify reaction mixtures obtained in the chemical synthesis of triacylglycerols from highly unsaturated fatty acid esters (14). Not surprisingly, the major by-products in these mixtures were di- and monoacylglycerols, as well as free fatty acids. Recent data (22) suggest that the latter presents no special difficulty, but there is a need to better understand optimum conditions of pressure and temperature for selective removal of the lower acylglycerols from such mixtures.

To provide such information, two different mixtures containing MO, DO, and TO were prepared from high purity materials. In order to interpret quaternary (MO-DO-TO-CO₂) data obtained with these mixtures, we follow the usual procedure (21) of defining the partition

coefficient K_i for a component i :

$$K_i = \frac{Y_i}{X_i} \quad [1]$$

where Y_i is the concentration of component i in the CO_2 -rich phase and X_i is the concentration of the same component in the lipid-rich phase. Any consistent concentration units may be used, but they must be specified. In this work, values for K_i will be given on a w/w basis.

TABLE 2

Partition Coefficients on a w/w Basis for a Monoolein/Diolein/Triolein 10:10:80 Mixture at 60°C

P (bar)	Monoolein	Diolein	Triolein
172	1.6×10^{-2}	2.4×10^{-3}	4.1×10^{-4}
206	2.3×10^{-2}	7.8×10^{-3}	1.4×10^{-3}
241	3.3×10^{-2}	1.4×10^{-2}	3.2×10^{-3}
274	5.8×10^{-2}	2.0×10^{-2}	5.2×10^{-3}
309	5.3×10^{-2}	2.2×10^{-2}	7.6×10^{-3}

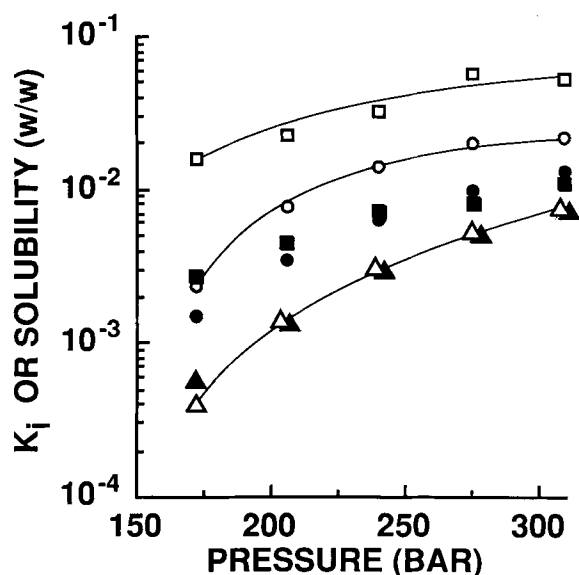


FIG. 2. Open symbols: Partition coefficients in supercritical fluid CO_2 for triolein (Δ), diolein (\circ), and monoolein (\square) obtained from a 10:10:80 mixture (w/w/w) at 60°C. Curves represent polynomial regression fits of the data included only to make the plot easier to interpret. Closed symbols, solubilities of pure triolein (\blacktriangle), diolein (\bullet), and monoolein (\blacksquare) in CO_2 at 60°C, also on a w/w basis.

TABLE 3

Partition Coefficients for Monoolein, Diolein, and Triolein in 10:10:80 and 33:33:33 (w/w/w) Mixture in CO_2 at 60°C^a

P (bar)	Monoolein			Diolein			Triolein		
	10:10:80	33:33:33	Pure	10:10:80	33:33:33	Pure	10:10:80	33:33:33	Pure
206	2.3×10^{-2}	1.6×10^{-2}	4.4×10^{-3}	7.8×10^{-3}	5.1×10^{-3}	3.5×10^{-3}	1.4×10^{-3}	1.3×10^{-3}	1.4×10^{-3}
240	3.3×10^{-2}	1.9×10^{-2}	6.9×10^{-3}	1.4×10^{-2}	9.0×10^{-3}	6.7×10^{-3}	3.2×10^{-3}	3.6×10^{-3}	3.1×10^{-3}
309	5.3×10^{-2}	2.7×10^{-2}	1.1×10^{-2}	2.2×10^{-2}	1.7×10^{-2}	1.3×10^{-2}	7.6×10^{-3}	9.1×10^{-3}	7.6×10^{-3}

^aThe solubilities of pure compounds are also included for comparison. All values are given on a w/w basis.

Since the bottom phase is not sampled in our method, the amount of CO_2 dissolved in the lipid-rich phase is not known and X_i , calculated from material balance considerations, is given on a CO_2 -free basis. Calculation of Y_i involves procedures identical to those used in obtaining solubilities for pure components.

Data in Table 2 summarize the results of several tests with a 10/10/80 (w/w/w) mixture of MO/DO/TO at 60°C and pressures between 172 and 309 bar. Each entry in Table 2 represents the mean of from 3–8 determinations performed sequentially on a single charge. It was found that sequential values of K_i were in good agreement for all three components in the early stages of a test. However, values of K_i for monoolein and diolein became quite erratic as the content of these components in the lipid-rich phase (i.e., X_i in eq. [1]) fell to levels of less than ca. 1% (w/w) and are therefore not included in the mean values reported in Table 2.

Data from Table 2 are plotted in Figure 2 (open symbols) along with curves representing polynomial regression fits to assist the reader in interpretation. Solid symbols represent solubility data reported in Table 1 for binary systems converted from a wt% to w/w basis. (As mentioned above, the composition of the bottom phase has been determined on a CO_2 -free basis in this work. Therefore, for pure components, $X_i = 1$, and K_i in equation [1] equals Y_i , i.e., the solubility of the pure component on a w/w basis [21]). It is apparent that while K_i for TO is unchanged in the binary and quaternary mixtures, the partition coefficients for di-, and especially monoolein, are higher in the quaternary mixture. One explanation of this positive deviation from ideal behavior would be the existence of hydrogen bonding between monoolein molecules in the condensed phase which also occurs (but to lesser degree) in the case of diolein. Dilution of the "solute" mono- and diolein molecules with the "solvent" triolein decreases hydrogen bonding between solute molecules, thus increasing their concentration in the vapor or CO_2 -rich phase. Such behavior is well-known for other systems, e.g., mixtures of hexane and methanol, the latter of which, of course, forms hydrogen bonds (30). Furthermore, Debye and Prins (31) and Debye and Coll (32) have shown that intermolecular hydrogen bonding occurs in solutions of α -monoglycerides and non-aqueous solvents such as benzene.

If this hypothesis holds, increasing the concentration of MO and DO in the lipid-rich phase from the 10% level is expected to result in a decrease in their respective partition coefficients. Tests were performed on a 33:33:33 (w/w/w) mixture of the three acylglycerols at 206, 241, and 309 bar. Results shown in Table 3 provide

support for this interpretation. Behavior similar to that illustrated by these data has also been noted for SCF CO₂ extraction of oleic acid from olive oils (22).

Whatever the origin of the observed concentration effect, it results in values for the selectivity of CO₂ for MO relative to TO (defined as the ratio of K_i values), ranging from ca. 10–15 at 206 bar to about 3–7 at 309 bar. The higher selectivities at a given pressure are found for mixtures with lower MO levels. Similarly, the selectivity for DO over TO ranges from about 4–6 at 206 to 2–3 at 309 bar. While values of K_i for more highly unsaturated acylglycerols will differ from those reported here, the selectivity of CO₂ for a monoglyceride of a highly unsaturated fatty acid relative to the triglyceride of the same fatty acid at 60 should be similar to those given above. Selectivities of this order of magnitude indicate that SCF CO₂ is an attractive media for fractionating highly unsaturated acylglycerol mixtures.

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