

Viscosities of Fatty Acids and Methylated Fatty Acids Saturated with Supercritical Carbon Dioxide

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The viscosities of several types of lipids saturated with supercritical carbon dioxide (SC-CO₂) were measured with a high-pressure capillary viscometer. Oleic acid and linoleic acid were evaluated from 85 to 350 bar at 40 and 60°C. The more SC-CO₂-soluble methylated derivatives of these fatty acids were evaluated from 90 to 170 bar at 40 and 60°C. The complex mixture of anhydrous milk fat (AMF) was evaluated from 100–310 bar at 40°C. The viscosities of the methylated fatty acids saturated with SC-CO₂ decreased between 5 and 10 times when the pressure increased from 1 to 80 bar, followed by a further decrease by a factor of 2 to 3 when the pressure was increased from 80 to 180 bar. The viscosities of the fatty acids and AMF saturated with SC-CO₂ had viscosity reduction similar to the methylated fatty acids between 1 and 80 bar, but they decreased much less between 80 and 350 bar. At constant pressure, the viscosity of the fatty acids and AMF decreased with increasing temperature, whereas the viscosity of the methylated fatty acids increased with increasing temperature. The lipid/SC-CO₂ mixtures were Newtonian, and their viscosities were best interpreted by using the mass concentration of dissolved SC-CO₂ in the lipids and the pure component viscosities.

KEY WORDS: Butter, carbon dioxide, fatty acids, high pressure, mixtures, supercritical, viscosity.

The design and scaleup of supercritical fluid extraction (SFE) processes require fundamental physical properties such as mixture viscosities. Such data are essentially nonexistent in the literature (1). The fluid viscosities are needed for calculating pressure drops in piping systems, determining the extent of mixing from turbulent flow or natural convection, and predicting other properties such as diffusion coefficients from such models as the Wilke-Chang expression (2). In many SFE processes, the material being extracted is a liquid, such as in vegetable oil modification or fractionation and in decholesterolization of butter and other animal fats (3–6), and the solvent is supercritical CO₂ (SC-CO₂). In these processes the liquid fat or oil becomes saturated with SC-CO₂. The design of efficient industrial extraction and separation systems requires an understanding of the viscosity of the fluid mixtures in the process. For more SC-CO₂ processing systems to be commercialized, a fundamental data bank of biomaterial/SC-CO₂ mixture properties needs to be established (1).

SC-CO₂ has a viscosity much lower than that of any liquid extraction solvent typically used, more than 10 times lower than water. This low viscosity lowers the viscosity of liquids into which it dissolves by up to one order of magnitude (7,8). The large difference in the viscosities of typical edible lipids and that of SC-CO₂ yields a large potential variation of the mixture viscosities.

Relationships have been proposed for modeling the viscosity of liquids saturated with gases (7). These relationships, although fairly successful in modeling the mixture viscosity, require experimental high-pressure viscosity data of the mixtures in order to determine correlation constants. Relationships that are based only on phase equilibrium data and pure component viscosities at the mixture conditions are more useful because they could be used to predict, not just model, the mixture viscosity (9).

Reid *et al.* (10) have reviewed many of the relationships available for modeling both gas and liquid mixture viscosities. For nonpolar liquid mixtures, Irving (9) suggested the predictive Arrhenius relation (11) in Equation 1:

$$\ln(\eta_{\text{mix}}) = \sum \omega_j \ln(\eta_j) \quad [1]$$

where η_{mix} is the mixture viscosity, ω_j is the mass fraction, and η_j is the viscosity of component j . For a binary mixture this reduces to (Equation 2):

$$\eta_{\text{mix}} = [\eta_1]^{\omega_1} [\eta_2]^{\omega_2} \quad [2]$$

Errors introduced with this relationship are typically $\pm 10\%$ (9). Liquid mixtures that follow this relationship are sometimes said to have ideal viscosity behavior because they do not require an interaction term to model their mixture viscosity. For binary mixtures containing polar materials, Irving (9) instead suggested the following relationship, known as the Grunberg equation (12) (Equation 3):

$$\eta_{\text{mix}} = [\eta_1]^{\omega_1} [\eta_2]^{\omega_2} \exp(G_{12}\omega_1\omega_2) \quad [3]$$

where G_{12} is an interaction parameter. This equation is the same as Equation 2 with an adjustment term added, which changes according to the composition of the mixture. G typically has negative values for liquid mixtures. This suggests that the molecules in the liquid mixtures interact with each other less than would be expected from the individual fluid viscosities. The absolute value of G is commonly observed to decrease with an increase in temperature. That is, the ideal mixture viscosity relation (Equation 2) becomes more accurate at higher temperatures.

Irving (9) has derived a relationship for determining G , based on a least squares method, which minimizes the error considering the magnitude of the viscosity. This relationship was derived for liquid mixtures where individual component viscosities are constant. This condition leaves composition as the only variable. In high-pressure saturated mixtures, the concentration of the mixture is altered by adjusting the pressure, which also changes the viscosity of the components in these mixtures. Under these circumstances, the value of G can be found by trial and error or by averaging.

There have been some attempts to attach a physical significance to the G term. Most of the work, however, has

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been conducted on liquid mixtures. Grunberg (13) has used the excess volume of liquids to predict G . The excess volumes must be measured accurately if they are to be used to correlate mixture viscosities. Any error in volume measurement causes a 10- to 20-fold error in the viscosity estimates. Typical errors of viscosity correlation are 5% for liquids of similar chemical structure differing in viscosity by less than 30%. The lack of mixture density data for gas/liquid mixtures makes these possible correlations for G difficult to evaluate. Isdale *et al.* (14) have proposed a molecular group contribution method to evaluate the effect of structure on liquid-mixture viscosities. They used an alternate form of Equation 3 where mole fractions were used instead of mass fractions. Their technique for modeling this molar G for Equation 3 was developed by observing a large data bank of liquid-mixture viscosity data and determining the effect of structure on mixture viscosity.

The ability of Equations 2 and 3 to model viscosities of liquids saturated with gases was evaluated in this work by using new data and data from the literature. These two models were evaluated because of their simplicity and accuracy. Equation 2 requires information that is readily available or easy to estimate and Equation 3 is the most accurate and versatile relationship currently available for modeling liquid-mixture viscosities (9). Although these relationships were developed and previously evaluated only for atmospheric-pressure liquid mixtures (9), it was proposed that the close intermolecular distances in high-pressure gas/liquid mixtures reasonably approximates liquid/liquid mixtures. The viscosity of squalene (C₃₀H₆₂) saturated with CO₂ has been measured at 40°C from 0 to 50 bar (7). Equation 2 overestimated the viscosity of this mixture by an average of 60%. The larger error of Equation 2 for gas/liquid mixtures compared to liquid/liquid mixtures could be partially attributed to the greater difference in viscosity between the components in gas/liquid mixtures. The use of Equation 3 with $G = -7.06$ reduced the percent average absolute deviation (PAAD) to 4%. Killesreiter (8) measured the viscosity of crude oil saturated with CO₂ at 80°C from 50–450 bar. He reported the solubility of CO₂ in the crude oil in mole fraction units but did not indicate the average molecular weight of the pure crude oil. The average molecular weight that yielded the smallest PAAD with Equation 2 was 580 g/mole. This is a reasonable value for the molecular weight of a crude oil. The PAAD of Equation 2 with this molecular weight was 18%. Equation 3 was not evaluated because the PAAD was minimized in order to calculate the average molecular weight with Equation 2.

If Equations 2 and 3 are to be used to calculate viscosities of high-pressure mixtures, the viscosities of the pure components at the pressure and temperature of the mixture are required. The viscosities of pure liquids at elevated pressures can be calculated from the relationship (15) (Equation 4):

$$\eta_p = \eta_o \exp(\alpha P) \quad [4]$$

where η_p is the high-pressure viscosity, η_o is the low-pressure viscosity, which is often taken as the atmospheric-pressure viscosity, P is the pressure, and α is a parameter that varies with both the compound and temperature but is independent of pressure. Little work has been conducted

on the viscosity of oils and lipids at elevated pressures. Bridgman (15), however, has measured α for oleic acid at 30 and 75°C at pressures up to 1,000 bar. The viscosity of CO₂ over a wide range of pressures and temperatures has been tabulated in the literature (16).

The major objective of this work was to measure the effect of pressure and temperature on the viscosity of the liquid fatty acids oleic acid (C_{18:1}) and linoleic acid (C_{18:2}) and their methylated derivatives (methyl oleate and methyl linoleate) saturated with SC-CO₂ in the two-phase region. The viscosities were measured in the two-phase region because, for a two-component system at equilibrium, the concentration of each phase is fixed by the system pressure and temperature and is independent of the total amount of each component in the system. The two fatty acids were chosen because they are widespread in nature as constituents of many triglycerides and differ only in their number of C-C double bonds. This work sought to quantify the effect of C-C double bonds on the viscosity of biomaterial/CO₂ mixtures. It was also desired to evaluate the effect of solvent power on viscosity of liquid/gas mixtures. Therefore, the methylated fatty acids were evaluated because they have structures similar to the parent fatty acids, but SC-CO₂ is much more soluble in the methylated fatty acids (17).

The viscosity of anhydrous milk fat (AMF) saturated with CO₂ in the two-phase region was also measured because of interest in its fractionation with SC-CO₂. With this information, a comparison between the viscosity behavior of multicomponent AMF and simple binary mixtures was possible.

The final objective was to evaluate two relationships for modeling the mixture viscosities. These relationships have been developed for liquid mixtures, but it was hypothesized that they could be used for SC-CO₂/liquid mixtures as well.

MATERIALS

The carbon dioxide used was 99.99 mole percent pure (Grade 4, Airco Gas Co., Murray Hill, NJ). The fatty acids oleic acid (No. O-1630) and linoleic acid (No. L-1268) were both 95% mass purity from Sigma Chemical Co., St. Louis, MO. The methylated fatty acids methyl oleate (O-4754) and methyl linoleate (L-1876) were both 99% mass purity from Sigma Chemical Co. Clarified AMF was prepared by melting a frozen 0.46-kg package of sweet unsalted butter (Sweet Butter from Hotel Bar, Hotel Bar Foods Division of Meadow Gold Dairies Inc., Secaucus, NJ) in a 57°C oven. The clear yellow liquid fraction of the melted butter (AMF) was decanted off and filtered 3 times through fresh qualitative filter paper (No. 1001-185, Whatman Int. Ltd., Maidstone, England) at 57°C. The AMF was frozen until needed and completely melted before use. Ethanol used to check the accuracy of the viscosity measuring apparatus was U.S.P. 200 proof punctilious dehydrated (Quantum Chemical Corp., Newark, NJ).

EXPERIMENTAL PROCEDURES

Measurement of atmospheric pressure viscosities. The kinematic viscosities of pure AMF, free and methylated fatty acids, and ethanol were measured at atmospheric pressure in a Cannon-Fenske glass capillary viscometer

(Industrial Research Glassware, Union, NJ). The viscometer was immersed in a constant-temperature circulating water bath (Model 73, Polyscience Corp., Niles, IL). The temperature was recorded to $\pm 0.2^\circ\text{C}$. In order to calculate the viscosity from the kinematic viscosity measured, the densities of the liquids were measured in this same water bath by using a 50 ± 0.1 mL volumetric flask. The level of liquid was adjusted to the mark and weighed to ± 0.01 g with a digital balance.

Measurement of high-pressure viscosities. The viscosities of the various lipids saturated with SC-CO₂ were measured with the closed-loop high-pressure capillary viscometer system shown in Figure 1. This apparatus measured viscosities within $\pm 5\%$ over the condition range studied. This accuracy was determined by using pure ethanol under pressure as a calibration fluid (15). Experimental errors are discussed in detail later in this paper. The repeatability of measurements taken with the apparatus was determined by measuring the standard deviation of two independent experiments at the same conditions and was less than 3% of the mean.

Operation of the capillary viscometer consisted of pumping the test fluid through a tube and measuring the

pressure drop at a known flow rate. The fluid viscosity was then determined from the Hagen-Poiseuille equation (Equation 5):

$$\eta = (\pi\Delta PD^4)/(128LQ) \quad [5]$$

where η is the viscosity of the fluid, ΔP is the pressure drop through the tube, D is the inside diameter of the tube, L is the length of the tube, and Q is the volumetric flow rate of the fluid through the tube. The viscosity of the fluid was calculated directly from system geometries and measured parameters.

To prepare the system (Fig. 1) for an actual viscosity measurement, the previously evacuated 200-mL windowed pressure vessel (view cell) was filled with 120 mL of the lipid to be evaluated. The system was then filled with CO₂ by using the high-pressure pump until the desired pressure was obtained. The lipid was saturated with high-pressure CO₂ by recirculating vapor through the lipid with the magnetic recirculation pump for 6 hr.

As soon as the lipid was saturated with CO₂ at the desired pressure and temperature, the actual viscosity measurement procedure was begun. The procedure consisted of pumping pure CO₂ out the bottom of the previously filled nonmagnetic cylinder (Model TOC1-60-w/piston, 1.524 m long, 2.629 cm inside diameter, HIP Inc., Erie, PA) with the gear pump (Model L-1409, Micropump Inc., Concord, CA). The CO₂ was pumped into the top of the view cell and it displaced the more dense lipid whose viscosity was to be measured out the bottom. The CO₂-saturated lipid then flowed through the viscometer capillary (3.658 \pm 0.004 m long, 0.29665 \pm 0.00058 cm inside-diameter stainless-steel tube) that was wound into a 22.9-cm diameter coil. The pressure drop in the coil was measured with a 0-2,500 \pm 1 Pa differential pressure transducer (Model TH-D, T-Hydraulics Inc., Westerville, OH). For these studies, a pressure drop of 50-300 Pa gave the most precise viscosity measurements. The CO₂-saturated lipid then flowed into the bottom of the fluid reservoir where it displaced CO₂ into the top of the nonmagnetic cylinder.

To calculate the viscosity of the fluid from Equation 5, the volumetric flow rate of the test fluid was also required. The volume of CO₂ pumped, which was the same as the volume of lipid pumped, was determined by the displacement of the free-floating magnetic stainless-steel piston fitted with a Teflon seal located inside the nonmagnetic cylinder. Whenever CO₂ was pumped out the bottom of the nonmagnetic cylinder, through the system, then back into the top of the cylinder, the piston was displaced to maintain equal pressure on both its faces. The piston position was followed with a doughnut-shaped magnet located on the outside of the nonmagnetic cylinder. The magnet travel (typically 8 cm) was determined from the displacement of the counterweight hooked to the magnet. The counterweight was located on the outside of the insulated box. The counterweight displacement was measured with a caliper to ± 0.013 cm. The volumetric flow rate was determined by dividing the volume of fluid pumped (typically 50 mL) by the run time of the experiments (typically 5 min), which was measured within ± 0.1 sec.

When the viscosities of a lipid saturated with CO₂ were to be measured at various pressures, the system was first pressurized to the highest pressure to be studied. After

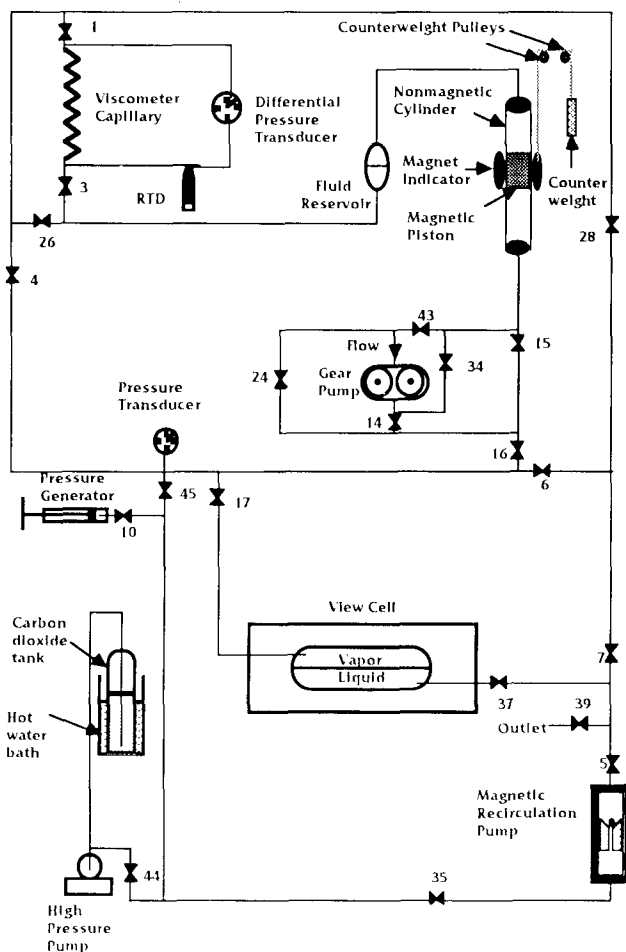


FIG. 1. Schematic diagram of system for measuring viscosities of liquids saturated with SC-CO₂.

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measuring the viscosity at the highest pressure, the pressure was reduced to the next lower desired pressure by bleeding CO₂ out of the system. When the lipid degassed to the new equilibrium pressure, which typically took 1 hr, its viscosity was measured. Equilibrium was attained when no more degassing bubbles formed, the system pressure rise stopped, and the lipid-rich phase was transparent with no internal refractive index variations throughout the view cell. Degassing was much faster than saturating and was therefore used whenever possible to obtain a new pressure mixture.

To determine if the viscosities of the fatty acids and the other component mixtures saturated with SC-CO₂ were Newtonian, the flow rates of the mixtures were varied by a factor of 2 or 3 between trials. The measured viscosities were independent of flow rate, thus indicating that the viscosities of all the mixtures were Newtonian. Newtonian viscosities were expected because single-phase fluids generally have Newtonian behavior if the backbone molecules in the fluid have fewer than 100 atoms (18). The longest carbon backbone length material was AMF which contains mostly triglycerides shorter than 60 atoms (19). The Reynolds numbers of the viscosity tests for the fatty acids and all the other components never exceeded 200, showing that the flow was always laminar (*i.e.* < 2,100).

In addition to measurement errors previously discussed, various other factors may have contributed errors to the high-pressure, capillary-tube, viscosity measurement apparatus (18). Most errors would have increased with the Reynolds number. The errors that could have been significant were all calculated at the maximum Reynolds number used, which was 200. The possible errors were: i) As mentioned previously, the true inside diameter of the viscometer tube was measured within $\pm 0.2\%$. This was determined by weighing in triplicate the amount of mercury inside a measured length of tubing. Because the viscosity equation (Equation 5) utilizes the diameter to the fourth power, this measuring error represents a $\pm 1\%$ uncertainty in the calculated viscosity. ii) The end effect errors (*i.e.* the tube length required for the fluid flow to develop its steady-state velocity profile) were calculated as being less than 1% of the capillary tube length (20). The length-to-diameter ratio of the tube was 1,200 and Bogue (21) found that a viscometer tube of length-to-diameter ratio 400 gives negligible end effects. iii) The maximum pressure drop of the fluid flowing through the tube was 0.01 bar. This pressure drop had no significant effect on the viscosity of the fluids throughout the pressure and temperature range studied. Also, this low pressure drop indicates negligible viscous dissipation effects and could not have heated up the fluid to change its properties. iv) The coiling of the viscometer tube did not affect the viscosity results. The coiling effect can be evaluated by checking the Dean number, which is calculated as (Equation 6):

$$N_{De} = N_{Re}(D/d)^{0.5} \quad [6]$$

where N_{De} is the Dean number, N_{Re} is the Reynolds number, D is the inside diameter of the tube, and d is the diameter of the coil. The same coil was used for all the experiments and had a d/D ratio of 77. The maximum Reynolds number used was 200 yielding a Dean number of 23. Srinivasan *et al.* (22) have found that for Dean

numbers less than 30 the pressure drop in a coil is the same as in a straight tube.

RESULTS AND DISCUSSION

Fatty acids. The effects of pressure and temperature on the viscosity of oleic acid and linoleic acid saturated with SC-CO₂ are shown in Figure 2. Each viscosity data point for the fatty acids and all the other components evaluated was an average of 3–6 measurements, yielding a standard error of less than 2% of the mean.

In Figure 3 the viscosity of oleic acid saturated with CO₂ is plotted, along with that of pure oleic acid (15) and of pure CO₂ (16). As shown, the viscosity of CO₂ was about 2 orders of magnitude smaller than that of oleic acid. Since the oleic acid/CO₂ mixture was 24–42% CO₂ by mass, depending on the pressure and temperature, there was a large potential for variation in the expected viscosity of the mixture. This plot was typical for all the lipid/CO₂ mixtures studied.

In general, the viscosity of a mixture is related to both the mixture composition and the pure component viscosities. Because pressure and temperature affect the viscosity differently, it is difficult to generalize how pressure and temperature will affect a mixture's viscosity unless actual mixture composition and component viscosity data are available. To understand the effect of pressure and

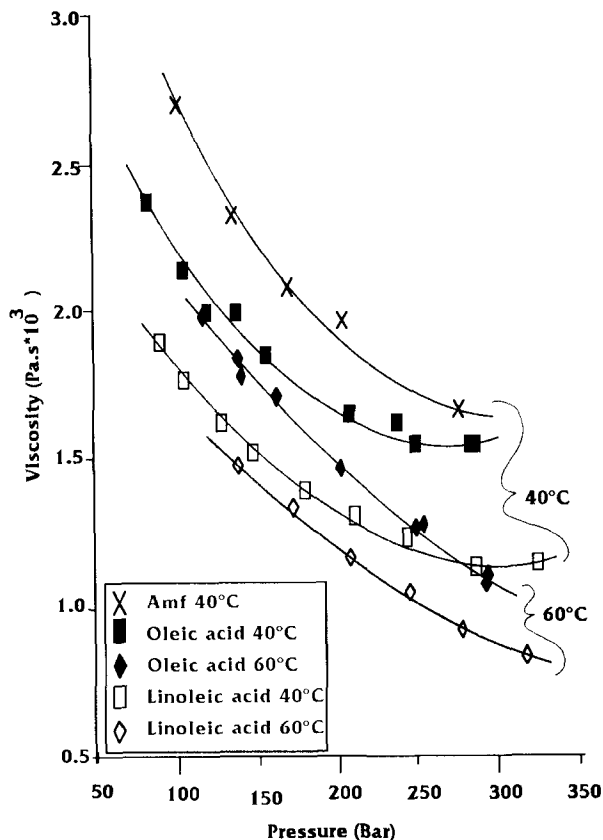


FIG. 2. Viscosity of oleic acid, linoleic acid, and AMF saturated with SC-CO₂ at 40 and 60°C.

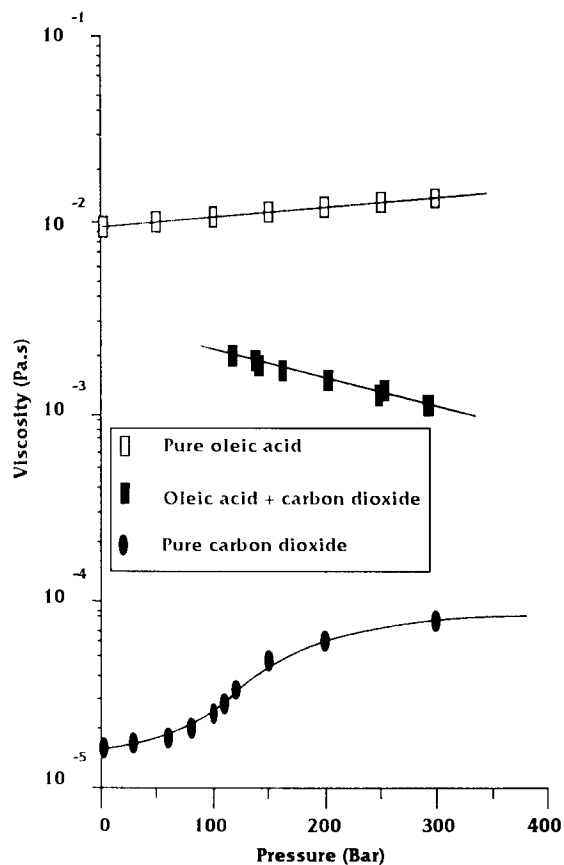


FIG. 3. Viscosity of pure oleic acid, pure CO₂, and oleic acid saturated with SC-CO₂ at 60°C.

temperature on the viscosity of a high-pressure liquid/supercritical fluid mixture, various interrelating factors must be considered, such as: i) The viscosity of a dense fluid increases with increasing pressure and decreasing temperature (15) and ii) The solubility of SC-CO₂ in a liquid fatty acid increases with increasing pressure and decreasing temperature (17).

Based on this information, several general observations can be made about the data in Figure 2. The quantitative data used for these arguments can be calculated from the data in Tables 1 and 2. The liquid-phase compositions of

the saturated mixtures were calculated from linearized ($R^2 > 0.98$) phase equilibrium data for AMF (6) and free and methylated fatty acids (17). Table 1 contains the linear coefficients for the mixture compositions over the pressure range of mixture viscosities evaluated at 80–350 bar for AMF and the fatty acids, and 90 bar to (mixture critical pressure – 20 bar) for the methylated fatty acids. The critical pressures of the mixtures were obtained from (17). The linoleic acid/SC-CO₂ mixture had lower viscosities than oleic acid/SC-CO₂. This was expected because i) linoleic acid is more unsaturated, ii) CO₂ is more soluble in linoleic acid (Table 1), and iii) pure linoleic acid has a lower viscosity than oleic acid (Table 2). The viscosity of the fatty acid mixtures decreased with pressure because more CO₂ dissolved into the fatty acids at higher pressures, and therefore reduced their viscosity. This effect overpowered the fact that the viscosity of both the pure fatty acid and pure CO₂ increase with pressure (Fig. 3). It appeared that the mixture viscosities at 40°C might start to increase with pressure but at pressures slightly higher than those studied. Killesreiter (8) observed a viscosity minimum at 350 bar when crude oil was saturated with SC-CO₂ at 80°C. The viscosities of the mixtures decreased with increasing temperature. This was most likely due to the higher temperature lowering the individual component's viscosity. This effect overpowered the lower amount of dissolved CO₂ at the higher temperature, which tends to raise the viscosity of the mixture.

Methylated fatty acids. The effects of temperature and pressure on the viscosity of methyl oleate and methyl linoleate saturated with SC-CO₂ are shown in Figure 4. These viscosity results vary considerably from those obtained on oleic and linoleic acids. The largest difference was that temperature increased the viscosity of the methylated fatty acid mixtures. Data in Table 1 show that the solubility of CO₂ in the methylated fatty acids decreased by approximately 30% as the temperature increased from 40 to 60°C, whereas the solubility of CO₂ in the fatty acids decreased by only 5%. The large solubility decrease with temperature had a much stronger effect on raising the mixture viscosity compared to the reduction of component viscosities with temperature. The viscosity of a methylated fatty acid saturated with SC-CO₂ was also approximately five times lower than that of the corresponding fatty acid at a given pressure. This was due to the combination of lower pure

TABLE 1

Constants for the Linear Relationships Describing the Liquid Phase Composition of SC-CO₂/AMF^a (80–350 bar), Fatty Acids^b (80–350 bar), and Methylated Fatty Acids^b (90 bar to critical pressure – 20 bar)

Compound	Mass fraction CO ₂ = mP + b		P = pressure (bars)	
	40°C		60°C	
	m (1/bars * 10 ⁴)	b	m (1/bars * 10 ⁴)	b
Oleic acid	8.07	0.187	8.31	0.162
Linoleic acid	5.94	0.257	7.18	0.202
Methyl oleate	58.3	-0.0971	38.1	-0.0919
Methyl linoleate	69.6	-0.199	39.6	-0.125
AMF ^c	4.94	0.256	—	—

^aReference 6.

^bReference 17.

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TABLE 2

Constants^a (α and η_0) for Equation 4 to Determine the Effect of Pressure and Temperature on Pure Lipid Viscosities

Compound	η_0 (Pa.s * 10 ³)	
	40°C	60°C
Oleic acid	16.1	9.72
Linoleic acid	12.6	7.95
Methyl oleate	3.58	2.48
Methyl linoleate	3.08	2.23
AMF	29.3	—

Temperature (°C)	α (1/bar)	
	40	1.45*10 ⁻³
60	1.20*10 ⁻³	

^aZero pressure viscosities (η_0) extrapolated from atmospheric viscosity measurements, α interpolated from 30 and 75°C oleic acid data of Reference 15.

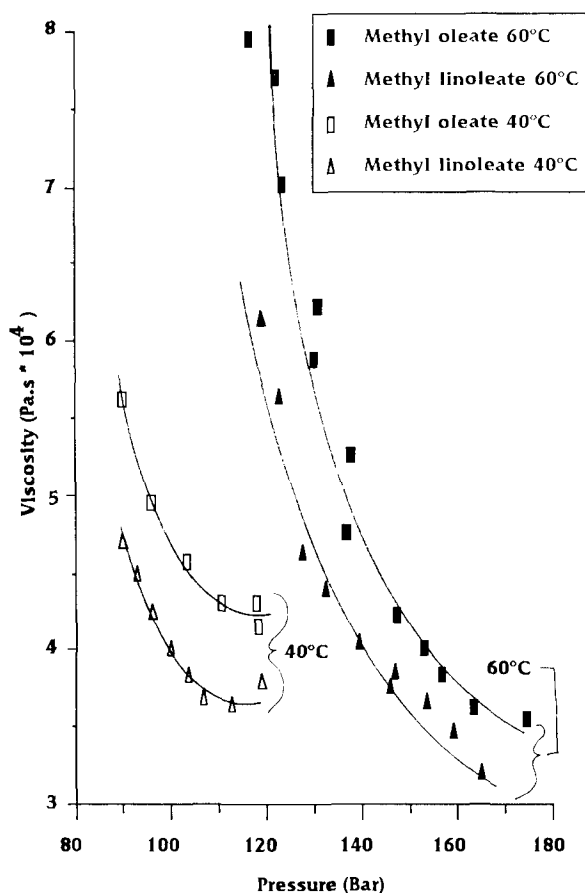


FIG. 4. Viscosities of methyl oleate and methyl linoleate saturated with SC-CO₂ at 40 and 60°C.

methylated fatty acid viscosities (Table 2) and the greater solubility of SC-CO₂ in methylated fatty acids (Table 1). The main similarity between the fatty acid mixtures and those of their methylated derivatives was that the more unsaturated linoleates had lower viscosities than oleates.

This was anticipated because pure methyl linoleate had a lower viscosity than methyl oleate and the solubility of CO₂ in the lipids was similar. The viscosities of the methylated fatty acid mixtures also decreased with pressure except near the mixture critical pressure.

The viscosities of the methylated fatty acid/CO₂ mixtures were not measured close to the mixture critical pressure (mutual solubility pressure). The near-critical region was avoided because it was difficult to obtain distinct phases in this region. Flow in the view cell induced intermixing of the similar density phases. Mixture viscosities were not measured above the critical point because concentrations could not be measured in the apparatus. The critical pressures of the two-phase methylated fatty acid/CO₂ systems studied in this work are around 145 bar at 40°C and near 230 bar at 60°C (17). These critical conditions limited the highest pressures at which the methylated fatty acid-rich phases could be measured in the two-phase region. The critical pressures of the fatty acid/CO₂ and AMF/CO₂ systems were over 350 bar at 40°C and even higher at 60°C (6,17). The pressures evaluated for the fatty acids and AMF, therefore, were limited instead by the maximum system-operating pressure of 350 bar, rather than by attainment of the mixture critical pressure.

Anhydrous milk fat. The viscosity of AMF saturated with CO₂ is shown in Figure 2. The 10-fold decrease in AMF viscosity when saturated with CO₂ can be seen by comparison to pure AMF viscosity calculated from Table 2. The viscosity behavior of the AMF saturated with CO₂ versus pressure was similar to both oleic acid and linoleic acid saturated with CO₂ at 40°C. The difference was that CO₂-saturated AMF had a higher viscosity than both CO₂-saturated oleic acid and linoleic acid. Based on these data, it appears that if mixture viscosity is linear with the number of C-C double bonds, stearic acid (C_{18:0}) saturated with SC-CO₂ perhaps would be a good material for modeling the viscosity behavior of the more complex mixture AMF saturated with SC-CO₂.

Comparison by mass fraction. The viscosities of all the lipids saturated with SC-CO₂ are compared on a mass fraction basis in Figure 5. These are the same data as in Figures 2 and 4, except that the viscosities are plotted against mass fraction CO₂. When mass fractions are used with this log format, all the lipid/CO₂ mixtures behaved similarly, with the 40°C oleic acid/CO₂ mixture differing most from the norm. Comparison of Figures 2 and 5 indicates little difference whether the data are evaluated on a mass fraction or pressure basis for the AMF and fatty acids studied. Conversely, Figures 4 and 5 show different behavior for methylated fatty acids when they are compared on a mass fraction or pressure basis. This difference in behavior is most likely due to the solubility of CO₂ in the methylated fatty acids decreasing 30% with a temperature increase from 40 to 60°C compared to a 5% CO₂ solubility decrease in the fatty acids over the same temperature change. Evaluating the viscosity of methylated fatty acids on a mass fraction instead of a pressure basis reduced the effect of temperature on mixture viscosities. It is significant to notice, however, that when evaluated by using mass fractions the viscosity of all the lipid/SC-CO₂ mixtures decreased with an increase in temperature. The similar viscosity behavior of

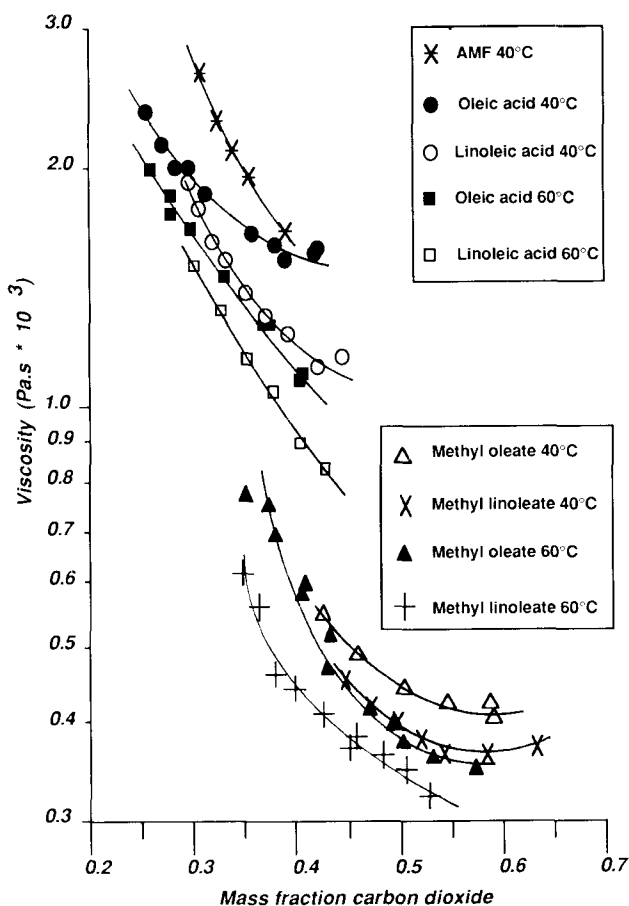


FIG. 5. Viscosities of various lipids saturated with SC-CO₂ at 40 and 60°C.

all the lipids tested, and the consistency of temperature effects indicate that it is better to evaluate high-pressure liquid/SC-CO₂ viscosities on a mass fraction rather than on a pressure basis.

Viscosity modeling. Fatty acids. To get a better understanding of the factors that affect the viscosities of SC-CO₂/lipid mixtures, both Equations 2 and 3 were evaluated. The viscosities of pure carbon dioxide at various pressures and temperatures were obtained from the literature (16), some of which are shown in Figure 3. Viscosities at pressures between those listed were interpolated by means of second-order polynomial. The viscosities of the pure lipids at elevated pressures were obtained by extrapolating the measured atmospheric-pressure viscosities (Table 2) with Equation 4. The α values reported by Bridgman (15) for oleic acid at 30 and 75°C were interpolated to 40 and 60°C and used to calculate the viscosity of all the pure lipids at elevated pressures. Experimentally measuring α with the viscosity measuring apparatus was unfeasible because this would have required filling the entire large-system volume with the pure lipids, which were too expensive. The estimated error in the viscosity by extrapolating α for oleic acid to the other lipids was $\pm 2\%$ for linoleic acid, $\pm 2\%$ for the methylated fatty acids, and $\pm 10\%$ for AMF at the highest pressures. This error estimation was based on the variation of the

α values with chemical structure of other pure liquids reported in the literature (15). The compositions of the lipid/SC-CO₂ mixtures were measured in this laboratory (17). A summary of these solubility data appears in Table 1.

The ability of Equation 2 to model the viscosities of the fatty acid/SC-CO₂ mixtures is shown in Table 3. For all the lipids, the errors were calculated at eight evenly spaced pressures throughout the pressure ranges evaluated. The highest R² second-order polynomial of the experimental data was used to calculate the viscosities at the discrete pressures. Equation 2 tended to overestimate the fatty acid viscosities by an average of 52%. It should be considered when evaluating this error that the viscosity of the SC-CO₂ is over 100 times lower than that of the fatty acids, so there was a potential for large variation. Equation 2 is useful for getting a first approximation of a mixture's viscosity at high pressure because phase equilibrium and pure-component viscosity data are much more available than high-pressure mixture viscosities.

The second relationship evaluated for modeling the mixtures' viscosities was Equation 3, where G is an experimentally determined adjustable parameter chosen to minimize the error for each lipid on each isotherm. The value of G for a given temperature and pressure saturated mixture was calculated by rearranging and substituting into Equation 3: i) the experimental mixture viscosity calculated with the best R² second-order polynomial, ii) component viscosities, and iii) mixture compositions. The optimum value of G for each isotherm was calculated by averaging the Gs at the same eight uniformly spaced pressures utilized previously.

Equation 3 was much more accurate at modeling the viscosity of the CO₂-saturated fatty acids than Equation 2 (Table 3). The data in Figure 6 show the increasing accuracy of Equation 3 at higher temperatures. Equation 3 was able to model the viscosities within a percent average absolute deviation (PAAD) of 8% and a maximum error of -26% . The optimum values of G varied between -1.47 and -2.35 , depending on the temperature and fatty acid (Table 4). The absolute values of G decreased with temperature but were always negative. These are commonly observed trends in liquid mixtures (9). Comparing the G values for the fatty acids in this study showed that the more saturated oleic acid had a more negative value than linoleic acid by 12 to 25%, depending on the temperature.

Equation 3 was able to model the viscosity better than that obtained by adding a multiplication factor to Equation 2. Adding this "correction factor" to Equation 2 resulted in a PAAD of 13% for oleic acid at 40°C, compared to 9% for Equation 3. In addition, Equation 3 meets the requirement that the viscosity of the mixture reduces to the pure component viscosity at a mass fraction CO₂ of 0 and 1.

Methylated fatty acids. The results of viscosity modeling on methyl oleate and methyl linoleate saturated with SC-CO₂ are shown in Table 3 and in Figure 7 for methyl oleate at 40 and 60°C. The error results of the models show that the fairly simple Arrhenius equation (Equation 2) was able to model the mixture viscosities of the methylated fatty acids much better than for the free fatty acids. The PAAD for the methylated fatty acids was less than 11%, compared with 52% for the free fatty acids.

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TABLE 3

Errors of Equations 2 and 3 for Modeling the Viscosities of Various Liquid Lipids Saturated with SC-CO₂

Material	Temperature (°C)	Error Equation 2		Error Equation 3	
		PAAD ^a	Max % ^b	PAAD ^a	Max % ^b
Oleic acid	40	66.4	83.3	8.97	-20.2
Oleic acid	60	44.9	59.5	4.42	-10.7
Linoleic acid	40	50.9	66.0	6.62	-25.7
Linoleic acid	60	42.3	64.0	9.85	-21.4
Methyl oleate	40	9.90	-26.3	8.10	-18.0
Methyl oleate	60	13.3	-32.4	12.7	-21.9
Methyl linoleate	40	10.3	-31.6	12.5	-25.4
Methyl linoleate	60	7.40	-14.9	7.96	-12.4
AMF	40	110	128	5.29	-14.9
AACD ^c		39.5	56.3	8.49	18.9

^a PAAD = percent average absolute deviation (PAAD) = $\sum |e|/N$; $e = \{(\text{measured viscosity} - \text{calculated viscosity})/\text{measured viscosity}\} * 100\%$; N = number of data points evaluated = 8.

^b Max % = largest $|e|$ encountered, percent absolute maximum deviation.

^c Average absolute column deviation = $\sum |\text{column error values}|/R$; R = number of rows (compounds and temperatures) = 9.

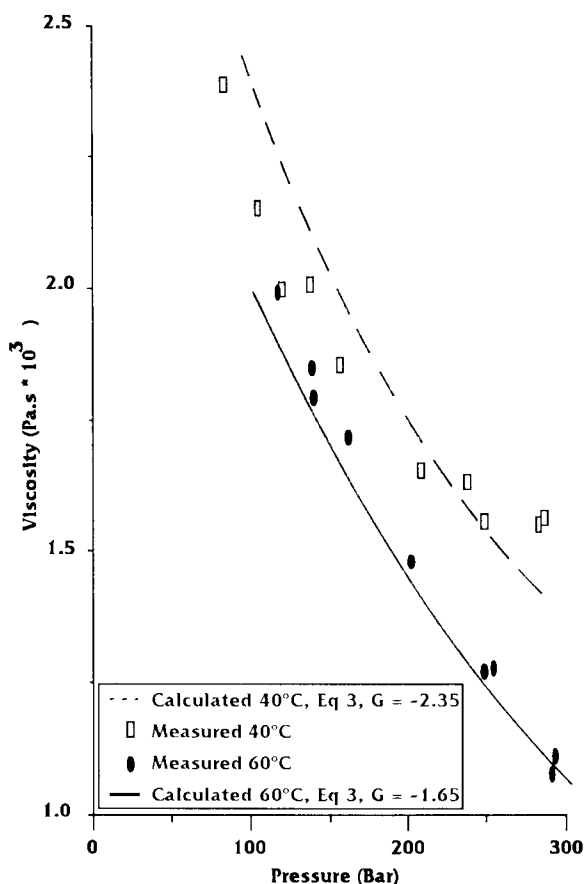


FIG. 6. Measured and calculated viscosities of oleic acid saturated with SC-CO₂ at 40 and 60°C.

TABLE 4

Experimentally Determined Best Fit G Values for Equation 3

Compound	G	
	40°C	60°C
Oleic acid	-2.35	-1.65
Linoleic acid	-1.87	-1.47
Methyl oleate	0.45	0.65
Methyl linoleate	0.38	0.12
AMF	-3.24	-

The Grunberg equation (Equation 3) was also used to model the viscosity behavior of the methylated fatty acid/CO₂ mixtures (Table 4, Fig. 7). The increased accuracy of the Grunberg equation, compared to the Arrhenius equation for the methylated fatty acids, was small compared to the increased accuracy for the fatty acids. The PAAD was reduced by only 1% for the methylated fatty acids. The G values for the methylated fatty acids were positive whereas the G values for the fatty acids were negative. The difference can be attributed to the higher CO₂ solubility in the methylated fatty acids, the smaller difference of component viscosities in the methylated fatty acid/CO₂ mixture, or the more polar nature of the fatty acids.

The absolute value of G for methyl linoleate decreased with temperature as was expected, but increased with temperature for methyl oleate, in direct contradiction to the fatty acid results and to what is typically observed for liquid mixtures (9). However, this contradiction was within experimental error. The absolute value of G for the

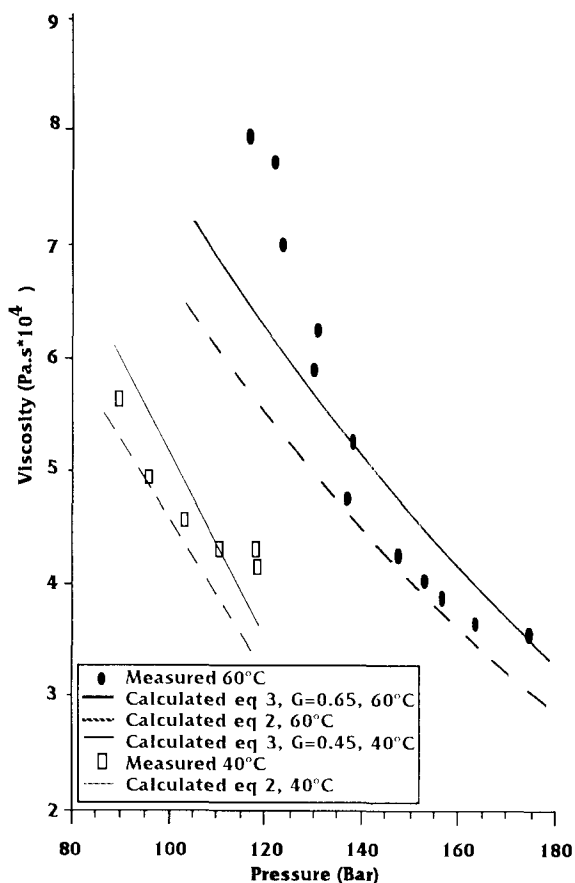


FIG. 7. Measured and calculated viscosities of methyl oleate saturated with SC-CO₂ at 40 and 60°C.

more saturated methyl oleate was larger than the G of methyl linoleate, which is consistent with the fatty acid results. The variation of G values for the free and methylated fatty acids showed that the absolute value of G was, on average, 20% smaller for the more double-bonded lipids.

Anhydrous milk fat. The ability of Equations 2 and 3 to model the viscosity of the AMF/CO₂ mixtures is shown in Table 3. Similar to the fatty acids, the results show that Equation 2 overestimates mixture viscosity, in this case by more than 100%. However, use of the Grunberg equation reduced the PAAD to less than 6% when the interaction parameter (G) was -3.24 . This AMF G , along with the G for 40°C oleic acid at -2.35 , and 40°C linoleic acid at -1.87 showed the general trend of G decreasing with a pure component viscosity increase. Because of their similar solubility behavior, only the fatty acids and AMF were compared here.

Success of the Grunberg and Arrhenius equations. In summary, Equation 2, a relationship modeling the viscosity of SC-CO₂-saturated lipids in which only pure component viscosities and mixture compositions are used, predicted the mixture viscosities within a PAAD of 52% for the fatty acids, 10% for the methylated fatty acids, and 111% for the AMF (Table 3). These large errors of Equation 2 can be attributed partially to the large difference in viscosity between the mixture components. Introduction of an experimentally determined adjustable parameter G (Equation 3, Table 4) reduced the PAAD to

8% for the fatty acids, 10% for the methylated fatty acids, and 5% for AMF (Table 3). The maximum deviations were typically 2 and 1.5 times the PAAD with and without an adjustable parameter, respectively.

Predicting G for Grunberg's equation. One of the few attempts to predict G without experimental data has been proposed by Isdale *et al.* (14). Their technique uses the molar form of Equation 3 in conjunction with calculating G from the molecular structure of the mixture components. The use of mole fractions in place of mass fractions with Equation 2 resulted in a large underestimation of the viscosities of all the lipid/CO₂ mixtures in Table 3. By using mole fractions, the viscosity of oleic acid/CO₂ at 40°C was underestimated by an average of 85% (estimated viscosity was only 15% of the measured viscosity), compared to only a 66% overestimation of the true viscosity when mass fractions were used. The corresponding percent average absolute deviation from the experimentally determined best-fitting G was 24% when using mole fractions and 10% when using mass fractions. The results at 60°C and for the other lipids were similar. The increased accuracy obtained from using mass fractions instead of mole fractions was also seen by modeling the gas/liquid mixture viscosity data of other researchers (7,8).

Since the G for Equation 3 typically must be determined from time-consuming and expensive experiments, Isdale and coworkers' (14) attempt to predict G could be insightful. Unfortunately, the G for mole fractions cannot be converted to the G for mass fractions, which for the gas/liquid mixtures in this work was found to be more accurate. However, because this represents one of the few attempts to determine G from readily available data, it was analyzed further. To test the ability of this group contribution method to predict G , the 40°C oleic acid data were analyzed in the form of mole fractions. The group contribution method predicted a G of 4.75, compared to the experimental best fit G of 11.51. This G of 4.75 results in underestimating the true viscosity by 67%, which is a slight improvement over not using any G at all (Equation 2). Without G , the viscosity is underestimated by 85%. This shows that qualitatively the group contribution method works, but the error is still much greater than that achieved from Equation 2 with mass fractions, which requires no G estimation.

There are two primary reasons why the technique of Isdale *et al.* (14) may have inaccurately predicted the viscosities of the lipid/CO₂ mixtures of this study. First, the difference in component viscosities and molecular weights was much greater for the gas/liquid mixtures studied in this work than those for the liquid/liquid mixtures Isdale *et al.* (14) used to develop their technique. Second, their group contributions could not account for the unique functional groups of CO₂.

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