Title
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Extraction of Fatty-Acid Methyl Esters with Supercritical Carbon Dioxide

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ABSTRACT

A flow apparatus was constructed to measure vapor-phase compositions of systems containing fatty-acid methyl esters as solute and supercritical carbon dioxide as solvent at 65 to 200 bar. The equilibrium cell consists of a packed bed of liquid (or solid) solute coated on an inert solid support which is commonly used in gas-chromatographic columns.

Experimental measurements were obtained for five binary systems containing methyl myristate, methyl stearate, methyl oleate, methyl linoleate or methyl laurate. Each system was measured at 40°C and 60°C and at a pressure below the critical of the mixture. In addition, a ternary system containing carbon dioxide, methyl oleate, methyl linoleate was measured at 60°C and 107 bar.

The measured solubility data were correlated using an equation of state which has a perturbation term of the van der Waals form and a reference system proposed by Boublik and Mansoori. A quadratic mixing rule with one binary parameter is suitable for these mixtures.

INTRODUCTION

Extraction with supercritical solvents provides an attractive separation technique.1,2 For extraction purposes, a supercritical solvent is a fluid at a temperature higher than its critical temperature and a pressure higher than its critical pressure.

Supercritical extraction is advantageous because the density of a supercritical solvent can be changed significantly with small changes in pressure and temperature. Changes in solvent density make it possible to vary solvent power and solvent selectivity, thereby increasing multi-stage extraction efficiency and solvent recovery.

An important advantage of supercritical-solvent extraction is provided by the ease of separation of the solvent from the extracted material. Further, supercritical fluids provide lower mass transfer resistance and lower pressure drops in flow systems than those in conventional liquid-liquid extraction. Supercritical solvents are superior to gases because of their significantly higher solvent power.

Carbon dioxide is a popular supercritical solvent because it is non-toxic, inexpensive, non-flammable and environmentally acceptable. Another advantage of carbon dioxide, of particular interest for our purposes, is its ability to extract thermally labile materials. This is possible because of the convenient critical temperature (31.05 °C) of carbon dioxide.
The solvent properties of supercritical fluids have been recognized for over 100 years but commercial applications have developed slowly, possibly due to the need for expensive high-pressure equipment. Extraction with supercritical carbon dioxide has been applied in the food processing industry for about one decade. Industrial applications include decaffeination of coffee and hop extraction for beer production. To improve the efficiency of design and optimization of extraction processes, quantitative phase equilibria are required.

There is much interest in separating naturally-occurring fatty acids because, for human nutrition and health, some acids are much more valuable than others. Most fatty acids exist in nature in the form of triglycerides. Triglycerides are triesters of glycerol and fatty acids; they are the predominant compounds in fats and fatty oils. It is advantageous to transesterify triglycerides with methanol to form methyl esters in order to separate different fatty acids. This transesterification can be achieved using either alkaline or acidic catalysts. The vapor pressures of methyl esters are about four orders of magnitude higher than those of triglycerides and about one order of magnitude higher than those of free fatty acids. Higher vapor pressures give higher solubilities in supercritical carbon dioxide. Thus, an extraction process using supercritical carbon dioxide can exert sufficient extraction power while avoiding thermal decomposition to the fatty acids, especially to the unsaturated ones.

To fractionate mixtures of fatty-acid esters, Suzuki et al. and Eisenbach proposed two different procedures. Suzuki suggested a continuous fractionation while Eisenbach proposed a batch-wise method to separate 8-component mixtures of ethyl esters. For fractionation, pressure gradients (isothermal), temperature gradients (isobaric) or a combination of both are possible.

The purpose of this work is first, to obtain new experimental data for the solubilities of saturated and unsaturated fatty-acid methyl esters in supercritical carbon dioxide and second, to correlate new and previously published solubility data using a suitable equation of state. These solubilities are needed for design and optimization of an extraction process.

**EXPERIMENTAL**

Figure 1 shows a schematic flow diagram of the continuous-flow apparatus. Liquid carbon dioxide is compressed by a cooled positive-displacement pump (LDC/Milton Roy model 396). On the outlet side of the pump, a back pressure regulator (Tescom model 26-1723-24) controls the pressure which is indicated by a
pressure gauge (Heise model CM-12"-5000psig) to better than ± 5 psi. The high-pressure liquid carbon dioxide flows into a heated water bath and becomes supercritical. The temperature controller (Omega RTD Digital Controller model 4201) of the water bath has an accuracy of ± 0.1°C. The supercritical carbon dioxide then enters the equilibrium cell.

The equilibrium cell consists of a 15-cm long stainless tube with 0.775-cm inner diameter (3/8"OD). Inert particles (Chromosorb P 60/80) coated uniformly with fatty-acid methyl esters are packed densely in the tube. Both ends of the tube are plugged with glass wool to keep the packings in place. To coat the particles, a known amount of solute (fatty-acid methyl ester) is dissolved in pentane and the mixture is added to a known amount of particles. Most of the pentane is removed under slow nitrogen flow with constant swirling. After overnight vacuum, we obtain free-falling coated particles. The particles are then filled into the cell. To remove the residual pentane, the cell is heated to 100°C for two hours under continuous nitrogen flow. Heating also makes the ester coating more uniform. The amount of ester is about 25 wt% of the finished packing.

After supercritical carbon dioxide flows past the equilibrium cell, the saturated-vapor phase enters the sampling valve where the vapor mixture can be sampled for its ester content. After the flow passes the sampling valve, it leaves the water bath and is expanded to atmospheric pressure by a micrometering valve (Nupro SS-SS2). The micrometering valve is also used to adjust the flow rate. The line between the water bath and the micrometering valve and the valve itself are heated to about 150°C to avoid condensed solute plugging up the valve. After the expansion, the condensed solute is collected in a vial and the carbon dioxide flow rate is then measured by a digital mass flow meter (Matheson model 8143A).

Since we took samples of a defined volume at process conditions, the flow rate is not required to calculate the solubility of the solute in CO₂. But it has to be controlled to make sure that we are in the region where the concentration does not depend on the flow rate, i.e. where the CO₂ is saturated with the fatty-acid methyl ester. It was found that saturation is attained for a flow rate not exceeding 10 ml/min at standard conditions. The experimental flow-rate was always less than 5 ml/min.

Figure 2 shows schematically the sampling valve (Valco liquid chromatography valve model 10UW-HC) for taking samples under process conditions. The sampling technique is similar to that used by McHugh and Paulaitis,¹¹ and by Dobbs et al. who used a single sampling loop.¹² The sampling valve consists of two sampling loops, LA and LB, each with 0.1 cc volume. Carbon dioxide, saturated with solute, flows either through the tubes indicated by the solid lines or through those indicated by the dashed lines, depending on the position of a switch above the valve. The
first sample is not taken until about five hours after start-up. After that, samples are taken about every two hours. Initially, valves V1, V2, V3 and V4 are closed. To make sure a loop is filled with carbon dioxide / fatty-acid methyl-ester mixture, the flow is allowed to pass through the loop for two hours before the sampling-valve switch is turned.

After flow had passed through loop LA, valve V1 is opened very slowly to expand the CO\textsubscript{2} to atmospheric pressure through a narrow glass column filled with about 3 to 4 cm\textsuperscript{3} of a proper organic solvent such as tetrahydrofuran. This organic solvent serves to trap any entrainment of solute in the carbon dioxide gas. After the pressure is released, valve V2 is opened and a small nitrogen pressure is applied to flush the organic solvent slowly from the glass column through loop LA into a vial attached to the outlet of valve V2. To assure that all solute is collected, an additional 3 to 4 cm\textsuperscript{3} of the organic solvent is used to flush through the sample loop. Each flush is collected and separately analysed separately by high-performance liquid chromatography (HPLC).

For each fatty-acid methyl ester, a HPLC calibration curve was established with standard solutions of various concentrations. For each standard solution or sample from the supercritical fluid experiment, five injections are made in the HPLC. The average peak area is used to calculate the concentration.

After THF solutions are collected from the sampling loop, the loop is dried with nitrogen flow. Valves V1 and V2 are closed. The loop is then ready for another sampling. In the meantime, loop LB is used in sampling.

Knowing the weight of each flush and the solute concentration, we calculate the amount of solute which was in the sampling loop at process temperature and pressure. To obtain the solute concentration in CO\textsubscript{2} at process conditions, the amount of CO\textsubscript{2} which was in the loop has to be known. This is obtained by multiplying the density of pure CO\textsubscript{2} (at the prevailing pressure and temperature) by the known volume (0.1 ml) of the sampling loop.

The density of CO\textsubscript{2} is obtained from the equation of state proposed by Huang \textit{et al.}\textsuperscript{13} which has an error of less than 0.2\% in density calculations. According to Reid and Debenedetti\textsuperscript{14}, it is reasonable to neglect the influence of the solute on the density for the low solute concentrations encountered here.

The sampling procedure was repeated at least five times for each temperature and pressure. Reported solubilities are averages of all measurements at the same conditions.
Although liquid-phase compositions cannot be analyzed in this apparatus, the small packed-bed design allows measurement of vapor-phase compositions using a very small amount of solute. Thus, the apparatus is useful for measuring solubilities of expensive solutes in supercritical carbon dioxide.

DATA CORRELATION

Many equations of state have been proposed. None of them is able to describe accurately phase equilibria in the critical region. It has been shown that an extension of the Carnahan-Starling reference system to mixtures (proposed by Boublík and by Mansoori et al.) may improve the accuracy of high-pressure phase-equilibria calculations, especially for asymmetric systems, i.e. those where the two components differ appreciably in molecular size.\textsuperscript{15,16} We use here an equation of the van der Waals-Boublík-Mansoori form.

The molar residual Helmholtz energy is conveniently separated into a theoretical reference term and a semiempirical perturbation term.

\[ A^r = A^{\text{ref}} + A^{\text{pert}} \]  

The expression proposed by Boublík and by Mansoori et al.\textsuperscript{17,18} is:

\[ \frac{A^{\text{ref}}}{R \, T} = \frac{3 \, D \, E}{F} \frac{\xi - \frac{E^3}{F^2}}{1 - \xi} + \frac{E^3}{F^2} \left( \frac{E^3}{F^2} - 1 \right) \ln(1 - \xi) \]  

\[ D, E \text{ and } F \text{ are defined as:} \]

\[ D = \sum_{i=1}^{m} x_i \, \sigma_i \]  

\[ E = \sum_{i=1}^{m} x_i \, \sigma_i^2 \]  

\[ F = \sum_{i=1}^{m} x_i \, \sigma_i^3 \]  

where \( x_i \) is the mole fraction, \( \sigma_i \) is the hard-sphere diameter of molecule \( i \), and \( m \) is the number of components. The reduced density \( \xi \) is defined as:

\[ \xi = \frac{b \, \rho}{4} \]  

with
Here, \( N_A \) is Avogadro's number and \( \rho \) is molar density.

The van der Waals perturbation term is:

\[
A^{\text{pert}} = -a \rho
\]

where \( a \) is an equation-of-state parameter which reflects intermolecular forces of attraction. This parameter depends on temperature and composition.

Compressibility factor \( Z \) can be derived from the equations above. It is given by:

\[
Z = \frac{1 + \left( \frac{3 D F}{F} - 2 \right) \xi + \left( \frac{3 E^3}{F^2} - \frac{3 D E}{F} + 1 \right) \xi^2 - \frac{E^3}{F^2} \xi^3}{(1 - \xi)^3}
\]

\[
- \frac{a \rho}{R T}
\]

For a pure component \( i \), van der Waals covolume parameter \( b_i \) is conveniently related to a dimensionless parameter \( b_i^{(0)} \) which is here considered to be independent of temperature.

\[
b_i = b_i^{(0)} \frac{R}{P_c,i} T_{c,i}
\]

where \( P_c \) and \( T_c \) are critical pressure and temperature, respectively. Parameter \( a_i \) is a function of temperature according to:

\[
a_i(T) = \frac{R^2 T_{c,i}^2}{P_{c,i}} \times \frac{a_i^{(0)} + a_i^{(1)} T_{r,i}^2}{1 + a_i^{(2)} T_{r,i}^2}
\]

where \( a_i^{(0)} \), \( a_i^{(1)} \) and \( a_i^{(2)} \) are dimensionless and where \( T_{r,i} = T/T_{c,i} \). For simplicity, we set \( a_i^{(2)} = 1 \).

For a mixture of \( m \) components, a quadratic mixing rule is used:

\[
a = \sum_{i=1}^{m} \sum_{j=1}^{m} x_i x_j \sqrt{a_i a_j} (1 - k_{ij})
\]
\[ k_{ij} = k_{ji} \]  \hspace{1cm} (13)

where \( k_{ij} \) is a dimensionless binary parameter.

**Determination of Pure-Component Parameters**

Experimental data used to determine the parameters for pure carbon dioxide fluid are from Vargaftik.\textsuperscript{19} Vapor pressure and density, one-phase density, supercritical density and critical properties have been used in the temperature range 220 to 400\(^\circ\)K.

For the fatty-acid methyl esters, only vapor pressures\textsuperscript{20} and liquid densities\textsuperscript{8} are available. The vapor pressures are given at temperatures near 200 \( ^\circ\)C. As described in Appendix 1, these vapor-pressure data are extrapolated to 40 and 60\(^\circ\)C for the determination of the equation-of-state parameters. The same extrapolation is used to estimate normal boiling points which are needed for estimating critical properties. Appendix 2 shows how critical properties and acentric factors were estimated. Experimental normal boiling points and critical properties are not available due to thermal instability of the esters.

Before determining the three equation-of-state parameters \( b, a^{(0)} \) and \( a^{(1)} \) for the fatty-acid methyl esters, van der Waals volume \( V \) is calculated using a group-contribution method developed by Bondi.\textsuperscript{21} The only information needed is the structure of the molecule. Table 1 shows calculated van der Waals volumes \( V \) for fatty-acid methyl esters.
Table 1
Van der Waals Volumes of Fatty-Acid Methyl Esters

<table>
<thead>
<tr>
<th>Methyl Ester</th>
<th>Formula</th>
<th>Molecular Weight (g/mole)</th>
<th>$V_w$ (cm$^3$/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stearate</td>
<td>C$<em>{19}$H$</em>{38}$O$_2$</td>
<td>298.5</td>
<td>206.2</td>
</tr>
<tr>
<td>Oleate</td>
<td>C$<em>{19}$H$</em>{36}$O$_2$</td>
<td>296.5</td>
<td>202.7</td>
</tr>
<tr>
<td>Linoleate</td>
<td>C$<em>{19}$H$</em>{34}$O$_2$</td>
<td>294.5</td>
<td>199.2</td>
</tr>
<tr>
<td>Palmitate</td>
<td>C$<em>{17}$H$</em>{34}$O$_2$</td>
<td>270.5</td>
<td>185.8</td>
</tr>
<tr>
<td>Myristate</td>
<td>C$<em>{15}$H$</em>{30}$O$_2$</td>
<td>242.4</td>
<td>165.3</td>
</tr>
<tr>
<td>Laurate</td>
<td>C$<em>{13}$H$</em>{26}$O$_2$</td>
<td>214.3</td>
<td>144.8</td>
</tr>
<tr>
<td>Caprate</td>
<td>C$<em>{11}$H$</em>{22}$O$_2$</td>
<td>186.3</td>
<td>124.4</td>
</tr>
<tr>
<td>Caprylate</td>
<td>C$<em>9$H$</em>{18}$O$_2$</td>
<td>158.2</td>
<td>103.9</td>
</tr>
<tr>
<td>Caproate</td>
<td>C$<em>7$H$</em>{14}$O$_2$</td>
<td>130.2</td>
<td>83.5</td>
</tr>
</tbody>
</table>

Van der Waals covolume $b$ and parameter $a^{(0)}$ are determined from regression analysis of thermodynamic properties of pure fluids without considering the third parameter $a^{(1)}$. Figure 3 shows results for van der Waals covolume $b$ for fatty-acid methyl esters and $n$-alkanes. As expected, van der Waals covolume parameter $b$ is nearly proportional to molecular size. Since parameter $a^{(0)}$ depends primarily on polarizability and since that (for a class of compounds) depends primarily on size, attractive force parameter $a^{(0)}$ should also be a linear function of the van der Waals volume. The correlation given in Figure 4 provides a good method for estimating parameter $a^{(0)}$. Thus, parameters $b$ and $a^{(0)}$ are determined by utilizing their linear relationships with respect to molecular size, without requiring high accuracy in correlating the liquid densities and vapor pressures of the fatty-acid methyl esters.

Finally, after $a^{(0)}$ and $b$ were determined, parameter $a^{(1)}$ was adjusted by minimizing the sum of squares of deviations in vapor pressures and liquid densities. The routine PFIT1 written by Topliss$^{22}$ has been used with slight modifications.

Table 2 gives all equation-of-state parameters for pure fluids. The deviations reported here are overall deviations in vapor pressure and liquid densities.

$^\dagger$ The correlation for the unsaturated fatty-acid methyl esters is shifted parallel from that for the saturated methyl esters. Instead of the constant 0.8706 for the saturated esters, the constant for the unsaturated esters is 0.7706.
Table 2
Pure-Component Parameters for Fatty-Acid Methyl Esters and for Carbon Dioxide

<table>
<thead>
<tr>
<th>Name</th>
<th>$a^{(0)}$</th>
<th>$a^{(1)}$</th>
<th>$b^{(0)}$</th>
<th>Temp.range ($^\circ K$)</th>
<th>Deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl Stearate</td>
<td>0.80420</td>
<td>0.13712</td>
<td>0.15931</td>
<td>300-400</td>
<td>3.2</td>
</tr>
<tr>
<td>Methyl Oleate</td>
<td>0.70534</td>
<td>0.28349</td>
<td>0.15513</td>
<td>300-400</td>
<td>3.9</td>
</tr>
<tr>
<td>Methyl Linoleate</td>
<td>0.70647</td>
<td>0.24016</td>
<td>0.15454</td>
<td>300-400</td>
<td>0.5</td>
</tr>
<tr>
<td>Methyl Palmitate</td>
<td>0.81079</td>
<td>0.09004</td>
<td>0.16116</td>
<td>300-400</td>
<td>1.4</td>
</tr>
<tr>
<td>Methyl Myristate</td>
<td>0.81737</td>
<td>0.11231</td>
<td>0.16399</td>
<td>300-400</td>
<td>2.2</td>
</tr>
<tr>
<td>Methyl Laurate</td>
<td>0.82395</td>
<td>0.02943</td>
<td>0.16299</td>
<td>300-400</td>
<td>3.0</td>
</tr>
<tr>
<td>Methyl Caprate</td>
<td>0.83053</td>
<td>0.02727</td>
<td>0.16812</td>
<td>300-400</td>
<td>4.4</td>
</tr>
<tr>
<td>Methyl Caprylate</td>
<td>0.83712</td>
<td>0.02759</td>
<td>0.17142</td>
<td>300-400</td>
<td>1.2</td>
</tr>
<tr>
<td>Methyl Caproate</td>
<td>0.84370</td>
<td>0.03362</td>
<td>0.17681</td>
<td>300-400</td>
<td>3.3</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>0.73485</td>
<td>0.31964</td>
<td>0.19521</td>
<td>220-400</td>
<td>8. *</td>
</tr>
</tbody>
</table>

The high deviation for carbon dioxide is not surprising because both vapor pressures and densities in the critical region were included in calculating deviations.

**RESULTS AND DISCUSSION**

Table 3 gives experimental vapor-phase compositions for five binary systems. These data are plotted in Figures 5 to 9, along with data measured by Hirohama$^{23}$ for methyl myristate and methyl stearate. For each carbon dioxide / fatty-acid methyl-ester system, the binary parameter $k_{12}$ is fitted to vapor-phase compositions measured in this work, and to estimated Henry's constants. Henry's constants have been estimated using solubility parameters as discussed in Appendix 3. For methyl myristate and methyl stearate, vapor-phase compositions and liquid-phase compositions measured by Hirohama$^{23}$ are also used to fit $k_{12}$. In general, there is very good agreement between the data measured in this work and those measured by Hirohama. Table 4 shows a set of binary parameters which are temperature independent over the temperature range considered here. The quadratic mixing rule correlates the experimental data well for all systems measured here except the system $CO_2 /$ methyl laurate.
Table 3
Solubilities of Fatty-Acid Methyl Esters in Supercritical Carbon Dioxide

<table>
<thead>
<tr>
<th>Solute</th>
<th>Pressure (bar)</th>
<th>Temperature (°C)</th>
<th>Mole Fraction of Solute ( \times 10^3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl Myristate</td>
<td>85.8</td>
<td>40.0</td>
<td>0.892</td>
</tr>
<tr>
<td></td>
<td>88.0</td>
<td>40.0</td>
<td>1.43</td>
</tr>
<tr>
<td></td>
<td>90.0</td>
<td>40.0</td>
<td>5.55</td>
</tr>
<tr>
<td></td>
<td>115.1</td>
<td>60.0</td>
<td>0.956</td>
</tr>
<tr>
<td></td>
<td>124.9</td>
<td>60.0</td>
<td>3.50</td>
</tr>
<tr>
<td></td>
<td>130.3</td>
<td>60.0</td>
<td>5.92</td>
</tr>
<tr>
<td></td>
<td>130.4</td>
<td>60.0</td>
<td>5.91</td>
</tr>
<tr>
<td></td>
<td>135.0</td>
<td>60.0</td>
<td>9.65</td>
</tr>
<tr>
<td>Methyl Stearate</td>
<td>120.3</td>
<td>40.0</td>
<td>7.60</td>
</tr>
<tr>
<td></td>
<td>150.7</td>
<td>60.0</td>
<td>1.42</td>
</tr>
<tr>
<td>Methyl Oleate</td>
<td>86.8</td>
<td>40.0</td>
<td>0.263</td>
</tr>
<tr>
<td></td>
<td>90.5</td>
<td>40.0</td>
<td>1.27</td>
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<tr>
<td></td>
<td>95.6</td>
<td>40.0</td>
<td>3.29</td>
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<td></td>
<td>100.0</td>
<td>40.0</td>
<td>6.10</td>
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<td></td>
<td>104.8</td>
<td>40.0</td>
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<td>11.0</td>
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<td>60.0</td>
<td>0.521</td>
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<td>1.97</td>
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<td>140.1</td>
<td>60.0</td>
<td>3.09</td>
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<td>60.0</td>
<td>6.01</td>
</tr>
<tr>
<td></td>
<td>154.8</td>
<td>60.0</td>
<td>7.36</td>
</tr>
<tr>
<td>Methyl Linoleate</td>
<td>85.1</td>
<td>40.0</td>
<td>0.146</td>
</tr>
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<td></td>
<td>93.9</td>
<td>40.0</td>
<td>2.13</td>
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<tr>
<td></td>
<td>100.0</td>
<td>40.0</td>
<td>3.76</td>
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<td>104.4</td>
<td>40.0</td>
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<td></td>
<td>150.3</td>
<td>60.0</td>
<td>3.43</td>
</tr>
<tr>
<td></td>
<td>159.7</td>
<td>60.0</td>
<td>4.99</td>
</tr>
<tr>
<td>Methyl Laurate</td>
<td>99.9</td>
<td>60.0</td>
<td>1.01</td>
</tr>
<tr>
<td></td>
<td>109.6</td>
<td>60.0</td>
<td>2.03</td>
</tr>
<tr>
<td></td>
<td>120.6</td>
<td>60.0</td>
<td>6.35</td>
</tr>
<tr>
<td></td>
<td>124.9</td>
<td>60.0</td>
<td>13.3</td>
</tr>
</tbody>
</table>
Table 4

<table>
<thead>
<tr>
<th>Fatty-Acid Methyl Ester</th>
<th>$k_{12} \times 10^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Myristate</td>
<td>3.00</td>
</tr>
<tr>
<td>Stearate</td>
<td>4.37</td>
</tr>
<tr>
<td>Oleate</td>
<td>5.13</td>
</tr>
<tr>
<td>Linoleate</td>
<td>7.16</td>
</tr>
<tr>
<td>Laurate</td>
<td>0.00</td>
</tr>
</tbody>
</table>

The experimental results show that the vapor-phase solubilities of fatty-acid methyl esters increase with pressure but decrease with temperature, probably due to the effect of solvent (carbon dioxide) density which is closely related to solvent power. The decreased solvent density at higher temperature apparently overrides the effect of a slight increase in solute vapor pressure.

For saturated fatty-acid methyl esters, the solubilities of the esters in the vapor phase decrease with increasing molecular size, as expected because larger molecules are less volatile and volatility is the predominant factor for determining solubility in a homologous series. For methyl laurate, only solubilities at 60°C were measured, because the critical pressure of the binary mixture at 40°C is too close to the minimum operating pressure of the apparatus (which is the pressure of the liquid carbon dioxide cylinder).

For the two unsaturated fatty-acid methyl esters measured, methyl oleate (one double bond) has higher solubilities than methyl linoleate (two double bonds). These two esters have the same carbon numbers as methyl stearate which has about the same solubilities as methyl linoleate. It is surprising that the change of solubility with increasing number of double bonds is not monotonic. To confirm this observation, a measurement was made for a two-solute system: methyl oleate and methyl linoleate.

An equimolar mixture of methyl oleate and methyl linoleate was used as the solute. The observed solubility is shown in Table 5. The solubility of methyl oleate was again higher than that of methyl linoleate. This supports the single-solute data. In this ternary system carbon dioxide(1), methyl oleate(2) and methyl linoleate(3), the binary parameter for the ester mixture, $k_{23}$, is assumed to be zero. Because of the similar structure of all fatty-acid methyl esters, the intermolecular potential between two different methyl esters is given by the geometric mean of those between identical esters. The binary parameters between carbon dioxide and
each ester were assumed to be the same as those used in binary systems. No ternary parameters were used. Figure 10 shows that the prediction by the equation of state matches the single-data point well.

<table>
<thead>
<tr>
<th>Table 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubility of Methyl Oleate and Methyl Linoleate in CO₂</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( P ) (bar)</th>
<th>( T ) (°C)</th>
<th>Mole Fraction Methyl Oleate ( \times 10^3 )</th>
<th>Mole Fraction Methyl Linoleate ( \times 10^3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>107.</td>
<td>60.0</td>
<td>3.68 ( \times 10^3 )</td>
<td>2.72 ( \times 10^3 )</td>
</tr>
</tbody>
</table>

**ACKNOWLEDGEMENTS**

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. A.S. is grateful to the Ernest-Solvay-Stiftung for financial support.
Figure 1. Schematic flow diagram of the apparatus.

![Schematic flow diagram of the apparatus.]

Figure 2. Schematic diagram of the sampling valve.

![Schematic diagram of the sampling valve.]
Figure 3. Covolume parameter \( b \) as a function of van der Waals volume.

\[
\frac{b}{V_w} = 3.469 + 2.75 \times 10^{-3} \left( \frac{V_w}{\text{cm}^3/\text{mol}} \right)
\]

- Fatty-acid methyl esters
- \( n \)-Alkanes

Figure 4. Parameter \( a^{(0)} \) as a function of van der Waals volume.

\[
a^{(0)} = 0.8706 - 3.217 \times 10^{-4} \left( \frac{V_w}{\text{cm}^3/\text{mol}} \right)
\]
Figure 5. Experimental and calculated vapor-liquid equilibria for CO$_2$(l) and methyl myristate(2)
Figure 6. Experimental and calculated vapor–liquid equilibria for CO\textsubscript{2}(1) and methyl stearate(2)
Figure 7. Experimental vapor compositions and calculated vapor–liquid equilibria for $\text{CO}_2(1)$ and methyl oleate(2)
Figure 8. Experimental vapor compositions and calculated vapor–liquid equilibria for CO$_2$(t) and methyl linoleate(2)
Figure 9. Experimental vapor compositions and calculated vapor-liquid equilibria for CO$_2$ (1) and methyl laurate (2)
Figure 10. Triangular diagram for CO₂ - methyl oleate - methyl linoleate
Appendix 1. Vapor-Pressure Extrapolation

Since the empirical Antoine equation cannot give reliable extrapolations of vapor pressures over several orders of magnitude, it is better to use a two-parameter equation from Abrams, Massaldi and Prausnitz (AMP) based on kinetic theory of fluids.\textsuperscript{24,25} has been used. In addition to the two adjustable parameters, the van der Waals volume as calculated earlier is required.

The vapor pressure $P_S$ (in atm) is given as a function of temperature $T$ (in °K) by

$$\ln P_S = \bar{A} + \frac{\bar{B}}{T} + \bar{C} \ln T + \bar{D} T + \bar{E} T^2$$

(1-1)

where

$$\bar{A} = \ln \left( \frac{R}{V_w} \right) + (s - \frac{1}{2}) \ln \left( \frac{E_0}{R} \right) - \ln [(s-1)!] + \ln(0.0966)$$

(1-2)

$$\bar{B} = - \frac{E_0}{R}$$

(1-3)

$$\bar{C} = 1.5 - s$$

(1-4)

$$\bar{D} = \frac{s - 1}{E_0/R}$$

(1-5)

$$\bar{E} = \frac{(s-3)(s-1)}{2(E_0/R)^2}$$

(1-6)

where gas constant $R$ is 82.06 cm$^3$-atm/mole/°K.

The parameters found for the fatty-acid methyl esters are listed in Table 1-1 together with the calculated normal boiling points.
Table 1-1
AMP parameters and calculated normal boiling points for fatty-acid methyl esters

<table>
<thead>
<tr>
<th>Methyl Ester</th>
<th>Formula</th>
<th>$E_0/R$ ($^{\circ}K$)</th>
<th>s</th>
<th>$T_b$ ($^{\circ}K$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stearate</td>
<td>C$<em>{19}$H$</em>{38}$O$_2$</td>
<td>14295.4</td>
<td>12.66</td>
<td>632.7</td>
</tr>
<tr>
<td>Oleate</td>
<td>C$<em>{19}$H$</em>{36}$O$_2$</td>
<td>12401.8</td>
<td>10.14</td>
<td>648.3</td>
</tr>
<tr>
<td>Linoleate</td>
<td>C$<em>{19}$H$</em>{34}$O$_2$</td>
<td>12335.1</td>
<td>10.01</td>
<td>649.7</td>
</tr>
<tr>
<td>Palmitate</td>
<td>C$<em>{17}$H$</em>{34}$O$_2$</td>
<td>13590.6</td>
<td>12.55</td>
<td>602.6</td>
</tr>
<tr>
<td>Myristate</td>
<td>C$<em>{15}$H$</em>{30}$O$_2$</td>
<td>13235.7</td>
<td>12.99</td>
<td>568.5</td>
</tr>
<tr>
<td>Laurate</td>
<td>C$<em>{13}$H$</em>{26}$O$_2$</td>
<td>13046.5</td>
<td>13.31</td>
<td>545.6</td>
</tr>
<tr>
<td>Caprate</td>
<td>C$<em>{11}$H$</em>{22}$O$_2$</td>
<td>11885.1</td>
<td>13.08</td>
<td>500.8</td>
</tr>
<tr>
<td>Caprylate</td>
<td>C$<em>{9}$H$</em>{18}$O$_2$</td>
<td>11488.8</td>
<td>13.83</td>
<td>460.4</td>
</tr>
<tr>
<td>Caproate</td>
<td>C$<em>{7}$H$</em>{14}$O$_2$</td>
<td>10930.4</td>
<td>14.82</td>
<td>411.9</td>
</tr>
</tbody>
</table>

Appendix 2. Estimation of Critical Properties

Three group-contribution methods have been considered. Ambrose's method$^{26}$ was found to be superior to the one by Lydersen$^{27}$ and also to the recent correlation of Klincewicz and Reid.$^{28}$

In addition to molecular structure Ambrose's correlation requires molecular weight and normal boiling point. Table 2-1 gives calculated critical properties for fatty-acid methyl esters together with the acentric factor as obtained from a correlation given by Lee and Kesler.$^{27}$
## Table 2-1

Calculated critical properties and acentric factors for fatty-acid methyl esters

<table>
<thead>
<tr>
<th>Methyl Ester</th>
<th>Formula</th>
<th>( T_c ) (°K)</th>
<th>( P_c ) (bar)</th>
<th>( V_c ) (cm³/mol)</th>
<th>( \omega )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stearate</td>
<td>C₁₉H₃₈O₂</td>
<td>788.6</td>
<td>12.6</td>
<td>1112.0</td>
<td>0.963</td>
</tr>
<tr>
<td>Oleate</td>
<td>C₁₉H₃₆O₂</td>
<td>810.1</td>
<td>12.8</td>
<td>1092.0</td>
<td>0.953</td>
</tr>
<tr>
<td>Linoleate</td>
<td>C₁₉H₃₄O₂</td>
<td>813.9</td>
<td>13.1</td>
<td>1072.0</td>
<td>0.943</td>
</tr>
<tr>
<td>Palmitate</td>
<td>C₁₇H₃₄O₂</td>
<td>762.0</td>
<td>13.8</td>
<td>1002.0</td>
<td>0.891</td>
</tr>
<tr>
<td>Myristate</td>
<td>C₁₅H₃₂O₂</td>
<td>730.7</td>
<td>15.4</td>
<td>891.0</td>
<td>0.816</td>
</tr>
<tr>
<td>Palmitate</td>
<td>C₁₅H₃₂O₂</td>
<td>714.7</td>
<td>17.3</td>
<td>781.0</td>
<td>0.737</td>
</tr>
<tr>
<td>Laurate</td>
<td>C₁₃H₂₆O₂</td>
<td>670.5</td>
<td>19.8</td>
<td>671.0</td>
<td>0.654</td>
</tr>
<tr>
<td>Laurate</td>
<td>C₁₃H₂₆O₂</td>
<td>632.5</td>
<td>23.1</td>
<td>561.0</td>
<td>0.569</td>
</tr>
<tr>
<td>Caproate</td>
<td>C₇H₁₄O₂</td>
<td>583.5</td>
<td>27.8</td>
<td>451.0</td>
<td>0.481</td>
</tr>
</tbody>
</table>

### Appendix 3. Estimation of Henry’s Constants

The definition of the Henry constant is:

\[
H_{i,\text{solvent}} = \lim_{x_i \to 0} \frac{f_i}{x_i} \tag{3-1}
\]

at constant temperature, or

\[
H_{i,\text{solvent}} = \frac{\Phi_i y_i P}{x_i} \tag{3-2}
\]

For a liquid, the solubility parameter \( \delta \) is defined as:

\[
\delta = \sqrt{-\frac{U}{V^L}} \tag{3-3}
\]

where \( U \) is the molar energy relative to that of an ideal gas at the same temperature and \( V^L \) is the molar volume of the liquid.

Prausnitz and Shair\(^29\) derived an expression for the equilibrium mole fraction of a gas 2 (in this case \( \text{CO}_2 \)) in a liquid 1:

\[
\frac{1}{x_2} = \frac{f^L_{\text{pure}2}}{f_2} \exp \left( \frac{V^L_2 (\delta_1 - \delta_2)^2 \zeta^2_1}{RT} \right) \tag{3-4}
\]
where $\zeta$ is the volume fraction and $f_{\text{pure}2}^L$ the fugacity of a hypothetical pure liquid 2. An expression for Henry's constant $H_{21}$ can be derived:

$$H_{21} = f_{\text{pure}2}^L \exp \left( \frac{V_2^L (\delta_1 - \delta_2)^2}{RT} \right)$$  \hspace{1cm} (3-5)

The fugacity $f_{\text{pure}2}^L$ is taken from Prausnitz and Shair, solubility parameter $\delta_2$ and volume $V_2^L$ both for CO$_2$ are taken from Barton$^{30}$ and solubility parameter $\delta_1$ for each fatty-acid methyl ester has been calculated using a correlation from Prausnitz et al.$^{30}$ This correlation requires critical properties and the acentric factor. The results are listed in Table 3-1.

<table>
<thead>
<tr>
<th>Methyl Ester</th>
<th>$H_{21}$ (bar) 40 °C</th>
<th>$H_{21}$ (bar) 60 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stearate</td>
<td>64.7</td>
<td>69.2</td>
</tr>
<tr>
<td>Oleate</td>
<td>63.7</td>
<td>67.6</td>
</tr>
<tr>
<td>Linoleate</td>
<td>64.1</td>
<td>68.0</td>
</tr>
<tr>
<td>Myristate</td>
<td>79.4</td>
<td>85.0</td>
</tr>
<tr>
<td>Laurate</td>
<td>86.9</td>
<td>91.7</td>
</tr>
</tbody>
</table>
NOTATION

Upper case

A  molar Helmholtz energy \((cm^3\cdot bar/mole)\)
\(\bar{A},\bar{B},\bar{C},\bar{D},\bar{E}\) defined in Appendix 1
\(D,E,F\) defined in equations (3) to (5)
\(E_0\) parameter in AMP equation \((J/mol)\) (see Appendix 1)
\(H\) Henry's constant \((bar)\)
\(N_A\) Avogadro number \((N_A = 6.02 \times 10^{23} \text{ mole}^{-1})\)
\(P\) pressure \((bar)\)
\(R\) gas constant \((R = 83.14 \ cm^3\cdot bar/mole/\degree K)\)
\(T\) temperature \((\degree K)\)
\(T_b\) normal boiling point \((\degree K)\)
\(V_w\) van der Waals volume \((cm^3/mole)\)
\(Z\) compressibility factor

Lower case

\(a,a_i\) equation-of-state parameter \((cm^6\cdot bar/mole^2)\)
\(b,b_i\) equation-of-state parameter \((cm^3/mole)\)
\(f\) fugacity \((bar)\)
\(k\) binary equation-of-state parameter
\(m\) number of components
\(s\) parameter in AMP equation (see Appendix 1)
\(x\) liquid-phase mole fraction
\(y\) vapor-phase mole fraction

Greek symbols

\(\delta\) solubility parameter \((bar^{0.5})\)
\(\omega\) acentric factor
\(\rho\) molar density \((mole/cm^3)\)
\(\xi\) reduced density, defined in equation (6)
\(\zeta\) volume fraction (see Appendix 3)
\(\Phi\) fugacity coefficient
Subscripts and superscripts

- **subscripts**
  - $c$: critical
  - $i,j,k$: integer numbers refer to component $i,j,k$
  - $L$: liquid-phase
  - $r$: reduced
  - $V$: vapor-phase
  - $1,2,3$: refer to component $1,2,3$

- **superscripts**
  - $L$: liquid
  - $pert$: perturbation
  - $ref$: reference
  - $r$: residual
  - $V$: vapor
References


25. A. B. Macknick, J. Winnick, and J. M. Prausnitz, "Vapor Pressures of Liquids as a Function of Temperature. Two-Parameter Equation Based on Kinetic


