# New Apparatus for Measurement of Supercritical Fluid-Liquid Phase Equilibria

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Over the past decade there has been rapidly increasing interest in the development of supercritical fluids as solvents for extraction and fractionation systems. Although there has been a significant amount of research on supercritical fluids in both industrial and academic laboratories, only a few such processes have found their way to commercialization. The main impediment to further applications of this technology is the lack of reliable methods by which solvent capacities can be estimated. Viable processes continue to appear only very slowly, since their development depends upon the complex procedure by which solvent capacities are experimentally determined.

Many experimental difficulties in measuring phase equilibria in supercritical fluid-liquid systems arise as a consequence of the molecular dissimilarity of the compounds composing such mixtures. As a result, relatively few data have accumulated on systems with potential for supercritical fluid extraction or fractionation. To partially address the paucity of data, an apparatus was developed to perform PVT $XY$ phase equilibria studies in the range of 300 to 400 K. The volumetric measurement capabilities of this apparatus are important, since almost all supercritical fluid process design would require phase density information. Another significant feature is provided by the sapphire pressure vessel, which permits direct observation of the phase behavior over wide temperature and pressure ranges. A third important feature of the apparatus is that multicomponent mixtures can be investigated by procedures that are nearly as straightforward as those followed for binary mixtures.

The performance of this apparatus was evaluated through measurements on the carbon dioxide + decane system. This system has been previously studied extensively by Reamer and Sage (1963) among others, and is suitable as a test mixture.

Supercritical fluid extraction and fractionation of esterified fatty acids is a potentially attractive method of separation in comparison to currently used methods such as vacuum distillation. In fact, a crudely operating process in this area has already been investigated by Eisenbach (1984). Measurement and correlation of the phase relationships exhibited by systems of supercritical fluid + methylated fatty acids would facilitate accurate design and optimization of a fractionation process. Phase equilibrium measurements of carbon dioxide + methyl linoleate are also reported here, and represent the first step in our program to study supercritical fluids and methylated fatty acids.

## Experimental Method

A diagram of the apparatus is shown in Figure 1, and it is described in detail by Adams (1986). It is of the dual recirculation type, and is composed, in part, of a central pressure vessel through which both liquid and vapor phases are continuously recirculated. For both liquid and vapor phases, quantitative analyses of the composition and density are made with a gas chromatograph. Because of the procedures by which mixtures are prepared and subsequently analyzed, the apparatus can be used with any compounds exhibiting the following characteristics:

1. Melting points that are below ambient temperature
2. vapor pressures that are on the order of 0.1 kPa or greater at temperatures less than 513 K

The dashed lines in Figure 1 mark the boundaries of temperature-controlled air baths. The temperatures of these air baths are measured with thin-film platinum thermometers calibrated in this laboratory to within 0.01 K against precise temperature standards. Each bath is well insulated and has two separate thermometers, as well as two metal-blade fans that facilitate

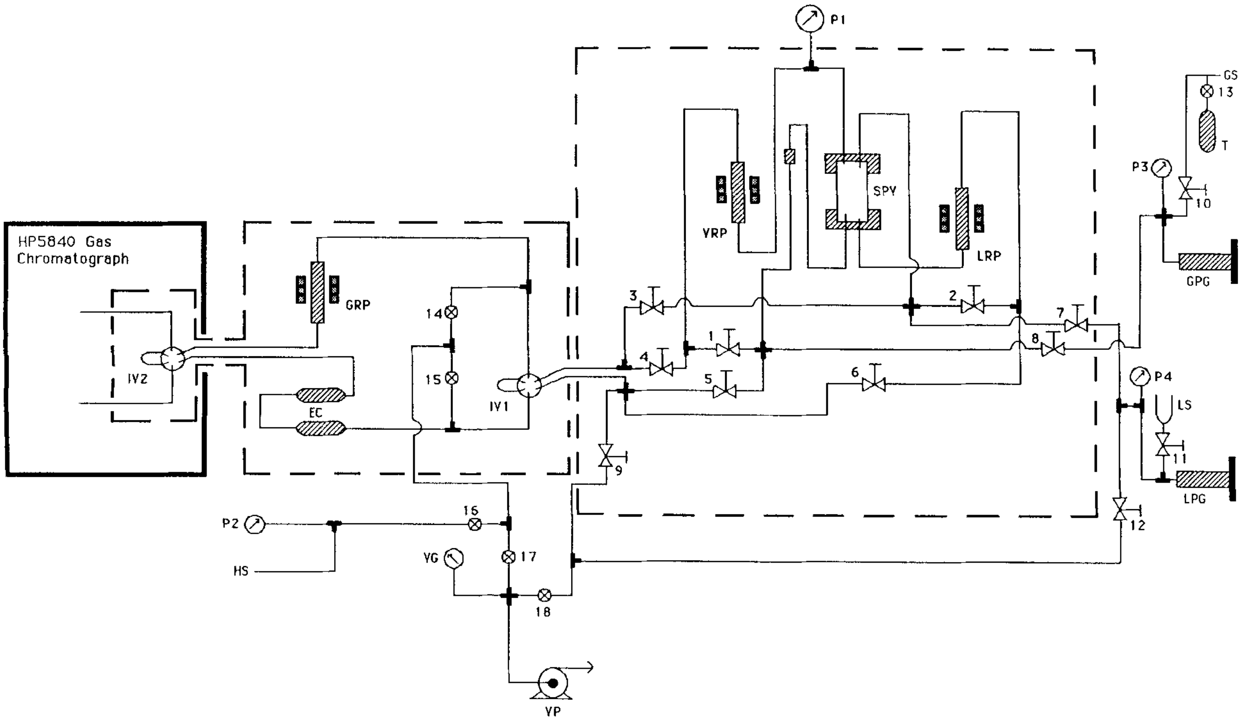

**Figure 1. Diagram of apparatus.**

EC, Expansion chambers
GPG, Gas pressure generator
GRP, Gas recirculation pump
GS, gas supply
HS, Helium supply
IV1, Rheodyne 6-port injection valve
IV2, Valco 6-port injection valve
LPG, Liquid pressure generator
LRP, Liquid recirculation pump
LS, Liquid supply
P(1-4), Pressure gauges
SPV, Sapphire pressure vessel
T, Trap
VG, Vacuum gauge
VP, Vacuum pump
VRP, vapor recirculation pump
1-18, Shut-off valves

thermal equilibration. Temperature gradients between the various thermometers are consistently controlled to less than 0.05 K. Two piston screw pump pressure generators are shown in the far right side of the diagram; these are used to pressurize and pump the mixture components into the sapphire pressure vessel. The pressure vessel consists of a 3.175 cm OD, 1.27 cm ID, by 10.16 cm long sapphire tube sealed against stainless steel end flanges by spring-loaded Teflon washers. After the vessel is charged with gas and liquid components, valves 1 and 2 are opened while valves 3 through 9 remain closed. To ensure thorough mixing, the vapor phase is drawn from the vessel top and driven by a magnetically actuated pump down through valve 1, up through a gas trap, and back into the bottom of the vessel. Similarly, the liquid is drawn from the vessel bottom and driven by a second magnetically actuated pump through valve 2 and back up into the top of the vessel. This method of dual recirculation establishes equilibration within 5 to 10 min. The mixture pressure is measured with a T-Hydronics transducer having triple ranges of 0 to 10.44, 24.23, and 34.58 MPa. The combined uncertainty due to nonlinearity and hysteresis is less than 0.15% of full scale in each range.

The equilibrated phases have to be sampled separately, but the same technique is employed in each case. Sampling is performed with a Rheodyne six-port sample injection valve of the type normally used in HPLC applications. To obtain a vapor phase sample for instance, valves 4 and 5 are opened and valve 1 is closed. The circulating vapor phase is thereby pumped through the sample loop of the injection valve and back into the bottom of the pressure vessel as before. In a similar manner, the sample loop of the injection valve can be filled with a liquid phase sample by opening valves 3 and 6, and closing valve 2; by this arrangement, liquid is driven through valve 6, the injection valve sample loop, valve 3, and on back to the vessel top.

The temperature-controlled region in which the injection valve is mounted serves to dilute, vaporize, and homogenize all the sample material for subsequent injection into the gas chromatograph shown in the far left side of Figure 1. With valves 14 and 15 closed, this section of tubing forms a closed loop. This loop extends from the Rheodyne sample injection valve through two 75 cm$^3$ expansion chambers, the GC sample injection valve, the magnetically actuated gas recirculation pump, and finally back to the Rheodyne valve. This section is initially maintained in thermal equilibrium with the section housing the pressure vessel and is filled with helium, which is also used as the GC carrier gas, at a pressure close to that prevailing at the GC column head. Rotation of the Rheodyne valve injects the high-pressure vapor or liquid sample into the dilution volume. During this sample expansion, most of the relatively nonvolatile components condense. To keep the dilution volume low and still vaporize all the mixture components, the temperature of this section of the apparatus is increased to a level at which the ratio of partial pressure to saturation pressure for all components is less than 0.1, a value at which physical adsorption effects should be insignificant.

Sample homogenization is promoted by the gas recirculation pump, which continuously circulates the gas mixture of helium + sample components around the circulation loop. Following a sufficient time period for vaporization and homogeniza-

Table 1. Phase Measurements of Carbon Dioxide + Decane at 313.15 K

| Pressure MPa | Mol. Frac. | Molar Vol. $cm^3 \cdot gmol^{-1}$ |
|---|---|---|
| | Liquid Phase Measurements | |
| 1.427 | 0.1474 | 177.5 |
| 3.438 | 0.3453 | 147.5 |
| 4.808 | 0.4960 | 133.6 |
| 6.184 | 0.6508 | 112.8 |
| 7.410 | 0.8259 | 84.3 |
| | Vapor Phase Measurements | |
| 5.672 | 0.9991 | 327.5 |
| 6.346 | 0.9990 | 270.8 |
| 6.969 | 0.9988 | 222.6 |
| 7.510 | 0.9982 | 190.7 |
| 7.835 | 0.9973 | 165.6 |

tion, a sample of the circulating gas stream is injected into the GC for quantitative analysis. The acquisition of time-invariant reproducible peak areas for all components indicates complete sample preparation. After the sample analysis is completed, valves 14, 15, and 17 are opened, and the sample-containing section is evacuated. Following a cooling period, it is prepared again for another sample.

The entire apparatus is calibrated as a unit for each of the individual components in the mixture. The sample loop of the Rheodyne valve is filled with one of the pure fluids at measured state conditions of temperature and pressure, and at a density that is calculated from an appropriate equation of state. Through the sample analysis procedure described above, a chromatographic peak area is obtained for the sample. Because the sample volume expansion is precisely reproduced, the peak areas obtained for pure samples at various known densities provide a direct calibration of peak area to sample density for each individual component. Furthermore, since the apparatus is calibrated for each component separately, the efficiency of the GC column imposes the only constraint on the number of substances that can be quantitatively analyzed in mixture samples.

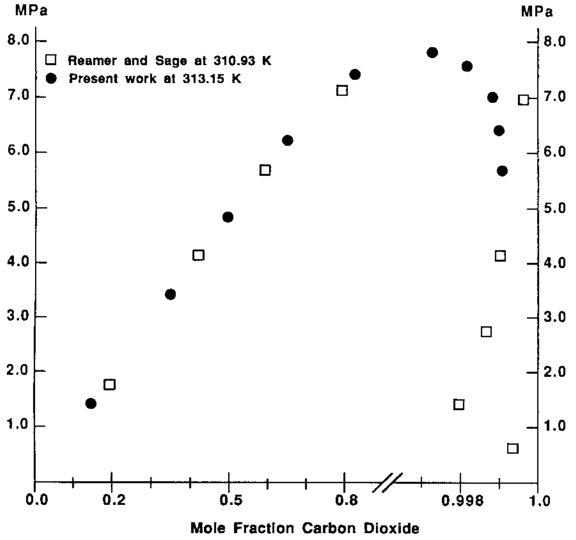

Figure 2. Pressure vs. composition of carbon dioxide + decane.

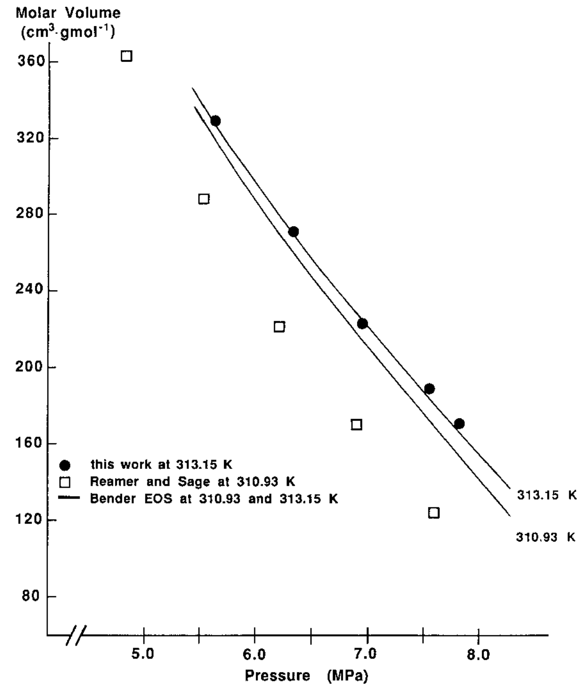

Figure 3. Molar volume vs. pressure for carbon dioxide + decane.

In this research, two loops were employed with the Rheodyne valve. A 0.018 $cm^3$ loop was used for liquid phase as well as for near critical, highly dense vapor phase samples, and a 0.455 $cm^3$ loop was used for the less dense vapor phase samples. The low-pressure circulation loop (sample expansion volume), was approximately 190 $cm^3$, and the sample loop on the GC injection valve was 0.58 $cm^3$: the fraction of the original sample that was injected into the GC for analysis therefore was 0.003. With such appropriately sized sample loops, the quantities injected were small enough to ensure that chromatography was performed in the linear elution mode; that is, in the linear portion of the adsorption isotherm where the retention time is independent of the concentration.

In this work, the manufacturer's stated purities of the compounds were 99.98 mol % for carbon dioxide (MG Industries), and 99.0 mol % for both decane and methyl linoleate (Alpha Products). The actual purity of the methyl linoleate as analyzed

Table 2. Phase Measurements of Carbon Dioxide + Methyl Linoleate at 313.15 K

| Pressure MPa | Mol. Frac. | Molar Vol. $cm^3 \cdot gmol^{-1}$ |
|---|---|---|
| | Liquid Phase Measurements | |
| 4.872 | 0.626 | 160.9 |
| 8.228 | 0.822 | 103.8 |
| 9.800 | 0.878 | 88.9 |
| 12.400 | 0.935 | 72.5 |
| | Vapor Phase Measurements | |
| 7.602 | 0.9986 | 185.1 |
| 11.088 | 0.9885 | 72.6 |
| 12.526 | 0.9806 | 62.4 |
| 12.859* | — | — |

*Mixture critical pressure

by GC with syringe injection, however, was only 95 mol %. The methyl linoleate was either received with the impurity or may have undergone slight degradation during storage. In any event, the impurities were apparently quite similar to methyl linoleate with respect to molecular weight and functionality: in GC analyses at 463 K with a 2 ft. (0.6 m) column packed with 12% stabilized di-ethylene glycol succinate on Anakrom support (Analabs), they appeared as small shoulders on the methyl linoleate central peak.

## Results and Discussion

The vapor and liquid phase compositions and molar densities measured for the carbon dioxide + decane test system at 313.15 K are presented in Table 1. The apparatus calibration equations relating peak area to density fit the data with RMS deviations of 2.0% for liquid decane and 0.5% for gaseous carbon dioxide. Assuming that the mixture density data are also accurate to within 2.0% for each component, the typical estimated mole fraction uncertainties for these experiments are 0.005 for liquid samples and 0.00005 for vapor samples. The phase composition data are plotted on the pressure-composition (*PXY*) diagram shown in Figure 2. Note that the abscissa is displayed on a broken scale in the diagram, so that all the relevant detail in the measurements can be appreciated. Two sets of data are plotted in the figure: the squares represent the experimental results of Reamer and Sage (1963) at 310.93 K, and the circles represent data obtained in this work.

Despite the 2.2 K difference, all the bubble point data appear to be in good agreement. On the scale of the diagram, one line can correlate all the data reasonably well. There are significant discrepancies in the dew point measurements, however, and these discrepancies cannot be completely accounted for by the 2.2 K difference. On close examination, it appears as if the present vapor phase measurements are more accurate than those of Reamer and Sage. This is not surprising, since the present analytical technique is certainly more sophisticated than the "partial condensation" procedure to which Reamer and Sage were restricted. Although the present measurements only extend between 5.6 and 7.9 MPa, there are five such measurements and they progress in an extremely smooth fashion, in contrast to the scatter apparent in the Reamer and Sage data. Perhaps a more convincing argument, however, can be developed through comparison of molar volume data. A plot of molar volume vs. mixture pressure is shown in Figure 3. In this figure, three sets of data are shown: circles denote data obtained in this work at 313.15 K, squares denote data of Reamer and Sage at 310.93 K, and the solid lines represent data generated from the Bender (1970) equation of state for carbon dioxide at 310.93 and 313.15 K. Within experimental uncertainty, the present results at 313.15 K fall on the curve generated by Bender's equation. This would certainly be expected, since the vapor phase samples were typically 99.9 mol % carbon dioxide and only 0.1% decane. The values of Reamer and Sage, on the other hand, deviate significantly from the corresponding values of Bender's equation for 310.93 K.

Table 3. Phase Measurements of Carbon Dioxide + Methyl Linoleate at 343.15 K

| Pressure MPa | Mol. Frac. | Molar Vol. $cm^3 \cdot gmol^{-1}$ |
|---|---|---|
| | Liquid Phase Measurements | |
| 4.138 | 0.500 | 237.7 |
| 6.923 | 0.656 | 170.2 |
| 11.709 | 0.769 | 119.5 |
| 17.238 | 0.881 | 92.2 |
| 21.305* | — | — |
| | Vapor Phase Measurements | |
| 9.031 | 0.9996 | 197.8 |
| 11.110 | 0.9992 | 131.3 |
| 14.789 | 0.9990 | 90.8 |
| 16.756 | 0.9965 | 74.5 |
| 18.769 | 0.9903 | 68.4 |
| 20.041 | 0.9823 | 66.7 |

*Mixture critical pressure

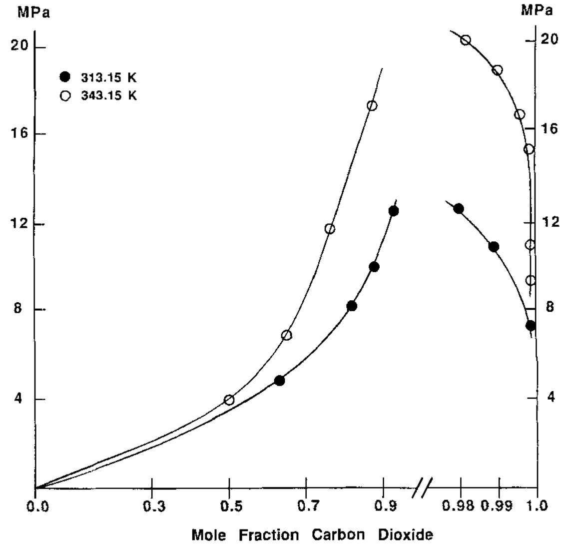

Figure 4. Pressure vs. composition for carbon dioxide + methyl linoleate.

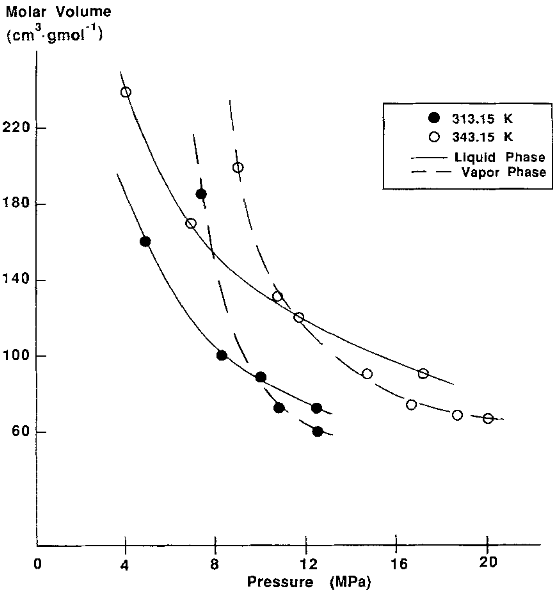

Figure 5. Volumetric data for carbon dioxide + methyl linoleate.

The vapor and liquid phase compositions and molar densities measured for the carbon dioxide + methyl linoleate system at 313.15 and 343.15 K are presented in Tables 2 and 3, respectively. The component density values are again estimated to be accurate to within 2%, and this uncertainty results in a typical mole fraction uncertainty of 0.005 for liquid samples and 0.00005 for vapor phase samples. The data for both isotherms are plotted on the pressure-composition (*PXY*) diagram shown in Figure 4. The mixture critical pressure was taken to be the pressure at which the maximum critical opalescence effects were observed, but phase sampling was not performed at this point. The occurrence of a mixture critical point at moderate pressures is interesting in itself. Although no comparable data are available on similar carbon dioxide + methylated fatty acid systems, some experiments have been performed with the free fatty acids. In these experiments, neither Brunner (1978) nor King et al. (1983) found mixture critical pressures in their studies up to 27.6 MPa. These facts suggest that the methylated form of the fatty acid is likely to be a much better candidate than the acid form for supercritical fluid extraction and fractionation processes.

Other interesting phenomena exhibited by this system are shown graphically in Figure 5, where vapor and liquid molar volumes are plotted against pressure. Although the mass density of the liquid phase was always greater than that of the vapor, it is readily apparent from the figure that the molar volumes for the vapor and liquid phases cross in their approach to equivalence at the critical point. This situation is a likely consequence of the widely differing molecular weights. We will interpret the phase behavior of this system more completely through equation of state correlation work that we expect to report in future publications.

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