Solubility of Surfactant Templates in Supercritical Carbon Dioxide Solutions

Brandon Smeltzer, Sermin G. Sunol, Aydin K. Sunol. University of South Florida, 4202 E. Fowler Ave., Tampa, FL 33620

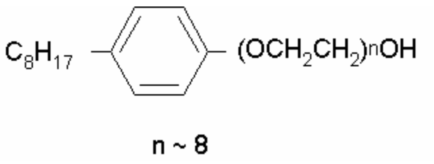
Abstract

Templates are key to the development of porous matrices with tailored pore size distribution and orientation. This presentation focuses on high surface area catalyst synthesis. A template that is soluble in supercritical carbon dioxide with or without an entrainer can be removed from the porous catalyst once the pore structure is formed. Therefore, the solubilities of non-ionic surfactants, Triton X-114 and Tergitol 15-S-9, are presented here. The solubility of each compound is determined using a variable volume, visual cell cloud point phase behavior set-up. Supercritical carbon dioxide plus an entrainer (alcohol) is used as the solvent. The results are modeled using PRSV and extended to other experimental conditions. The experimental mixtures range from 93.2 mol% to 97.6 mol% carbon dioxide with Triton X-114 compositions ranging from $1.93e^{-4}$ mol% to $4.56e^{-4}$ mol%. Observed cloud point pressures range from 95.6 bar to 173.1 bar at temperatures ranging from 35^oC to 60^oC.

Introduction

Supercritical fluids possess interesting and industry applicable characteristics that set them apart from typical solvents. The lack of surface tension, the mobility of a gas, and the solvation power of a liquid are three unique properties that make supercritical fluids very attractive as tunable solvents (McHugh & Krukonis 1986). Supercritical fluids can be used for the selective recovery of solutes by adjusting pressure and temperature.

One engineering field where selective solute recovery can have a major economic impact is novel catalyst design. One of the key components in porous aerogel catalyst production is the template - a surfactant, in this case tert-octylphenoxypolyethoxyethanol (commercially available as Triton X-114) and alkyloxypolyethyleneoxyethanol (commercially available as Tergitol 15-S-9). A template too soluble in a supercritical fluid will be removed too easily from the porous catalyst structure and result in collapsed pores. Too many collapsed pores yield a catalyst with a low surface area. A template completely insoluble in a supercritical fluid will not be removed until a calcination process. A template completely insoluble in a supercritical fluid is harmful in catalyst synthesis because the calcination process may have to be extended to allow for the template to breakdown. An extended calcination time can also lead to the undesired effect of lowering the catalyst surface area.



$CH_3(CH_2)_n(OC_2H_4)_9OH$

Triton X-114

Tergitol 15-S-9

Solubility Determination

The solubility of each surfactant was determined using a static variable volume solubility cell purchased from Thar Technologies. The solubility cell volume can be adjusted from 5 ml to 15 ml. The operating pressure and temperature limits monitored by the controller are 413 bar and 150°C, with an error of ± 0.1 bar and ± 0.1°C, respectively. Figure 1 shows the experimental set-up in its entirety:

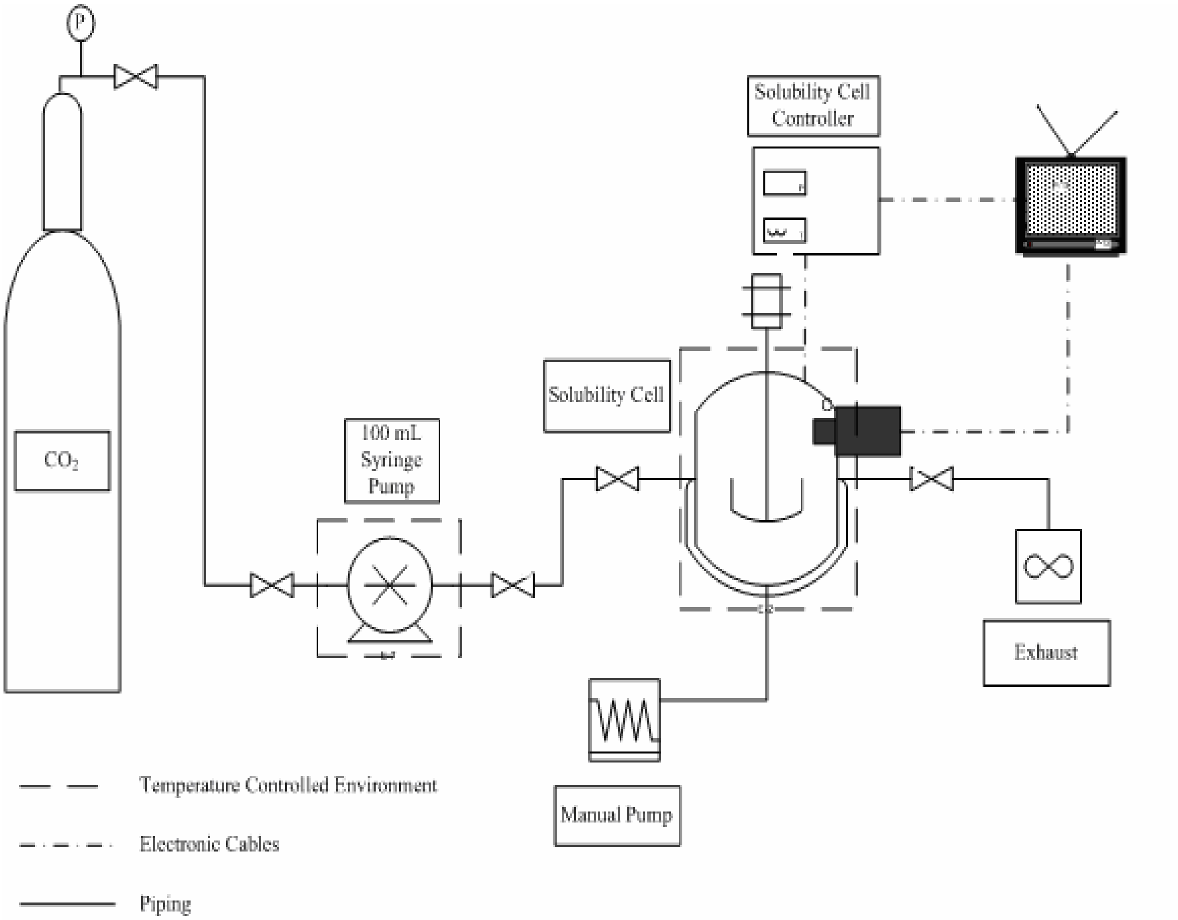


Figure 1. Experimental Set-Up

Carbon dioxide is pumped into an Isco 100DX Syringe Pump. A Lauda Econoline Low-Temperature Thermostat RE120 cools syringe pump to –3°C by circulating antifreeze. The cooling of the syringe pump is done to ensure that the carbon dioxide is in the liquid phase when it is pumped into the solubility cell. The surfactant, Triton X-114 or Tergitol 15-S-9 (Aldrich) is weighed in a beaker then transferred to the open solubility cell. The beaker is reweighed and recorded. HPLC grade ethanol (Aldrich), the entrainer, is weighed in a separate beaker and transferred to the solubility cell. The ethanol beaker is reweighed and recorded.

The solubility cell is then brought to a minimum volume using a Ruska manual pump while still open. Adjusting the solubility cell to a minimum volume is done so that the presence of air can be considered negligible. The solubility cell is then sealed with the magnetic stirrer. Low-pressure carbon dioxide is pumped into the solubility cell while the outlet valve is open to vacate the solubility cell of air completely. The outlet valve is closed and liquid carbon dioxide is pumped into the solubility cell. Once liquid carbon dioxide is visible on the television, the solubility cell volume is slowly expanded to its maximum volume. Liquid carbon dioxide flow into the solubility cell is shut off when the pressure inside the solubility cell increases one to two bars per second.

The pressure inside the solubility cell is allowed to reach equilibrium. After five to ten minutes, the initial pressure and temperature are recorded. The solubility cell is then shifted to a horizontal position such that the liquid-liquid interface is visible in the camera view cell. The magnetic stirrer is turned on to achieve homogeneity and the solubility cell is heated to temperature (35^oC, 40^oC, 45^oC, 50^oC) with the controller and heating element. Once the mixture reaches the experiment temperatures listed above the magnetic stirrer is turned off. A Ruska manual pump then pressurizes the solubility cell by forcing an incompressible fluid (deionized water) to move the piston inside the variable volume solubility cell. Pressurization continues until a cloud is observed in the view cell and the mixture becomes clear again with no discernable liquid-liquid interface. This procedure is continued until five cloud point pressures have been recorded at the experiment temperature. When the mixture is heated from one experimental temperature to the next experimental temperature the magnetic stirrer is turned on.

In between each experiment to determine surfactant solubility in supercritical carbon dioxide, the solubility cell undergoes a detailed cleaning process. The cleaning process is necessary to ensure that no contamination occurs in subsequent runs. After sufficient data points have been collected at experimental temperatures the heating element is turned off and the cell is returned to a vertical position. The outlet valve of the solubility cell is opened such that depressurization occurs at approximately two to three bars per minute. The slow depressurization rate is necessary to prevent clogging in the outlet valve and line.

Once pressure inside the solubility cell is completely released, the magnetic stirrer is unsealed from the top of the machine. The solubility cell is then inverted 180^o to remove the rest of the ethanol-surfactant mixture. The camera, inlet and outlet valves, thermocouple, and light are unplugged from the solubility cell. The solubility cell is then unscrewed from the base of the Supercritical Phase Analyzer. The two o-rings on the bottom of the solubility cell are removed and rinsed thoroughly with deionized water followed by denatured ethanol (Fischer). The o-rings are then allowed to air-dry.

The frit on the movable piston is unscrewed next. The frit is washed thoroughly with deionized water followed by denatured ethanol. The frit is then allowed to air-dry. The piston is rinsed with deionized water followed by denatured ethanol, wiped dry. The piston is then allowed to air-dry.

The stirrer is removed from the magnetic stirrer and rinsed thoroughly with deionized water followed by denatured ethanol. The stirrer is then allowed to air-dry. The solubility cell cap that houses the stirrer is rinsed thoroughly with deionized water followed by denatured ethanol. The solubility cell cap is then allowed to air-dry.

The solubility cell is rinsed thoroughly with deionized water followed by denatured ethanol. The solubility cell is then allowed to air-dry. Air-drying times for all components were a minimum of ten minutes.

After air-drying is complete, the solubility cell components are reassembled. A second cleaning is done at this point with pure carbon dioxide. Liquid carbon dioxide is pumped into the solubility cell, which is at its maximum volume. The flow of liquid carbon dioxide is shut off once the solubility cell is full as evident from pressure increases of one to two bars per second noted on the controller. The magnetic stirrer is turned on to improve cleaning efficiency. This solubility cell cleaning process with liquid carbon dioxide continues for ten minutes, then the solubility cell is depressurized two to three bars per minute.

After the pure carbon dioxide cleaning process, the magnetic stirrer and the solubility cell are removed from the Supercritical Phase Monitor and once again allowed to air-dry.

Results

Experiments were conducted with carbon dioxide and both surfactants, Triton X-114 and Tergitol 15-S-9 as binary systems. At all temperatures, 35^oC to 50^oC, the surfactant Triton X-114 is insoluble in supercritical carbon dioxide up to 320 bar. Similar results were obtained with the carbon dioxide – Tergitol 15-S-9 binary system. Tergitol 15-S-9 is insoluble in supercritical carbon dioxide up to 320 bar at all temperatures from 35^oC to 50^oC. Pressurization beyond 320 bar for both systems was not achieved because the variable volume cell had already reached the five-milliliter minimum volume.

The addition of ethanol as an entrainer to the carbon dioxide-Triton X-114 mixture allows for Triton X-114 to become soluble in supercritical carbon dioxide. Various compositions were examined for the ternary mixture. Table 1 displays the mixture compositions studied for this work.

Table 1. Ternary Mixture Compositions Studied with Triton X-114

Mixture	x_1	x_2	x_3
1	0.9769	0.0229	0.0002
2	0.9466	0.0530	0.0005
3	0.9321	0.0675	0.0004

Carbon dioxide is represented by x_1. Ethanol is represented by x_2. Triton X-114 is represented by x_3. Observed cloud point pressures for the carbon dioxide-ethanol-Triton X-114 ternary mixtures range from 95.6 bar at 35^oC to 143.8 bar at 50^oC. Table 2 shows the cloud pressures reported in bars, observed for each mixture at each temperature.

Table 2. Observed Cloud Point Pressures of Triton X-114 Mixtures

Mixture	35°C	40°C	45°C	50°C
1	99.9	114.65	128.63	143.1
2	95.6	107.43	122.2	134.27
3	n/a	n/a	129.1	143.8

Cloud point pressures are not reported for mixture three at 35°C and 40°C because one phase had already been achieved before the experiment temperature had been attained. Figure 2 shows a P-x diagram for Triton X-114 in the carbon dioxide-ethanol mixture.

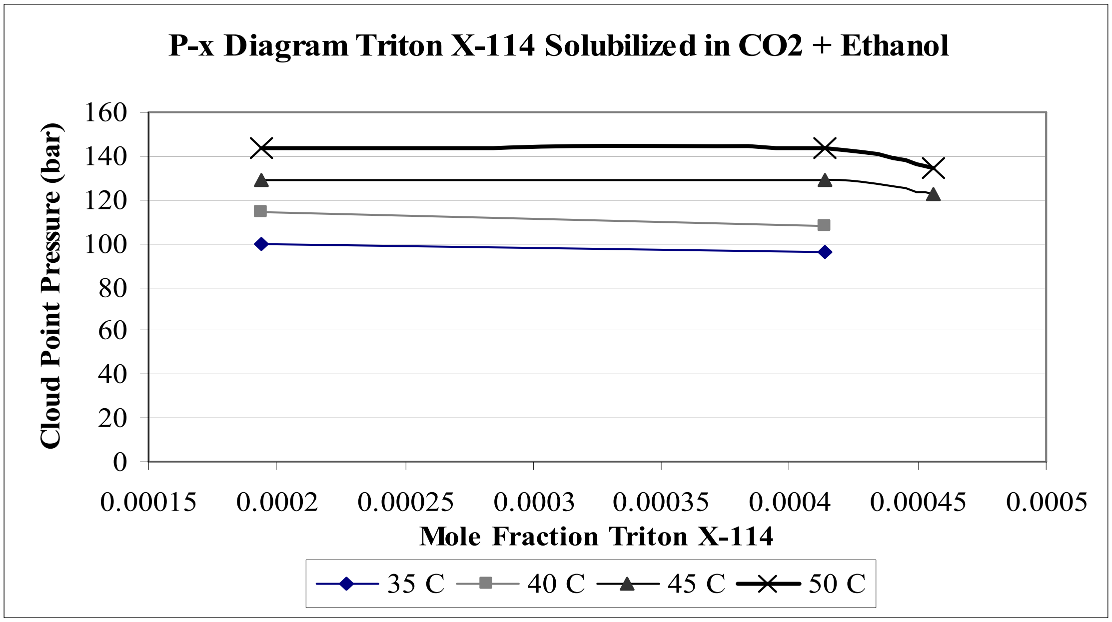


Figure 2. P-x Diagram of Triton X-114 in Carbon Dioxide-Ethanol

Five measurements for cloud point pressure were taken for each temperature. This was done to ensure accuracy and precision in observations. One measure of precision is standard deviation. A lower standard deviation of measurements means precision has been achieved. The highest standard deviation in cloud point pressure measurements at any temperature for this study is ± 0.2588 bar. Table 3 shows the standard deviations of the cloud point pressure measurements in bars for each mixture at each temperature.

Table 3. Standard Deviations of Cloud Pressure Measurements

Mixture	35°C	40°C	45°C	50°C
1	0.2588	0.1225	0.1095	0.1871
2	0.1226	0.2074	0.0707	0.1817
3	n/a	n/a	0.2345	0.1414

The addition of ethanol as an entrainer to the carbon dioxide-Tergitol15-S-9 mixture allows for Tergitol 15-S-9 to become soluble in supercritical carbon dioxide. Various compositions of the ternary mixture were studied. Table 4 shows the compositions of ternary mixtures examined in this study.

Table 4. Ternary Mixture Compositions Studied with Tergitol 15-S-9

Mixture	x_1	x_2	x_3
1	0.9441	0.0557	0.002
2	0.9231	0.0766	0.0003

In this case carbon dioxide is represented by x_1. Ethanol is represented by x_2. Tergitol 15-S-9 is represented by x_3. Observed cloud points for these mixtures range from 89.58 bar to 154.36 bar. Table 5 displays the observed cloud point pressures in bar of the ternary mixtures

Table 5. Observed Cloud Point Pressures of Tergitol 15-S-9 Mixtures

Mixture	35°C	40°C	45°C	50°C
1	125.26	154.36	127.29	116
2	89.58	120	n/a	n/a

Cloud point pressures are not reported for mixture two because one phase had already been achieved before the experiment temperature could be attained. Figure 3 shows a P-x diagram for the carbon dioxide-ethanol-Tergitol 15-S-9 system.

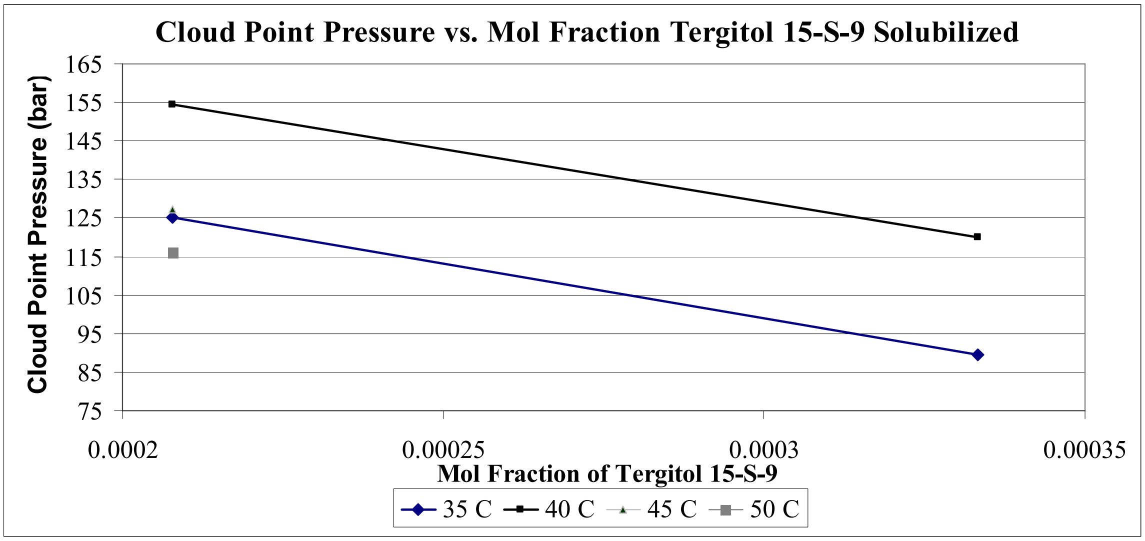


Figure 3. P-x Diagram for Tergitol 15-S-9 in Carbon Dioxide-Ethanol Mixture

Table 6 shows the standard deviations of the cloud point measurements in bar for each mixture at each experiment temperature.

Table 6. Standard Deviations of Cloud Point Pressure Measurements

Mixture	35°C	40°C	45°C	50°C
1	0.2302	0.1342	0.3782	0.1483
2	0.2702	0.1789	n/a	n/a