SUPERCRITICAL CARBON DIOXIDE DETERMINATION OF BENZOPHENONE CLOUD POINT

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INTRODUCTION

Benzophenone is a white crystalline organic substance with a slightly sweet rose geranium scent. In industry it is typically utilized as a photo-initiator, since it breaks down UV light into free radicals when exposed to light. Benzophenone's protects a range of products from inks, perfumes, cleaning products, to pharmaceuticals, and soaps. Adding benzophenone to clear plastic packaging such as food containers prevents UV damage to the contents inside. Benzophenone has also been utilized as biochemical probe to map certain peptide interactions.

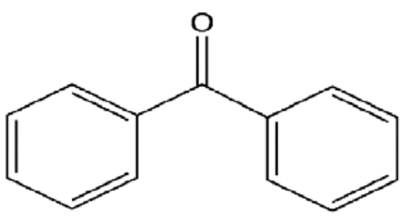

Figure 1. Benzophenone

Utilizing the SFT-Phase Monitor II SFT developed a process to determine the cloud point of benzophenone. The cloud point of a fluid is the temperature at which dissolved solids are no longer completely soluble, precipitating as a second phase giving the fluid a cloudy appearance. Direct, visual observation of materials under supercritical conditions is an important first step in the development and refinement of supercritical fluid extraction, reaction, and chromatographic processes.

The SFT-PM II has a specially designed phase equilibrium view cell is used to observe the dissolution, melting, precipitation, swelling and crystallization of compounds at a wide range of pressures and temperatures. Observations of materials are performed in the supercritical region, under precisely controlled conditions. The SFT-Phase Monitor II simplifies the determination of critical point for binary, tertiary, or complex mixtures. Through a better understanding of phase behavior as a function of temperature, pressure, and sample concentration, a significant time and cost savings for supercritical process development is realized.

Figure 2. SFT-Phase Monitor II

Over the last few decades, a considerable amount of solubility data has appeared in the literature. However, lack of reliable phase equilibrium data has been one of the major obstacles in the progress of SCF technology. In the presence of the solute, the vapor pressure curve for pure CO_2 is shifted ending in a critical end point. The SFT-PM II solves these issues.

Solid solutes when in contact with supercritical CO_2 can exhibit complex phase behavior such as depression in melting point resulting in multiple phases. This depression in melting point can considerably influence the determination of solid solubility. In addition, density inversion could occur which would result in erroneous solubility data. This emphasizes the need for checking the phase equilibrium when measuring solid solubility data. The knowledge of phase behavior of solutes of interest under the SCF conditions is also essential for the development of any SCF process.

Equipment and Materials

- Analytical Balance
- SFT-Phase Monitor II Unit
- Benzophenone

Experimental Procedure

Turn on the power to the SFT-Phase Monitor II. Weigh 0.1 gram of benzophenone and place into the SFT-PM II 30 cc vessel. Seal the SFT-Phase Monitor II 30 cc processing vessel with a 1" wrench. Start the computer and click the SFT Phase Monitor DAQ software icon. Turn Light Control Dial until sample can be properly viewed in screen of SFT Phase Monitor DAQ software.

Open the carbon dioxide with helium headspace tank valve (allowing carbon dioxide to come into the Unit).
Slowly open the inlet valve ½ turn, the 30 cc will fill with gas quickly and pressurize to 1740-1780. Close the inlet and wait for temperature to reach 36ºC. Notice that the pressure will increase into the low 2000 psi range as the cell is being heated.

Once the temperature has reached 36ºC, turn the wheel clockwise until the pressure reaches approximately 6100 psi. Ensure that the pressure doesn't exceed 15 psi/second. Turning the wheel will take approximately 7 minutes.

After approximately 3-4 minutes, turn the wheel clockwise to decrease the pressure to approximately 4900 psi. Continue to turn the wheel clockwise and counterclockwise in the range of 4600-5200 psi*. Oscillating the wheel between 4600-5200 psi will show the transition between the soluble (cloud point) and non-soluble (dissolved) states.

When cloud point is visible, press the stop log button on the DAQ software. Turn the mixer and light control dials to the off position. Set the temperature to ambient and turn wheel counterclockwise to the "0" position on the dial. Slowly open the outlet valve. When pressure and temperature have returned to ambient, shut down the SFT-PM II and the computer. Remove the SFT-Phase Monitor II 30 cc processing vessel with a 1" wrench. Clean out any naphthalene particulates with solvent if necessary.

*See SFT's benzophenone's cloud point video at http://www.supercriticalfluids.com/technical-resources/videos

Results

The following pictures are from the Phase Monitor and DAQ Package experiment of benzophenone. It follows the sequence from dissolved to cloud point back returning to the dissolved state.

Figure 3 depicts dissolved benzophenone in its CO_2 soluble state at 5435 psi.

Figure 3. Dissolved Benzophenone Sample at 5435 psi

Figure 4 depicts the benzophenone sample as pressure is decreased. Precipitation of the sample begins at approximately 5100 psi. The emerging white haze indicates the sample transitioning to the cloud point stage.

Figure 4. Benzophenone Sample at 5108 psi

As the sample is decompressed to the 4800 psi range there is a visible thick white cloud in the view cell of the SFT-PM II. Figure 5 illustrates the fully precipitated and non-soluble benzophenone.

Figure 5. Cloud Point of Benzophenone at 4800 psi

Increasing the pressure will force the sample from transition into the non-soluble to soluble state. The cloud will disappear; the view cell will look clear like in figure 3. You can continue to oscillate the pressure between 5200 psi and 4600 psi to repeat the process as many times as you wish.

CONCLUSIONS

Solubility of materials, including benzophenone, can be determined utilizing the SFT-PM II. The 30 cc view cell will allow visualization specific component's solubility with slight adjustments to temperature or pressure to determine the perfect experimental conditions.

REFERENCES

"Benzophenone." IARC Monographs. International Agency for Research on Cancer, n.d. Web.

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