Solubility of Metal Complexes in Supercritical Carbon Dioxide Solutions

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Abstract

Impregnation of the active component onto the catalyst support and its functionalization is a key step in preparation of catalysts. Impregnation at supercritical conditions is far superior to conventional wet impregnation. The key prerequisite for this process is the solubility of the metal complexes in supercritical fluids. Carbon dioxide, which is the most widely used supercritical fluid fails to dissolve some of these inorganic and organic metal complexes. For this reason modifiers such as alcohols are used.

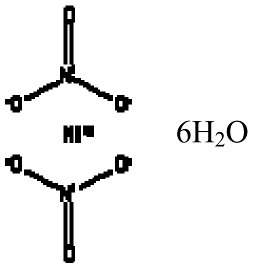
Here, cloud points of materials that are difficult to solubilize are determined. The materials include organic and inorganic catalyst precursor complexes such as Nickel Nitrate and Nickel Acetate. Supercritical carbon dioxide plus and entrainer (alcohol) is used as the solvent. The results are modeled using PRSV and extended to other experimental conditions.

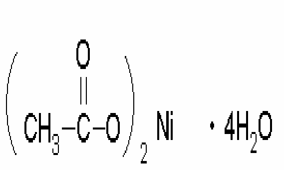
Introduction

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 or deposition of solutes by adjusting pressure and temperature.

One engineering field where supercritical fluid selectivity can have a major economic impact is porous catalyst functionalization. One technique used to functionalize catalyst support is supercritical fluid impregnation to deposit specific groups inside the catalyst pores. In supercritical fluid impregnation the compound with the desired functional group is solubilzed in the supercritical fluid and then passed over the porous catalyst support. The supercritical fluid passes through the porous matrix without collapsing its pore structure while the dissolved substrate is deposited into the pores. The result is a highly porous functionalized catalyst.

To make the supercritical impregnation of a functional group into a porous catalyst a success, the key aspect of the process is the knowledge of the functional group solubility in the supercritical fluid. In this case, the compounds of interest are inorganic metal complexes – nickel nitrate and nickel acetate. The solubility of each nickel complex in the supercritical fluid will play a huge factor in determining how long an impregnation process will take for a specific concentration of nickel inside the porous catalyst matrix.





$$(CH_3-\overset{O}{\overset{\|}{C}}-O)_2Ni \cdot 4H_2O$$

Nickel Nitrate Hexahydrate

Nickel Acetate Tetrahydrate

Solubility Determination

The solubility of each metal complex 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:

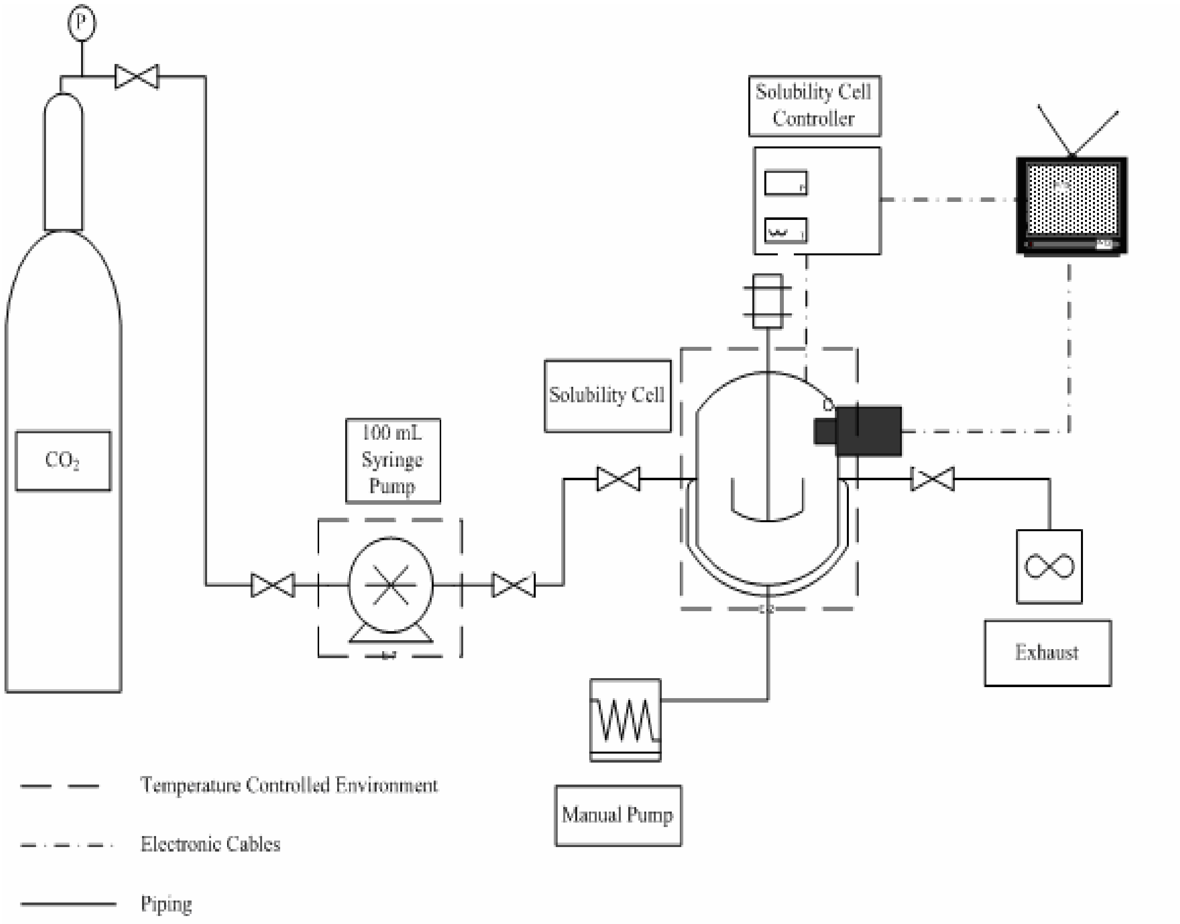


Figure 1. Experimental Set-Up

Carbon dioxide is pumped into an Isco 100DX Syringe Pump. A Lauda Econoline Low-Temperature Thermostat RE120 cools syringe pump to –3^{o}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 metal complex, Nickel Nitrate or Nickel Acetate (Aldrich) is weighed and then transferred to the open solubility cell. The beaker is reweighed and recorded. HPLC grade methanol (Aldrich), the entrainer, is weighed in a beaker and transferred to the solubility cell. The methanol 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°C, 40°C, 45°C, 50°C) 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 metal complex 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° to remove the rest of the methanol-metal complex 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 metal complexes, Nickel Nitrate and Nickel Acetate as binary systems. At all temperatures, 35°C to 50°C, the metal complex Nickel Nitrate is insoluble in supercritical carbon dioxide up to 350 bar. Similar results were obtained with the carbon dioxide – Nickel Acetate binary system. Nickel Acetate is insoluble in supercritical carbon dioxide up to 350 bar at all temperatures from 35°C to 50°C. Pressurization beyond 350 bar for both systems was not achieved because the variable volume cell had already reached the five-milliliter minimum volume.

The addition of methanol as an entrainer to the carbon dioxide-nickel nitrate mixture allows for nickel nitrate to become soluble in supercritical carbon dioxide at relatively low temperatures. 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 Nickel Nitrate

Mixture	x_1	x_2	x_3
1	0.8108	0.1875	$1.7108e^{-3}$
2	0.9058	0.0935	$6.6652e^{-4}$
3	0.9588	0.0411	$1.0969e^{-4}$

Table 2 displays the observed cloud point pressures for each ternary mixture. Above 40°C in each mixture one phase had been observed without further pressurization.

Table 2. Observed Cloud Point Pressures of Nickel Nitrate Mixtures

Mixture	35°C	40°C
1	84.7	83.2
2	84.2	94.5
3	93.6	103.1

The standard deviation for the observed cloud points did not exceed 0.63 bar in any case. Figure 2 shows a P-x diagram of carbon dioxide-methanol-nickel nitrate for this work.

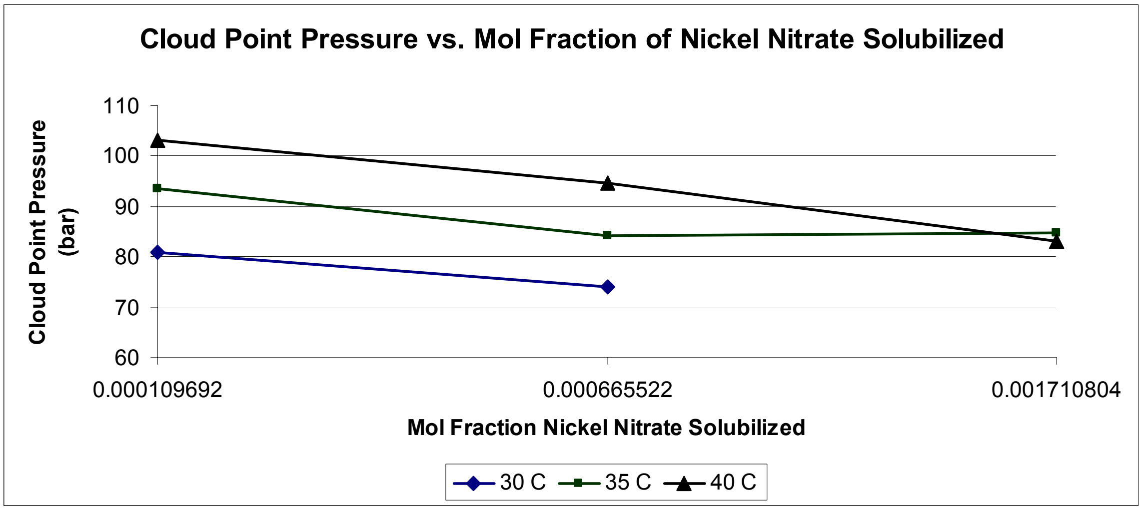


Figure 2. P-x Diagram of Carbon Dioxide-Methanol-Nickel Nitrate

The addition of methanol as an entrainer to the carbon dioxide-nickel acetate mixture allows for nickel acetate to become soluble in supercritical carbon dioxide at relatively low temperatures. Various compositions were examined for the ternary mixture. Table 3 displays the mixture compositions studied for this work.

Table 3. Ternary Mixture Compositions Studied with Nickel Acetate

Mixture	x_1	x_2	x_3
1	0.9410	0.0581	$8.8230e^{-4}$
2	0.9375	0.0621	$4.1863e^{-4}$
3	0.8767	0.1230	$2.5129e^{-4}$

Table 4 displays the observed cloud point pressures for each ternary mixture. Above 40°C in each mixture one phase had been observed without further pressurization.

Table 4. Observed Cloud Point Pressures of Nickel Acetate Mixtures

Mixture	35°C	40°C
1	81.7	80.4
2	83.1	83.7
3	80.6	95.6

The standard deviation for the observed cloud points did not exceed 0.27 bar in any case. Figure 3 shows the P-x diagram of carbon dioxide-methanol-nickel acetate.

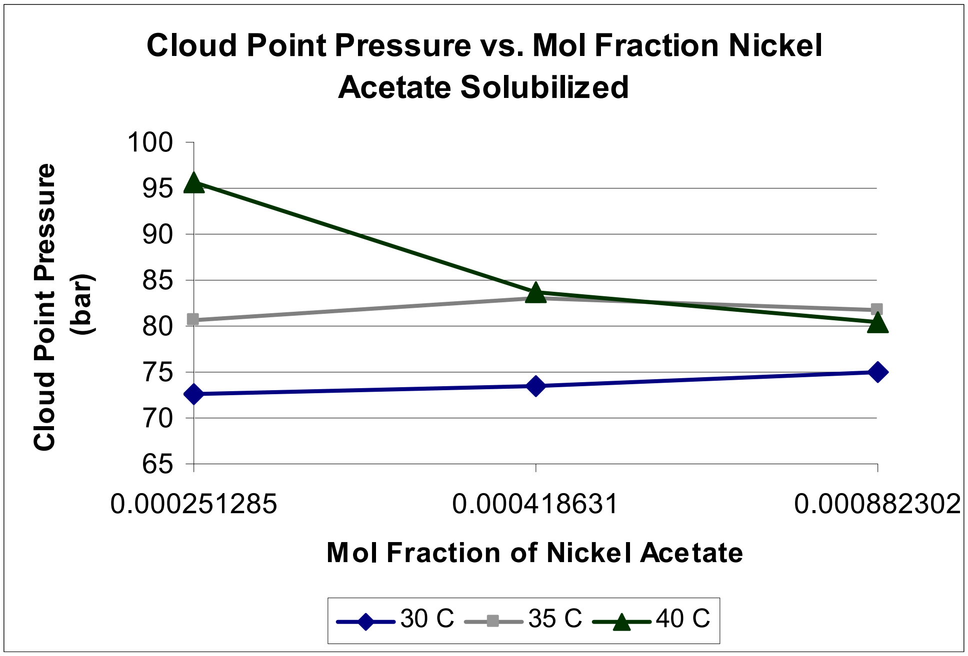


Figure 3. P-x Diagram of Carbon Dioxide-Methanol-Nickel Acetate