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Solubility Measurements of Ferrocene and Acetylferrocene in Supercritical Carbon Dioxide

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INTRODUCTION:

Addressing environmental issues with emissive losses, it is of great importance to use non-volatile solvents for carrying out reactions and separations. For instance, a new method has recently been developed based on miscibility switch phenomena, in which reactions and separations are carried out efficiently in one step in presence of two types of alternative solvents i.e., ionic liquids (ILs) and supercritical carbon dioxide (scCO₂) [1].

When using ILs as solvent for the reaction, in combination with scCO₂ as co-solvent, the reaction can be performed in a homogenous phase by selection of suitable pressure, temperature and CO₂ concentration. After the completion of the reaction, adaptation of the conditions result in a multi-phase system, wherein one of the phases is an IL and at least one of the other phases is a carbon dioxide rich phase, substantially free of IL.

It is our intention to apply the new method on the Friedel-Crafts acylation of Ferrocene (Fc) to Acetylferrocene (AcF) as shown in Figure 1. Previously, it was found that ILs can improve the yield and the conversion of this reaction [2], and that they are also safer than conventional volatile organic solvents, such as dichloromethane, which encounter environmental and health concerns. However, the separation of the product was not straightforward. Here, we investigate the separation of Fc and AcF from the IL phase by using scCO₂ as separation medium. In order to obtain the optimum operational condition of the extraction of the product, it is crucial to study the phase behavior of Fc and AcF in presence scCO₂.

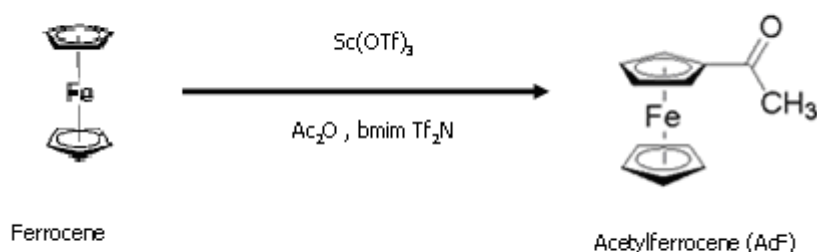


Figure1. Acetylation of Ferrocene to Acetylferrocene

The aim of this work is to measure the solubility data of the above-mentioned organometallic compounds in scCO_2 . The phase behavior of the binary system consisting of $\text{Fc}/\text{AcF} + \text{scCO}_2$ was measured by using an analytical method with a quasi-flow apparatus at (308, 318, 328, 338 and 348) K and pressures between (8 and 24) MPa. High-performance liquid chromatography (HPLC) was applied through an online sampling procedure to determine the concentration of Fc/AcF in the scCO_2 phase.

MATERIALS AND METHODS:

Acetylferrocene was purchased from Merck Schuchardt OHG with a purity of 95%. Ferrocene was purchased from Acros Organics N.V with 98% purity. Carbon dioxide with a quality of 2.7 (99.7% purity) was purchased from Hoek Loos (currently known as Linde Gas Benelux). An analytical method with a quasi-flow apparatus was used to measure the solubility of Fc and AcF in scCO_2 which is illustrated schematically in Figure 2 [3].

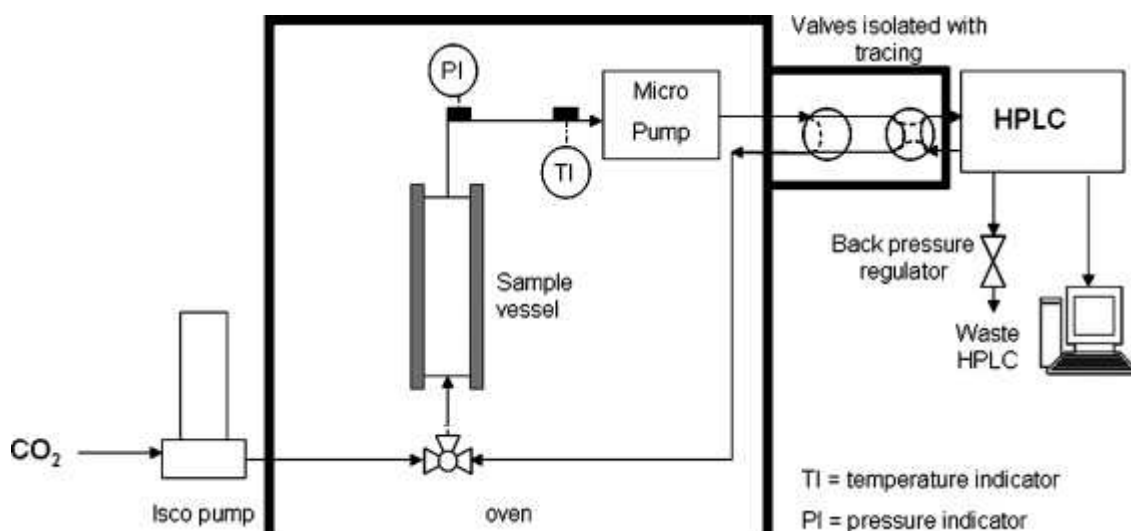


Figure 2. Schematic presentation of the high pressure quasi-flow apparatus [3].

The apparatus is composed of a sample vessel made of sapphire, a micro pump for CO_2 circulation (Micropump INC, model 380), a thermocouple PT-100 with an accuracy of ± 0.1 K and a pressure sensor (EFE-type VLE 700) with an accuracy of ± 0.05 MPa. In order to maintain the constant temperature within the system, all the components were positioned in an oven (Mettmert-type VLE 700).

An online sampling equipped with high performance liquid chromatography (HPLC) was used to measure the concentration of the solutes in the scCO_2 stream during the experiments. A chiral CHIRALPACK[®] (type AD-H, 4.6×250 mm) was used as analytical column with amylose tris (3,5-dimethylphenylcarbamate) as adsorbent and coated on $5 \mu\text{m}$ silica-gel. The mobile phase composed of a mixture of *n*-hexane and ethanol in the proportions 85/15 (v/v) and the flow rate was $1.0 \text{ mL} \cdot \text{min}^{-1}$.

For the solubility measurements first solid samples of Fc/AcF was placed in the sapphire view cell and then system was closed. Then the temperature of the oven was set at desired value. Subsequently, after reaching set point temperature and in order to achieve the required pressure, the system was filled with CO₂ using ISCO pump (model 260D). Circulation of the CO₂ in system was started when the temperature and pressure were stable.

A fixed amount of sample was taken after 4 h for HPLC, and this procedure was successively repeated every 45 min. Once the difference between two consequent measured sample concentrations was less than 0.09×10^{-4} , it was supposed that equilibrium was achieved.

In order to determine the concentration of the solutes in the scCO₂ using HPLC, a calibration line was used. This is possible due to the fact that the peak areas of the compounds obtained from chromatograms are linearly associated to their concentrations by the Lambert-Beer law. Calibration lines were obtained using 6 standard samples with known concentrations where each was injected three times and the average amount were used for the linear regression.

RESULTS AND CONCLUSIONS:

The experimental solubility data of Fc and AcF in scCO₂ was measured using a quasi-flow apparatus. The solubility of Fc and AcF at 308 K is presented in Figure 3. The experimental molar solubility of the product AcF in scCO₂ ranged from 2.5 to $44.5 \cdot 10^{-4}$ at 308 K, which is sufficiently high for separation using the new process set-up.

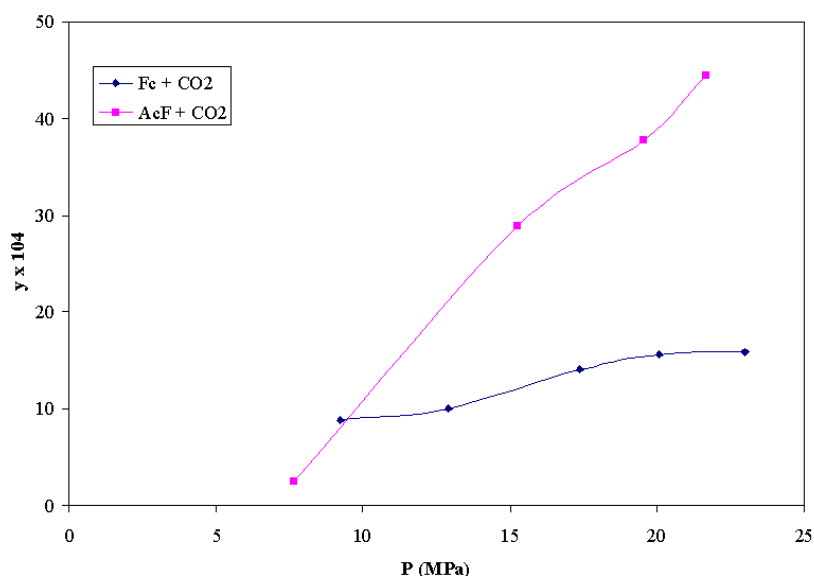


Figure 3. Comparison between solubility of Fc and AcF in scCO₂ at 308 K

The results are used to find the optimal operating conditions for the reaction of Fc to AcF in IL + CO₂ systems and the subsequent separation. Results at other temperatures and the existence of a cross over area will be presented at the conference.

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