

SOLBILITY MEASUREMENTS OF ANTHRACENE TO SUPERCRITICAL CARBON DIOXIDE USING BOTH VALUABLE-VOLUME VIEW CELL WITH ULTRA LOW VOLUME AND HPLC TECHNIQUE

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Introduction

Supercritical carbon dioxide (scCO₂) technology has reached a practical stage. A variety of new substances have been employed in scCO₂ systems with development of the technology. Appropriate solubility data are a key to scCO₂ process design and thus efficient solubility measurement technique for new substances are required. Reducing the amount of sample for the measurement is important, because expensive, toxic or highly flammable reagents are often among the substances for which data is required.

Spectroscopic methods often provide the first approach to solubility measurements with small amount of samples. However, when we choose such methods, we need to consider the change of molar adsorptivity (ϵ) and the spectrum shift occurring with the change of scCO₂ density [1-3]. Thus the molar adsorptivity of the new substances in scCO₂ should be confirmed using appropriate alternative method. This involved procedure complicates solubility measurement of new substances in scCO₂.

We have developed a solubility measurement technique for small amounts of sample using high-performance liquid chromatography (HPLC) and small sized variable volume view cell. Combination of HPLC and scCO₂ systems has been proved to be a beneficial method for solubility measurements [4-6] and, since scCO₂ is dissolved in HPLC eluent before detection, the scCO₂ density and pressure basically do not affect the analysis. In other words, the analysis is independent of molar adsorptivity changes.

In this work, we demonstrate solubility measurement using our newly-developed high pressure equipment, valuable-volume view cell with ultra low-volume (ULV3C) and HPLC. Anthracene (ANT) was employed as a model substance for the solubility measurement, since solubility data have been measured by many research groups [1, 7, 8]. Details of ULV3C are discussed in the other talk in the conference (645e, T. Furuya, et. al.).

Experimental

Figure 1 shows schematic diagram of the sample introduction to ULV3C cell. ANT (Aldrich) dissolved in hexane was introduced to the cell using a syringe. The ANT was then precipitated on the cell window by evaporating the hexane using a nitrogen gas flow through the cell. The ULV3C cell

containing ANT was filled with scCO₂ at 8-20 MPa, 313 K and left to equilibrate for at least 3 hours. Saturation of ANT was confirmed by observing the presence of ANT remaining on the cell window.

Figure 2 shows the interface between ULV3C and the HPLC system. The interface includes an inner-volume type sample injector (sample loop size 2 μl, Valco) and pipework for washing the sample loop. We have designed the system and procedure to minimize reverse flow of HPLC eluent to scCO₂ system and its effect on solubility. The outlet of the sample injector was connected to a silica capillary tube (1 m and 0.15 mm i. d.) for providing back-pressure. The ANT-scCO₂ solution introduced in the sample loop was thus moved slowly and refreshed continuously. Sample injection to HPLC was conducted by manually. The cell pressure was maintained constant by adjusting the piston during these steps. After each injection, the 6-port valve position was changed to flush out the sample loop with CO₂ gas.

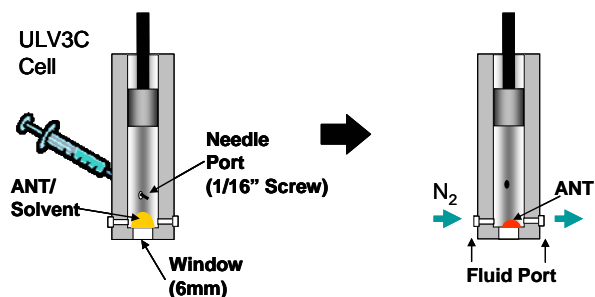


Fig. 1 Schematic diagram of sample introduction to ULV3C cell

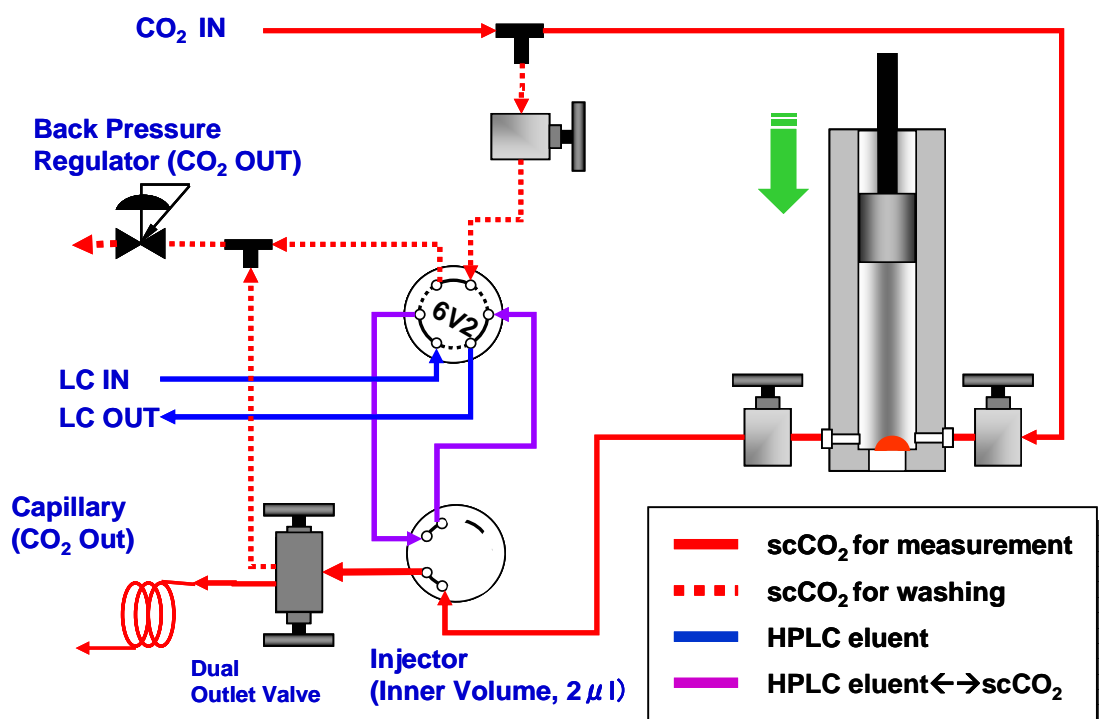


Fig. 2 Schematic diagram of the interface between ULV3C and the HPLC system.

The HPLC system was the same as that in our previous work. The normal-phase (NP) method with silica gel column (GL Science Inertsil SIL100A, 250 mm and 4.6 mm i.d.) and dichloromethane/methanol/hexane (45:45:10 v/v/v) were employed for ANT analysis. A calibration curve for ANT dissolved in the eluent was established before starting analysis with the scCO₂ solution. The injected ANT-scCO₂ solution was mixed and dissolved into the HPLC eluent, and then detected at the detector

after passing through the analytical column. The absorbance at 254 nm was used for analysis. The HPLC analysis was conducted at least 5 times for each condition and the data was processed statistically. The following equation, including the molar concentration of the sample C_2 derived from the analytical curve on the HPLC, defines the solubility y_2 :

$$y_2 = \frac{C_2 \cdot V_{loop}}{(\rho_1 / M_1)V_{loop} + C_2 \cdot V_{loop}} = \frac{C_2}{\rho_1 / M_1 + C_2} \quad (1)$$

Here, V_{loop} is the volume of the sample loop, ρ_1 is the density of the scCO₂ at the measurement temperature and pressure, and M_1 is the molecular weight of CO₂. Because the solubility of the ANT is not particularly high ($y_2 < 10^{-4}$), we assumed that the volume of the solute in the sample loop was negligible. The density of CO₂, ρ_1 , was calculated from the equation of state developed by Span and Wagner [9]. All other details are described in the literature [6].

Results and Discussion

Figure 3 shows the typical appearance of ANT on the cell window (6 mm diameter) before and after the experiment. A few mg of ANT was clearly observed on the window and was enough to confirm saturation.

Table 1 shows the solubility of ANT measured with 7.5 mg of sample. The measurement was conducted five times at each condition and the mean of three data points was used to calculate the average and relative standard deviation (RSD). The RSD value of similar solubility measurements in our previous work, which was acquired using 100mg ANT in a dynamic flow method and HPLC [6], were also shown. Figure 4 compares the solubility profiles at 313 K and 8-20 MPa in this work, with that in our previous work [6] and that in the literature [7-9] are also shown. The data taken using only 7.5 mg sample was in good accordance with other data. The RSD value of this work was comparable to that taken with 100mg ANT on each data point except at 8MPa. Poor reproducibility around 8 MPa may be due to instability of supercritical phase in our experiment. Except in this region our system is confirmed to be useful for solubility measurements with limited sample amounts.

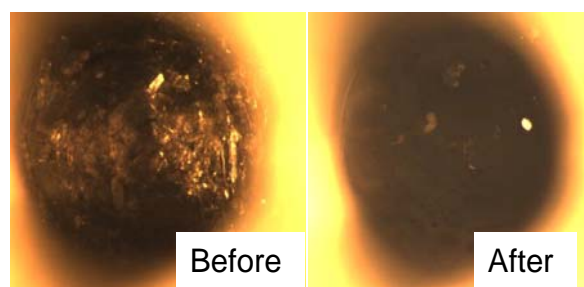


Fig. 3 ANT on the ULV3C cell window (6 mm diameter): Before and after the measurement.

Table 1 Solubility y_2 of antheracene (ANT) (2) in supercritical carbon dioxide (1) at 313K

| P MPa | y_2 | *RSD % | *RSD (100 mg)[6] % |
|----------------------|-----------------------|-----------|-----------------------|
| 8.1 | 1.15×10^{-6} | 66.1 | 58.4 |
| 8.6 | 1.04×10^{-5} | 3.4 | - |
| 9.1 | 2.27 | 5.8 | 20.9 |
| 10.1 | 3.52 | 0.2 | 1.8 |
| 12.5 | 4.98 | 4.3 | 1.4 |
| 14.9 | 5.70 | 2.4 | 3.2 |
| 17.3 | 6.42 | 2.0 | 4.9 |
| 19.8 | 7.93 | 5.1 | 4.2 |
| RSD Average | | 11.1 | 13.5 |
| RSD Average (> 9MPa) | | 3.3 | 6.1 |

**RSD of the data at the similar pressure on the measurement using 100mg antheracene, cyclic dynamic flow method and HPLC [6].

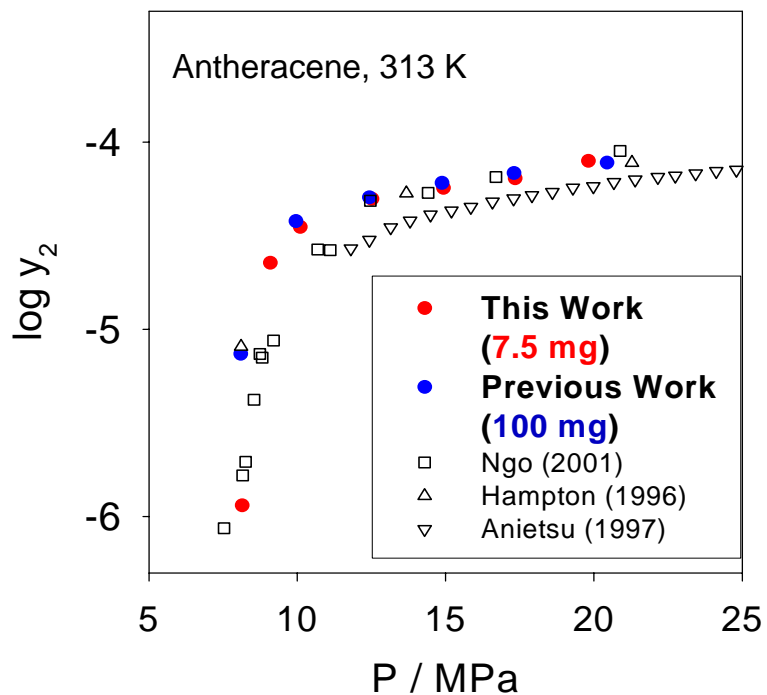


Fig. 4 Profiles of ANT solubility y_2 in $scCO_2$ at 313K, 8-20 MPa using 7.5 mg sample. Reference data were taken from our previous work [6] (using 100 mg ANT) and in the literature [1, 7, 8].

Conclusion

Measurement of the solubility of anthracene in supercritical carbon dioxide using sample sizes of <10 mg, a valuable-volume view cell with ultra low-volume (ULV3C) and HPLC has been performed. This system is promising for solubility measurement of expensive, toxic, flammable and instable substances such as drugs, biomedical reagents, organo-metal complexes and explosives.

Acknowledgement

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