

Measurement of Solubility of Rubrene in Supercritical CO₂ by the Determination of Saturation States Using UV-Visible Spectroscopy and the Correlation

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Organic semiconductors such as an organic thin film transistor (OTFT) have become established as one of the most promising materials to produce thin, lightweight, and flexible electronic devices in the future [1]. Recently, supercritical CO₂ has been used to produce organic thin films by crystallization [2] and to improve the performance of OTFT by surface treatment of thin films [3]. To optimize the operating conditions in the techniques, it is necessary to know the solubility of materials in supercritical CO₂.

The spectroscopic measurement technique is one of powerful tools to measure solubility of solutes (e.g., OTFT materials) poorly dissolved in supercritical CO₂. It requires no sampling of the solutes, which overcomes many of the deficiencies of the flow method. Takahara and Uchida [4, 5] have succeeded in measuring solubility of anthracene and tetracene (naphthacene) in supercritical CO₂ in the pressure range from 8 to 25 MPa and at the temperatures 313.2–373.2 K using the determination of the saturation states (i.e., equilibrium pressures) with a UV-visible spectroscopy, which was the modified method based on the method proposed by Ngo *et al.* [6]. The method can obtain solubility data without performing any calibration prior to the experiments or making any assumptions on the constancy of the molar absorptivity.

In the present work, solubilities of rubrene (5,6,11,12-tetraphenyltetracene) in supercritical CO₂ of pressure range from 18 to 22 MPa and at the temperatures 333.2, 353.2 and 373.2 K were measured by the determination of the saturation states using a UV-visible spectroscopy. Rubrene is a tetraphenyl derivative of tetracene and has attracted much attention because it revealed the highest carrier mobility of all organic semiconductors reported so far ($\mu = 40 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [7]).

A static equilibrium apparatus was used in this work as shown in Fig. 1. Known amounts of solutes were introduced into a high-pressure optical cell (7), having a direct path with two sapphire windows. After loading, the cell was heated to a desired temperature by heating mantle (8). The pressurized CO₂ was then introduced into the cell to a desired pressure, and stirred constantly. The supercritical CO₂ was in contact with solid solutes at the pressure and temperature. Equilibrium of the mixture was observed *in situ* by periodically taking UV spectra of the solution (12). The CO₂ pressure was increased up until there was no further increase in the peak absorbance. The absorbance was plotted versus pressure. As the pressure increased, there was a large increase in solubility. Once all the solute in the cell dissolved, there was an abrupt change in the slope and the absorbance became almost constant. The pressure at saturation was then determined from the intersection of the two linear regions on the graph. At this point, solubility can be calculated by knowing the mass of solute in the cell, the fluid density at saturation, and the cell volume.

The experimental solubilities of rubrene were shown in Fig. 2 together with the solubility of tetracene. The solubilities obtained at the present conditions were in the range from 1.8×10^{-8} to 1.7×10^{-7} in mole fraction, those were about an order of magnitude lower than those of tetracene. The solubilities were correlated by the Soave-Redlich-Kwong (SRK) equation of state with the van der Waals type mixing rules using the binary interaction parameters. The binary interaction parameters were determined to give a good representation of the experimental solubility. The present model gave good correlation results for the experimental data as shown in Fig. 2.

References

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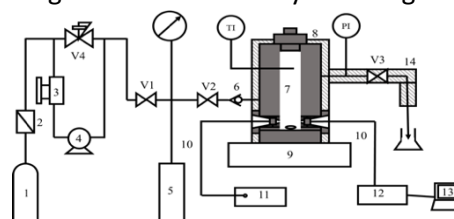


Fig. 1 Schematic diagram of the experimental apparatus.

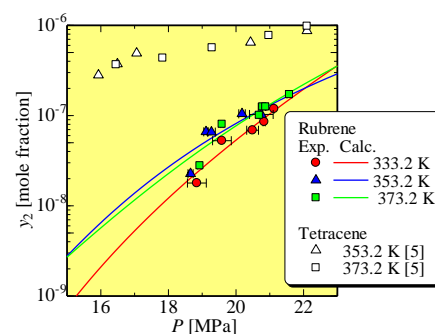


Fig. 2 Experimental and calculated solubilities of rubrene in supercritical CO₂.