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Measurement and correlation of solubility of anthraquinone dyestuffs in supercritical carbon dioxide

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ABSTRACT

Solubility data of 1,4-diaminoanthraquinone (C.I. Disperse Violet 1) and 1,4-bis(ethylamino)anthraquinone (C.I. Solvent Blue 59) in supercritical carbon dioxide (sc-CO_2) have been measured at the temperatures of (323.15, 353.15, and 383.15) K and over the pressure range from (12.5 to 25.0) MPa by a flow-type apparatus. The solubility of two anthraquinone dyestuffs was obtained over the mole fraction ranges of $(1.3 \text{ to } 26.1) \cdot 10^{-7}$ for 1,4-diaminoanthraquinone (C.I. Disperse Violet 1) and $(1.1 \text{ to } 148.5) \cdot 10^{-7}$ for 1,4-bis(ethylamino)anthraquinone (C.I. Solvent Blue 59). The experimental results have been correlated with the empirical equations of Mendez-Santiago–Teja and Kumar–Johnston expressed in terms of the density of sc-CO_2, and also analyzed thermodynamically by the regular solution model with the Flory–Huggins theory and the Peng–Robinson equation of state modified by Stryjek and Vera (PRSV-EOS) with the conventional mixing rules. Good agreement between the experimental and calculated solubilities of the dyestuffs was obtained.

1. Introduction

Recently the supercritical dyeing processes for a waterless dyeing of polyester fibre have come to be newly operated on a commercial and industrial scale after the invention and pioneer work of Schollmeyer group [1] during the last two and half decades. CO_2 is benign and non-flammable and capable of relative easy access to supercritical carbon dioxide (sc-CO_2) due to the lower critical properties. It is well-known that the supercritical CO_2 can dissolve the solid dyestuffs and the solubility of the dye changes with the density increment of CO_2. Eventually supercritical CO_2 is able to separate from the dye mixtures as gas-like CO_2. The supercritical CO_2 dyeing processes benefit by saving the energy of drying process and the waste treatments and by making a recovery and reuse of dyes. In this manner, the supercritical CO_2 dyeing technology has advantages over the conventional wet dyeing process, which needs a large amount of water in a dyeing medium as well as dispersing agents and surfactants in addition to the need to disperse the dye emit wastewater with various toxic chemical additives to the environment. To design and develop proper supercritical dyeing processes, the saturated solubility of dyestuffs in supercritical fluids becomes practically more important. However, the solubility of several anthraquinone dyestuffs and azo dyes in sc-CO_2 has been individually examined and then only a limited number of experimental values for solubilities of dyestuffs in sc-CO_2 is available in the literature [2–9]. A systematic study for the solubility of anthraquinone dyestuffs in sc-CO_2 has been performed from the viewpoints of a series of experimental results and calculation methods so far [10–13]. Therefore we made an attempt to examine the effect of substituent groups onto the anthraquinone to study the solubility difference between substituted anthraquinone and anthraquinone in sc-CO_2 because anthraquinone compounds have a crucial important role in the dyestuffs industry. The present study focused on the solubility of 1,4-diaminoanthraquinone (C.I. Disperse Violet 1) and 1,4-bis(ethylamino)anthraquinone (C.I. Solvent Blue 59) in sc-CO_2 over the temperature range of (323.15 to 383.15) K and the pressures from (12.5 to 25.0) MPa. We examine the solubility of two substituted anthraquinone in sc-CO_2 with respect to the substituent groups onto the anthraquinone. The solubilities of these compounds were analyzed with four different types of correlations: the semi-empirical equations proposed by Mendez-Santiago–Teja [14], Kumar–Johnston [15]; the regular solution model [16] with the Flory–Huggins theory; and the Peng–Robinson equation of state modified by Stryjek and Vera (PRSV-EOS) [17,18] with the conventional mixing rules based on the thermodynamic framework of (solid + liquid) equilibria and (solid + gas) equilibria. The calculated results are compared with the experimental values.

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2. Experimental

2.1. Materials

The dyestuffs of 1,4-diaminoanthraquinone (C.I. Disperse Violet 1, $C_{14}H_{10}N_2O_2$) and 1,4-bis(ethylamino)anthraquinone (C.I. Solvent Blue 59, $C_{18}H_{18}N_2O_2$) used in the experiment are listed in table 1, together with carbon dioxide and other reagents. These compounds were used directly without further purification.

2.2. Apparatus and procedures

The solubility measurement of anthraquinones was carried out using a flow-type apparatus. The apparatus used was the same as in previous works for the solubility experiments [19–21]. The flow diagram of the experimental setup is shown in figure 1. The solid anthraquinone was loaded in the equilibrium cell (150 mm long by 4.4 mm i.d.) packed with glass beads and plugged with glass wool at both inlet and outlet sides of the equilibrium cell to make a uniform flow distribution of the supercritical fluids. Temperature was controlled within ±0.1 K in the oven, and pressure was within ±0.1 MPa, controlled with a back-pressure regulator. Carbon dioxide was delivered from the gas cylinder into the cell at the desired pressure by a high-pressure pump. A liquid carbon dioxide flow rate of 2.5 $cm^3 \cdot min^{-1}$ was determined from preliminary experiments made at different flow rates of (1.5, 2.0, 2.5, 3.0, and 3.5) $cm^3 \cdot min^{-1}$. For the compounds used, the required equilibration and saturation time was around 30 min. at the flow rate of 2.5 $cm^3 \cdot min^{-1}$. After the carbon dioxide in the system reached the equilibrium pressure and temperature, a six-way valve (Rheodyne, model 7060) was turned to permit the flow of carbon dioxide into the cell. The line from the exit of the oven to the back pressure regulator and cold trap was temperature controlled by a flexible heater to prevent it from clogging with dry ice or deposited dye in the flow lines. After every experimental run, the whole line of the apparatus was rinsed with acetone and ethanol, respectively. The solvent remaining in the line was completely removed by flowing fresh carbon dioxide through the line heated at $T = 373.15$ K with the oven and flexible heater. The solutes dissolved into supercritical carbon dioxide were collected by a two-step ice-cold trap filled with ethanol. Absorbance of the absorbed anthraquinone in solution was measured using a UV–visible spectrophotometer (Shimadzu, BioSpec-1600), the anthraquinone concentration was directly determined from the UV-absorbance of the dye. The wavelengths of the light source were set to (549 and 645) nm for the solutions containing 1,4-diaminoanthraquinone and 1,4-bis(ethylamino)anthraquinone. respectively. The solubility of the dyes was calculated from the anthraquinone concentration and volume of carbon dioxide measured by a wet gas meter (Shinagawa, W-NK-1B). Three replicates at least were performed at each experimental condition, and the average uncertainty of the solubility measurements was estimated to be less than ±5.0%.

2.3. Experimental solubility data

The solubilities of the anthraquinone dyestuffs in supercritical carbon dioxide at the temperatures of (323.15, 353.15, and 383.15) K and over the pressure range from (12.5 to 25.0) MPa are given in table 2, along with the supercritical pure CO_2 density calculated by the Span–Wagner equation of state [22]. As shown in figures 2 and 4, the solubility data of 1,4-diaminoanthraquinone (C.I. Disperse Violet 1) at the temperature 353.15 K is in good agreement with the literature [9]. figures 3 and 5 illustrate the experimental results of 1,4-bis(ethylamino)anthraquinone show the same trend in comparison with those measured by Kautz *et al.* [13] at the different temperatures. Our results cover the wide

TABLE 1
Source and purity of chemicals.

Chemicals	Source	Mass fraction purity
1,4-diaminoanthraquinone (C.I. Disperse Violet 1)	Wako Pure Chemicals	>0.96
1,4-bis(ethylamino)anthraquinone (C.I. Solvent Blue 59)	Aldrich	>0.98
Carbon dioxide	Uno Sanso	>0.999
Ethanol	Japan Alcohol Trading Company	>0.99
Acetone	Wako Pure Chemicals	>0.98

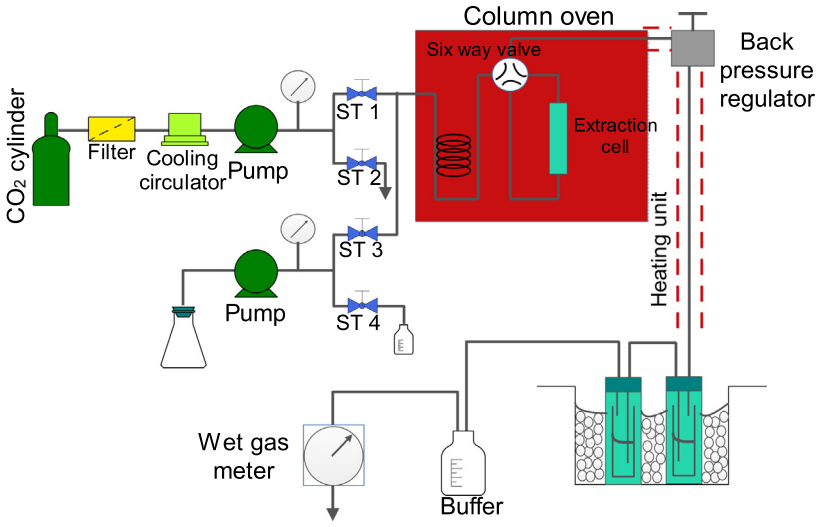

FIGURE 1. The flow diagram of experimental apparatus.