



# Solubility of anthraquinone derivatives in supercritical carbon dioxide



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## ABSTRACT

Solubility data of 1-amino-4-hydroxyanthraquinone and 1-hydroxy-4-nitroanthraquinone in supercritical carbon dioxide have been measured at the temperature of 323.15, 353.15 and 383.15 K and over pressure ranges 12.5–25.0 MPa by a flow – type apparatus. The solubility of 1-amino-4-hydroxyanthraquinone was significantly higher than that of 1-hydroxy-4-nitroanthraquinone. It was found that amino group in 1-amino-4-hydroxyanthraquinone can enhance the solubility of anthraquinone derivatives in supercritical carbon dioxide compared with nitro group in 1-hydroxy-4-nitroanthraquinone. The experimental results were correlated satisfactorily by four types of the density-based models, namely, Mendez-Santiago–Teja, Kumar–Johnston, Chrastil, and Sung–Shim. Moreover accurate representation of the solubility of anthraquinone dyestuffs was obtained by the regular solution model with the Flory–Huggins theory as well as the Peng–Robinson equation of state modified by Stryjek and Vera with the van der Waals one-fluid mixing rule.

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## 1. Introduction

Supercritical Fiber Dyeing (SFD) process [1,2] promising as a water-free dyeing treatment brings a new innovation in the textile dyeing technology from a viewpoint of rising the environmental and energy saving concerns. Currently, the up-to-date SFD system is designed to produce in a commercial scale and is applied to polyester fabrics and polypropylene fiber, but cotton and other natural fibers [3,4]. It is highlighted that SFD can benefit from decreasing emissions of wastewater including various toxic chemical additives to the environment, from reducing excess energy consumption for the drying treatment after dyeing fiber, and from the separation and recycle of excess amount of solid dyes after dyeing treatment through a release of the pressure from the supercritical state to an atmospheric gas, compared with the conventional wet dyeing process that needs a large amount of water in a dyeing medium. Supercritical carbon dioxide (sc-CO<sub>2</sub>) falls into a green solvent and is benign and non-flammable and capable of relatively easy access due to the lower critical temperature and pressure. sc-CO<sub>2</sub> used in the SFD process is a main dyeing medium where the solid dye stuffs can dissolve and plays an important role in the impregnation of the dye into the fiber as well as the

plasticization of the fiber. In particular the density of sc-CO<sub>2</sub> affects significantly the solubility and diffusion of dyes in sc-CO<sub>2</sub>. Besides, the solubility and diffusion of dyes are affected greatly by the affinity due to the molecular interaction between the dyestuff and CO<sub>2</sub> molecule. For these reasons, to find out the physical properties of the dyestuffs in sc-CO<sub>2</sub> have a crucial importance in the design and development for a new dyestuff applicable to the supercritical dyeing process. Among the dyestuffs there are a number of colorant compounds derived from anthraquinone as a backbone. As the experimental data for solubilities of the anthraquinone derivatives in sc-CO<sub>2</sub> available in the open literature is still limited [5–16], our group has ever revealed the solubility of several kinds of anthraquinone derivatives in sc-CO<sub>2</sub> and the solubility change in terms of the functional units on anthraquinone backbone molecule.

The aim of this work is a continuation to examine the effect of functional substituent groups addition onto the anthraquinone to the solubility changes in sc-CO<sub>2</sub>. We focused on the solubility of two anthraquinone dyestuffs; namely, 1-amino-4-hydroxyanthraquinone (C.I. Disperse Red 15) and 1-hydroxy-4-nitroanthraquinone. The solubilities of these compounds were measured and correlated with not only a semi-empirical type of the equations proposed by Mendez-Santiago–Teja [17], Kumar–Johnston [18], Chrastil [19], and Sung–Shim [20], but the thermodynamic framework of solid–liquid and solid–gas equilibria incorporating the regular solution model with the Flory–Huggins theory [5,21] and the Peng–Robinson equation of state modified by Stryjek and Vera (PRSV-EOS) [22,23] with the van der Waals one-fluid mixing rule.

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**Table 1**  
The chemical name, source, and purity of the chemicals.

Chemical name	Supplier	Mass fraction purity/%
1-amino-4-hydroxyanthraquinone (C.I. Disperse Red 15), (C <sub>14</sub> H <sub>9</sub> NO <sub>3</sub> )	Tokyo Chemical Industry CO.,LTD	>98
1-hydroxy-4-nitroanthraquinone (C <sub>14</sub> H <sub>7</sub> NO <sub>5</sub> )	Tokyo Chemical Industry CO.,LTD	>97
Carbon dioxide	Uno Sanso	>99.9
Ethanol	Japan Alcohol Trading Company	>99
Acetone	Wako Pure Chemicals	>98

## 2. Experimental

### 2.1. Materials

The chemical name, supplier, and purity of 1-amino-4-hydroxyanthraquinone (C.I. Disperse Red 15, C<sub>14</sub>H<sub>9</sub>NO<sub>3</sub>, CAS No.: 116-85-8), 1-hydroxy-4-nitroanthraquinone (C<sub>14</sub>H<sub>7</sub>NO<sub>5</sub>, CAS No. 81-65-2), carbon dioxide, ethanol, and acetone used are given in Table 1. These compounds were used directly without further purification.

### 2.2. Apparatus and procedures

The solubility measurements of anthraquinone derivatives were performed using a flow-type apparatus. The flow diagram of the experimental setup and procedure were described in details elsewhere [5,24–26]. Liquefied carbon dioxide was pressurized by a high-pressure liquid pump and delivered into the equilibrium cell placed in a thermostatic oven. Temperature of the oven was controlled with  $\pm 0.1$  K. The equilibrium cell (150 mm long by 4.4 mm i.d.) packed with glass beads was plugged with silica glass wool at both inlet and outlet sides of the equilibrium cell to make a uniform flow distribution of the supercritical fluid. Pressure-control in the cell was carried out by a back pressure regulator (JASCO, 880-81) within  $\pm 0.1$  MPa. Carbon dioxide flow rate of 2.5 cm<sup>3</sup> min<sup>-1</sup> was determined among 1.5–3.5 cm<sup>3</sup> min<sup>-1</sup> from preliminary experiments, and then measuring time needs for a equilibration of the saturated solubility was around 0.5 h. After the system temperature and pressure reached to the equilibrium, a six-way valve (Rheodyne, 7060) was turned to flow the carbon dioxide

into the cell. The flow line from the exit of the back pressure regulator and to the inlet of a cold trap was temperature-controlled by a flexible heater to prevent deposited solid dye from clogging with dry ice in the stream line as the carbon dioxide gas expanded to atmospheric pressure through the back pressure regulator. After every experimental run, the whole line of the apparatus was rinsed with appropriate solvents. The solute remaining in the line was completely removed by flowing carbon dioxide with ethanol through the line heated at 373.15 K with the oven and flexible heater. The solute dissolved into supercritical carbon dioxide was collected by a two-step trap immersed in an ice bath. The trap was filled with ethanol to dissolve the solute and separate from carbon dioxide gas. The concentration of the solute in the ethanol 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 for the absorbance of anthraquinone dyes were set to 533 and 398 nm for the solutions containing 1-amino-4-hydroxyanthraquinone and 1-hydroxy-4-nitroanthraquinone respectively. The solubility of the dyes was calculated from the anthraquinone concentration and gas 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 solubility obtained is the average of these results. The average uncertainties of the solubility measurements for 1-amino-4-hydroxyanthraquinone and 1-hydroxy-4-nitroanthraquinone systems were within 3.1% and 4.4%, respectively.

## 3. Results and discussion

### 3.1. Experimental solubility data

Table 2 shows the solubilities of two anthraquinone dyestuffs in supercritical carbon dioxide measured at the temperature of 323.15, 353.15, and 383.15 K and over the pressure ranges 12.5–25.0 MPa, along with the CO<sub>2</sub> density calculated from the Span–Wager equation of state [27]. In whole the experimental solubility increases with the rise of the system temperature and pressure. The solubility isotherm at 323.15 K has a crossover at pressures of about 17–19 MPa for the isotherms at 358.15 and 383.15 K. It is to be noted that the solubility increases with increasing temperature above the crossover pressure, but below

**Table 2**  
Solubilities of 1-amino-4-hydroxyanthraquinone (C.I. Disperse Red 15) and 1-hydroxy-4-nitroanthraquinone in sc-CO<sub>2</sub>.

T = 323.15 K			T = 353.15 K			T = 383.15 K		
P (MPa)	y <sub>2</sub> <sup>a,b</sup> (× 10 <sup>7</sup> )	ρ <sup>c</sup> (mol·m <sup>-3</sup> )	P (MPa)	y <sub>2</sub> (× 10 <sup>7</sup> )	ρ (mol·m <sup>-3</sup> )	P (MPa)	y <sub>2</sub> (× 10 <sup>7</sup> )	ρ (mol·m <sup>-3</sup> )
<i>1-amino-4-hydroxyanthraquinone (C.I. Disperse Red 15)</i>								
12.5	18.4 ± 0.1	13929.4	12.5	4.33 ± 0.2	7217.7	12.5	9.81 ± 0.7	5385.9
15.0	33.6 ± 0.4	15899.9	15.0	13.6 ± 0.1	9705.9	15.0	19.8 ± 0.0	6887.1
17.5	45.2 ± 0.8	17025.1	17.5	39.1 ± 1.4	11883.8	17.5	51.9 ± 1.3	8441.5
20.0	61.7 ± 1.0	17820.8	20.0	68.4 ± 1.3	13494.5	20.0	94.1 ± 1.6	9926.1
22.5	72.6 ± 0.4	18442.0	22.5	113.5 ± 0.7	14679.4	22.5	138.0 ± 1.4	11247.3
23.5	82.0 ± 2.2	18657.7	23.5	132.5 ± 7.8	15070.8			
25.0	93.2 ± 0.7	18954.7	25.0	177.5 ± 9.2	15592.5	25.0	244.5 ± 3.5	12376.3
<i>1-hydroxy-4-nitroanthraquinone</i>								
15.0	12.2 ± 1.3	15899.9	15.0	6.26 ± 0.2	9705.9	15.0	8.05 ± 0.04	6887.1
17.5	17.2 ± 1.8	17025.1	17.5	17.6 ± 1.2	11883.8	17.5	17.6 ± 0.6	8441.5
20.0	21.7 ± 2.4	17820.8	20.0	28.1 ± 0.3	13494.5	20.0	30.3 ± 0.1	9926.1
22.5	30.1 ± 0.4	18442.0	22.5	39.2 ± 1.0	14679.4	22.5	56.6 ± 0.1	11247.3
25.0	35.9 ± 3.3	18954.7	25.0	53.9 ± 1.8	15592.5	25.0	86.4 ± 2.6	12376.3

<sup>a</sup> Average values of mole fraction taken from triplicate runs.

<sup>b</sup> ±Uncertainties refer to standard deviation.

<sup>c</sup> CO<sub>2</sub> density calculated by Span–Wagner equation of state [24].

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