DYE SOLUBILITY IN SUPERCRITICAL CARBON DIOXIDE FLUID

by

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Supercritical carbon dioxide fluid is an alternative solvent for the water of the traditional dyeing. The solubility of dyestuff affects greatly the dyeing process. A theoretical model for predicting the dye solubility is proposed and verified experimentally. The paper concludes that the pressure has a greater impact on the dyestuff solubility than temperature, and an optimal dyeing condition is suggested for the highest distribution coefficient of dyestuff.

Key words: *supercritical CO_2, disperse dyes, solubility, phase equilibrium, Chrastil association model, distribution coefficient*

Introduction

Carbon dioxide capture, storage, and utilization become the hottest topic in the world as one of the main alternatives for sustainable energy infrastructure development [1, 2]. Supercritical carbon dioxide (SC-CO_2) dyeing is a new clean technology for textile industry, and the dyestuff is recyclable [3]. Solubility of dyestuff is extremely important to develop the SC-CO_2 dyeing process, and much preliminary work was conducted [4-11]. The affinity between dyes and fabric in SC-CO_2 is usually expressed by distribution coefficient of dyestuff, the higher of the coefficient, the higher efficiency of dye utilization and better dyeing effect. However, the theoretical insight into the coefficient is rare and very much preliminary. Therefore, the theoretical and experimental studies on the coefficient are much needed. This paper develops a theoretical model, and an experiment is verified by experimental data.

Experimental

Cotton/polyester (65/35) fabrics, C. I. disperse red 127 ($\geq$ 98%), fig. 1, and pure CO_2 (99.99%) were used in the experiment.

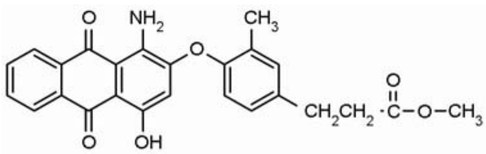

Figure 1. The constitutional formula of C. I. disperse red 127

Experimental set-up includes the reaction unit, control unit, recycle unit, pressure unit, and temperature unit [1].The reaction unit was consisted of a high pressure reaction kettle for dyestuff dissolving. The control unit took the monitoring role of the whole reaction process by controlling the flow rate of CO_2, pressure

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and temperature. The recycling unit referred to separate the dyestuff and CO_2 by decreasing the pressure and temperature, which the dyestuff could be gathered. After recycled, the CO_2 could be used again by increasing pressure, achieving the effect of recycle utilization.

There were two kinds of solubility measurement equipment for the disperse dyestuff in SC-CO_2: continuous and intermittent. Intermittent sampling was referred to put the dyestuff in a sealed container first and the CO_2 is introduced through the pipe. The dyestuff was taken out for analysis after the conditions of high pressure reaction kettle reached the phase equilibrium. But because of the intermittent sampling was more difficult to judge whether all dyestuff is dissolved in the kettle or not, so the continuous sampling device was adopted in this work.

Solubility of dyestuff

The solubility of dyestuff can be expressed by the Chrastil equation [10]:

$$\ln c = k\ln\rho + \left(\frac{a}{T} + b\right) \tag{1}$$

where c is the solubility of solid solute, ρ – the fluid density, T – the temperature, and k, a, and b are constants.

Peng-Robison equation of state (PR-EOS) is adopted hereby:

$$P = \frac{\mathrm{R}T}{v-b} - \frac{a}{v(v+b)+b(v-b)} \tag{2}$$

where

$$a = \frac{0.45724\mathrm{R}^2 T_c^2 \alpha(T_r)}{P_c} \tag{3}$$

$$\alpha(T_r) = [1 + m(1 - T_r^{0.5})]^2 \tag{4}$$

$$m = f(w) = 0.37464 + 1.54226w - 0.26992w^2 \tag{5}$$

$$b = \frac{0.0778\mathrm{R}T_c}{P_c} \tag{6}$$

where a and b are the gravity parameter and repulsion parameter, respectively, R is the universal gas constant for the value of 8.314 J/molK, P – the pressure, T – the temperature, v – the molar volume, P_C – the critical pressure, T_C – the critical temperature, T_r – the reduced temperature, and w – the acentric factor.

Compression factor Z is expressed in the form:

$$Z = \frac{PV}{\mathrm{R}T} \tag{7}$$

The density of CO_2 is defined as:

$$\rho = \frac{M}{V} \tag{8}$$

where M is 44.011 g/mol, and V is the molar volume of CO_2 [cm^{-3}mol^{-1}].

Combining eqs. (7) and (8), eq. (8) becomes:

$$\rho = \frac{MP}{ZRT} \tag{9}$$

When the critical temperature is 304.26 K, critical pressure is 7.39 MPa, ρ_c is 0.448 g/m^3, Z_c is 0.7870. The density of the CO_2 is given in tab.1.

Table 1. The density of SC-CO_2

373.2 [K]	ρ	378.2 [K]	ρ	383.2 [K]	ρ	388.2 [K]	ρ
P [MPa]		*P* [MPa]		*P* [MPa]		*P* [MPa]	
21	497.26	21	473.65	21	445.16	21	430.84
22	523.39	22	489.92	22	465.54	22	452.52
23	554.28	23	516.74	23	483.77	23	471.90
24	579.79	24	532.88	24	501.89	24	492.24
25	602.24	25	556.29	25	524.05	25	512.74

Results and discussion

The solubility of C. I. disperse red 127 in SC-CO_2 was measured under CO_2 flow rate of 500 kg/h, at the temperature of 373.2 K to 388.2 K and pressure of 21 MPa to 25 MPa in the work. The results of the solubility under different condition were shown in fig. 2.

Comparison between the experimental solubility and theoretical prediction is presented as AAD%, which is defined as:

$$AAD\% = \frac{1}{np}\sum_{i=1}^{np}\frac{y_{2i}^{\text{exp}} + y_{2i}^{\text{calc}}}{y_{2i}^{\text{exp}}}100 \tag{10}$$

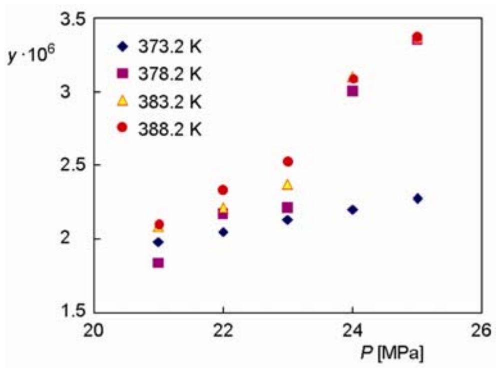

Figure 2. The experimental values of C. I. disperse red 127 in SC-CO_2

where *np* is the experimental number of points, and y_{2i}^{exp} and y_{2i}^{calc} are the solubility of dyestuff obtained from experimental data and calculated by thermodynamic model, respectively. The values of AAD% are listed in tab. 2.

Table2. The parameters of Chrastil equation and average relative error

C. I. disperse red 127	*K*	*b*	*a*	AAD%
			K	
373.2 K	1.979	–547.777	200077.633	8.72
378.2 K	3.6679	–547.777	200077.633	5.17
383.2 K	3.1873	–411.210	166002.295	4.81
388.2 K	2.8242	–411.210	166002.295	2.42
Average value	2.915	–479.494	183039.964	5.28

The continuous sampling method was used to measure the solubility data of C. I. disperse red 127 in SC-CO_2, it is concluded that the solubility in the range of 1.842-3.373·10^{-6} mol/mol in the work. The solubility was increasing when the pressure increased. And because of the solubility increased obviously between 23 MPa and 24 MPa, it indicated that the transition pressure of C. I. disperse red 127 was 23 MPa.

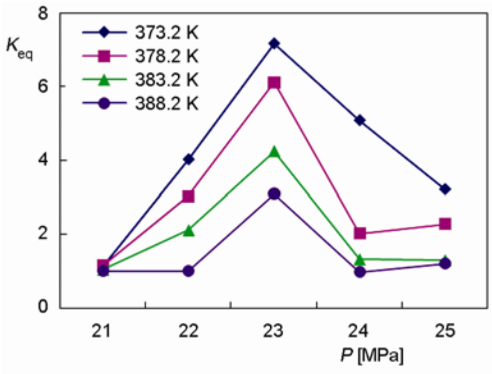

Figure 3. The relation chart between distribution coefficient and pressure in ternary system of C. I. disperse red 127, fabric and SC-CO_2

The distribution coefficient between fabric and CO_2: The cotton/polyester (65/35) fabric was dyed with C. I. disperse red 127 by self-developed SC-CO_2 dyeing equipment. According to the data, the relation among temperature, pressure and distribution was shown in fig. 3.

From fig. 3, the distribution coefficient (K_{eq}) reached the highest at the pressure of 23 MPa. But with the increase of temperature, the distribution coefficient decreased and the change of distribution coefficient was relatively stable under the range of high pressure, showing the rate of dye uptake on the fabric almost equal to the dissolved rate of dyestuff in CO_2.

At the temperature of 373.2-383.2 K, pressure of 21-23 MPa, the concentration of dyestuff both in CO_2 and fabric increase and K_{eq} increased obviously. It was shown that most of dyestuffs dissolved in CO_2 were in combination with fabric and this process was the key period to the dyeing. However, the rate of dyes uptakes on the fabric slowed down with the increase of pressure, even dyestuff desorption appeared. And the distribution coefficient decreased.

Conclusions

The measurement of solubility in SC-CO_2 was studied in this paper. In the experimental conditions, the solubility range of C. I. disperse red 127 was 1.842-3.373·10^{-6} mol/mol for the SC-CO_2-dyestuff binary phase equilibrium system. At the same temperature, when the pressure was lower than 23 MPa, the increase rate of solubility was slower, but the pressure was higher than 23 MPa, the increase rate of solubility was quicker. At the same pressure, with the increase of the temperature, the solubility increased smoothly. From mentioned above, the pressure had a greater impact on the dye solubility relative to the temperature. The results showed that the turning point of C. I. disperse red 127 pressure was 23 MPa. Chrastil associating model, cube state model PR equation and Van der Waals mixed rules were used to do experimental data correlation. Through the model above, the average relative error between the calculated value and experimental value was less than 10%. It was proved to be successful through correlation calculation.

The distribution coefficient of C. I. disperse dyes between fabric and SC-CO_2 was also discussed. Combining with the dyeing data of C. I. disperse red 127 and cotton/polyester (65/35) fabric in SC-CO_2, it was showed that at the temperature of 373.2-388.2 K, pressure of 21-25 MPa, the distribution coefficient of SC-CO_2-dyestuff-fabric ternary phase equilibrium system was 1.006-7.178. At the temperature of 388.2 K, the pressure of 23 MPa, the distribution coefficient was highest, showing the dyestuff had a good affinity on the fabric. The concentration of dyestuff in fabric was higher than in SC-CO_2, which is about $10^2 \sim 10^4$ orders of magnitude. Because of SC-CO_2 dyeing is an exothermic chemical process, raising temperature will reduce distribution coefficient at the same pressure.

Acknowledgments

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