GREEN DYEING OF COTTON FABRICS BY SUPERCRITICAL CARBON DIOXIDE

by

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Green dyeing process with zero waste water emission is a hot topic recently. This paper reveals that supercritical carbon dioxide is the best candidate for this purpose. Effects of thermodynamic parameters, such as enthalpy and entropy of activation, on dyeing process are studied experimentally.

Key words: *supercritical carbon dioxide, cotton fabric, reactive dye, thermodynamics*

Introduction

The conventional aqueous textile dyeing process uses large amounts of clean water. However, waste effluent containing colored compounds and concentrated electrolytes has caused serious environmental problems [1]. In order to overcome this disadvantage, supercritical carbon dioxide (SC-CO_2) dyeing technology was firstly proposed by E. Schollmeyer in 1988. Using SC-CO_2 as solvent to replace water presents the advantages of high uptake rate, short dyeing process, recycling of dyes and CO_2, and zero waste water emission in textile dyeing procedures, which fully complies with clean, green, and environmental manufacturing concept [2].

To date, dyeing of synthetic fibers with SC-CO_2 has been realized successfully, which has high color yields and fastness data with commercially available disperse dyes. However, until now, there are few reports on dyeing procedure of cotton fabrics with reactive dyes in SC-CO_2. In this paper, the dyeing mechanism of cotton fabrics with reactive golden yellow K-2RA was investigated by employing water as the entrainer in SC-CO_2. In addition, thermodynamic properties of reactive golden yellow K-2RA was also studied in SC-CO_2 to better understand the dyeing mechanism of cotton fabrics.

Experimental

Materials and dyeing procedure

Cotton fabrics were obtained from Liaoning Chaoyi Industry & Trade Group. Reactive golden yellow K-2RA ($\geq$ 98%) were supplied by Zhejiang Shaoxing fine chemical industry.

A self-developed batch-type dyeing apparatus was used in the dyeing procedure of SC-CO_2. Water-scoured cotton fabrics were fixed onto a porous dyeing beam and then placed

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into the dyeing kettle. Reactive golden yellow K-2RA dye with a ratio of 5% o. m. f. was packed into a dye cylinder and placed into the dye kettle. The solid dyes were then dissolved with water in SC-CO_2 and flowed through the dyeing kettle in which cotton fabrics would be dyed. The experiments were conducted at dyeing pressure 18 MPa for 10-90 min at dyeing temperatures ranging from 60-120 °C.

Results and discussion

Diffusion coefficient and activation energy diffusion

In the dyeing process, dyes cannot spread into the internal of fibers when the dyeing time is relatively short. According to the diffusion of Fick's second law & Crank, eq. (1), the amount of dye in the fiber at any time is directly related to the square root of dyeing time *t* [3]:

$$\frac{C_t}{C_\infty} = 2\sqrt{\frac{D_f t}{\pi}} \tag{1}$$

In the experiments, C_∞ can be regarded as a constant at a certain temperature, eq. (2) [4]. The values of diffusion coefficient *D* at different temperatures were calculated from the slope of corresponding linear plot by eq. (2) in tab. 1:

$$C_\mathrm{t} = D\sqrt{t} \tag{2}$$

Table 1. Diffusion coefficients of reactive golden yellow K-2RA

Temperature	60 °C	80 °C	100 °C	120 °C
$D \cdot 10^{12}/(\mathrm{m^2 s^{-1}})$	1.0218	1.2086	1.5621	1.6437

From tab. 1, the results indicated the diffusion coefficient was increased as the dyeing temperature increased. This is mainly because the increase of temperature can enhance the proliferation of dyes and promote the diffusion of dyes into fibers, which improves the dye uptake. In addition, when dyes diffused into the cotton fibers, dye concentration on fiber surface was gradually reduced. More dyes could reached the surface of fiber by CO_2 fluid, and then continually diffused into the internal of fibers, thus improving the dye uptake further.

The activation energy of the diffusion was calculated by Arrhenius equation, eq. (3):

$$\ln D = \ln D_0 - \frac{E}{\mathrm{R}T} \tag{3}$$

where D_0 is the Arrhenius factor, R – the constant of air, and *E* – the diffusion activation energy.

It can be seen from fig. 1 that R^2 was 0.9922. Thus, this confirmed that the range of error was small. The activation energy of reactive golden yellow K-2RA was 31.05 kJ/mol. The result showed that as the temperature increased, the activation energy which was related to the diffusion coefficient decreased. Meanwhile, the reaction was occurred in a homogeneous supercritical phase, which is

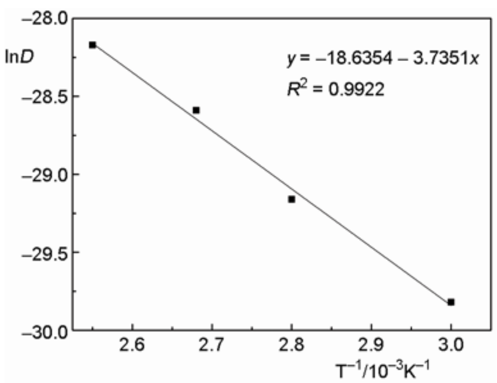

Figure 1. Plot of ln*D* against 1/*T* for determination of diffusion activation energy

less densely than the liquid phase. SC-CO_2 as a dyeing medium had a significant influence on the reaction of the cotton fabrics and reactive dyes.

Enthalpy and entropy of activation

The partition coefficient and standard affinity were calculated by eq. (4) and eq. (5), respectively:

$$K = \frac{q_\infty^f}{q_\infty^s} \tag{4}$$

$$-\Delta\mu^0 = \mathrm{R}T \ \ln \frac{q_\infty^f}{q_\infty^s} = \mathrm{R}T \ \ln K \tag{5}$$

where q_∞^f is the dye uptake of cotton fabrics at the equilibrium, q_∞^s – the dye concentration at the equilibrium in SC-CO_2, $-\Delta\mu^0$ – the affinity of dye molecules to the fiber, R and T are the gas constant and the absolute temperature, respectively. K is the partition coefficient of dyeing reaction.

The enthalpy change ΔH^0 and the entropy change ΔS^0 were calculated using eq. (6):

$$-\Delta\mu^0 = -\Delta H^0 + T\Delta S^0 \tag{6}$$

$$\ln K = -\frac{\Delta H^0}{\mathrm{R}T} + \frac{\Delta S^0}{\mathrm{R}} \tag{7}$$

where ΔS^0 [kJmol^{-1}K^{-1}] is the entropy change of adsorption at different temperature, $-\Delta\mu^0$ [kJmol^{-1}] – the standard affinity, and ΔH^0 [kJmol^{-1}] – the heat of adsorption.

Figure 2 shows the linear relationship between ln$K$ and 1/T for fibers. According to the fitting eq. (7) of fig. 2, the values of the enthalpy ΔH^0 and entropy of activation ΔS^0 for the dye were –14.4 kJ/mol and –35.9 J/molK, respectively. The change of the enthalpy and the entropy are usually employed to describe the dyeing ability of given dyes on a solid substrate according to thermodynamic theory. The value of enthalpy was negative, which indicated that the adsorption of dyes on fibers was an exothermic process and the heat energy was released [5, 6]. The entropy change of dye bath implied the entropy difference between the dye molecules within the fibers and dyeing solution. The thermal motion of dye molecules was limited because of the interaction between dye molecular and fiber, and the degree of chaos was decreased in this thermodynamics system.

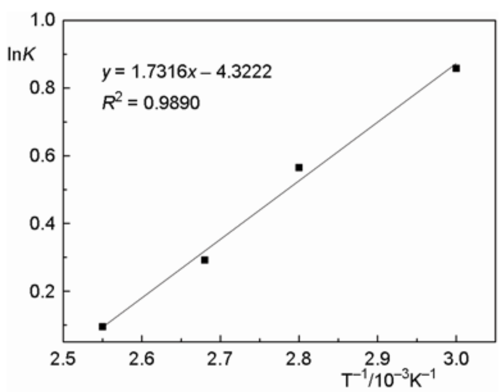

Figure 2. The plot of relationship between ln*K* and 1/*T*

Conclusions

Kinetic and thermodynamic parameters of reactive golden yellow K-2RA for cotton fabrics were investigated in SC-CO_2. The diffusion coefficient was increased as the temperature increased, but diffusion activation energy decreased, which effectively reduce the energy resistance of the dye diffusing into fabrics. Meanwhile, the values of the enthalpy $\Delta H°$ and entropy of activation $\Delta S°$ for the dye were –14.4 kJ/mol and –35.9 J/molK, which demonstrated that the adsorption of reactive golden yellow K-2RA was an exothermic process. Therefore, the mobility and freedom of dye molecules is appreciably reduced after completion of dyeing.

Acknowledgments

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