Diffusion Coefficients of Disperse Dye to PE and PET Films in Supercritical Carbon Dioxide

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The diffusion coefficients of C. I. Disperse Red 13 and C. I. Disperse Blue 134 to polyethylene and polyethylene terephthalate films in supercritical carbon dioxide were measured to understand the dyeing mechanism of the disperse dyes into polymer. Experiments were performed at the pressures from 15 to 25 MPa and the temperatures from 363.15 to 383.15 K. The time dependence was not observed and the diffusion of dyes to polymer films in supercritical carbon dioxide was controlled by the Fick's low within experimental time ranges. The diffusion coefficients of the disperse dyes to polyethylene and polyethylene terephthalate films in supercritical carbon dioxide increase with elevating temperature and pressure.

INTRODUCTION

Recently, the dyeing process using supercritical carbon dioxide has been developed in place of a conventional dyeing. The use of supercritical carbon dioxide dyeing processes expected the decreasing of wastewater compared with the conventional method. Moreover, neither surfactant nor dispersing agent is used, and the drying process is not necessary in the supercritical carbon dioxide dyeing process. Carbon dioxide and the dyes used in the supercritical dyeing process would be recycled and reused.

The solubility and the diffusion coefficient of dyes in supercritical carbon dioxide are essential for the design of supercritical dyeing processes. In our previous works [1-3], the solubility of dyes in supercritical carbon dioxide have been measured and correlated by a cubic equation of states. Sciradi et al. [4, 5] applied a film roll method to measure the diffusion coefficients of dyes to polyethylene terephthalate film in supercritical carbon dioxide. In this work, the diffusion coefficients of disperse dyes to polyethylene (PE) and polyethylene terephthalate (PET) films in supercritical carbon dioxide were measured by using a film roll method in order to understand the dyeing mechanism to polymer in supercritical carbon dioxide.

THEORY [4, 5]

The film roll method was used to determine the diffusion coefficients of the dyes to PE and PET films in supercritical carbon dioxide. **Figure 1** shows the schematic image of film roll method. The film was wrapped tightly around a stainless steel tube of 0.4 cm in diameter. The end of roll was pressed firmly by a thin stainless rod. The top and the bottom of roll were fixed by thread wire. Considering that the dye diffuses into polymer by the

Fick's law and the diffusion is performed above the polymer's glass transition temperature of the polymer, we can derive the following equation.

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \quad (1)$$

The initial and boundary conditions can be expressed as follows.

$$t = 0 \quad x > 0 \quad C = 0 \quad (2)$$

$$t \geq 0 \quad x = 0 \quad C = C_0 \quad (3)$$

$$t \geq 0 \quad x \to \infty \quad C = 0 \quad (4)$$

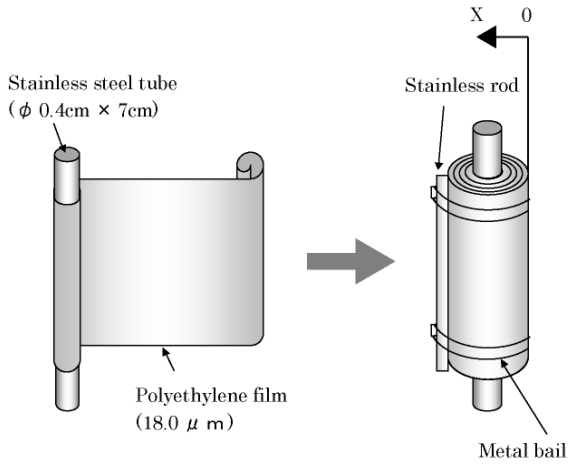

Figure 1 Image of film roll method.

Eq. (1) can be solved using the initial and boundary conditions eq. (2) to (4) and the following equation is obtained [6].

$$\frac{C}{C_0} = erfc\left(\frac{x}{2t^{1/2}D^{1/2}}\right) \quad (5)$$

where C is the dye concentration of each layer, C_0 is the first layer's concentration, x is the radial distance from the surface of roll showed in **Figure 1**, t is the dyeing time, D is the diffusion coefficient.

EXPERIMENT

Materials

C.I. Disperse Red 13 (supplied by Aldrich Chem. Co.) and C.I. Disperse Blue 134 (supplied by Arimoto Chem. Co., Ltd.) were used in this work. LLDPE film supplied by Komatsu Seiren Co., Ltd. (18μm in thickness) was used as the polyethylene film and PET film supplied by Mitsubishi Polyester Film Co., Ltd. (C600-3F, 3μm in thickness) was used as the polyethylene terephthalate film. Carbon dioxide (purity 99.999 %) was obtained from Uno Sanso Co., Ltd.

Experimental Apparatus and Procedure

A flow type apparatus shown in **Figure 2** was used for the experiment. The two columns were set in an oven. After the oven was heated up to the experimental temperatures, carbon dioxide was pumped to the system and pressure regulated by a back pressure regulator. As carbon dioxide flowed through the dyeing column, the film packed in the column was swollen by carbon dioxide before the diffusion experiment. After a steady state was established, a six-way valve was turned around and the dyeing experiment was started. Then the dye packed in the dissolving column was dissolved in supercritical carbon dioxide and supercritical carbon dioxide containing the dye was introduced into a dyeing column for dyeing a polymer film. The dye diffused into the film.

Analysis

After the dyeing experiment was finished, the film was unrolled and cut into the section pieces representing the successive layers. These films of each layer were dipped in test tubes including ethanol. The dye concentration extracted from the section pieces was determined using a UV-spectrometer (SHIMADZU Co., BioSpec-1600).

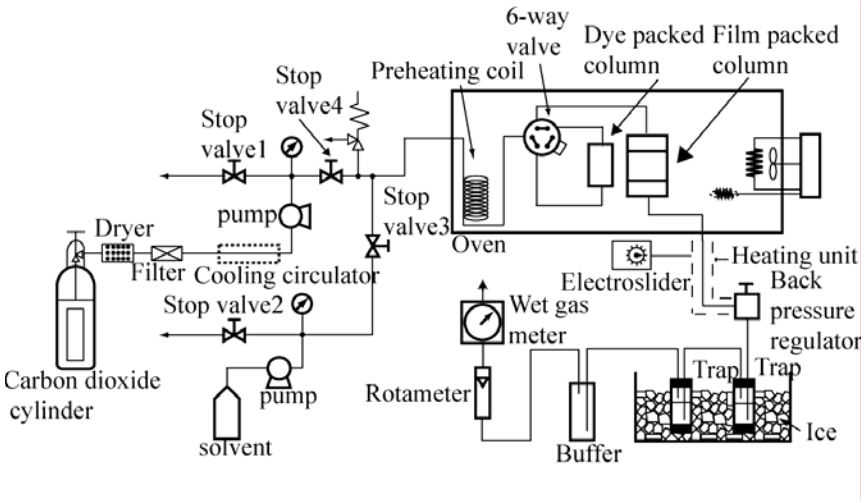

Figure 2 Experimental apparatus.

RESULTS AND DISCUSSION

The diffusion coefficients of the disperse dyes to PE and PET films in supercritical carbon dioxide were measured at the temperatures from 363.15 K to 373.15 K and at the pressures from 15 MPa to 25 MPa. The differences of the diffusion coefficients for the diffusion time, temperature and pressure were considered. Experimental results of diffusion coefficients were listed in **Table 1**.

Influence of diffusion time

The concentration profiles for C. I. Disperse Blue 134 in PE film at 373.15 K and at 25 MPa are shown in **Figure 3**. The diffusion times were 5 and 10 min. The experimental diffusion coefficients for each diffusion time are almost the same values. The time dependence of diffusion coefficients was not also observed for C. I. Disperse Red 13. There are no time dependence in the results for PET film. I It was confirmed that the disperse dyes diffuse into PE and PET films by the Fick's law in supercritical carbon dioxide in these

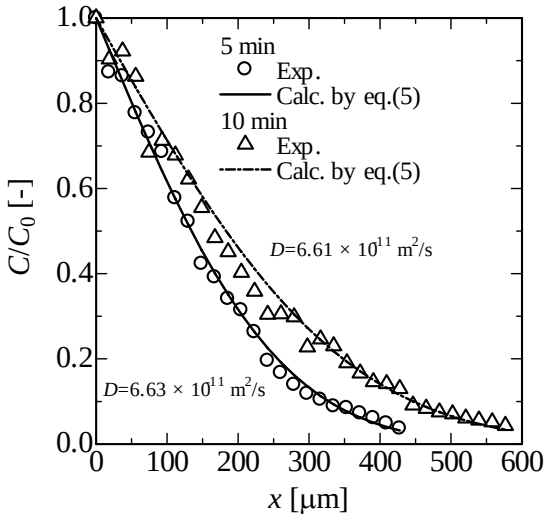

Figure 3 Concentration profiles C. I. Disperse Blue 134 at 25 MPa and 373.15 K dved for 5 and 10 min.

experimental time ranges.

Influence of temperature

The experimental results of diffusion coefficient to PE at 25 MPa are shown in **Figure 4** as a function of temperature. The measuring time was set to 10 min. The results showed linear expression of the Arrhenius equation and the diffusion coefficients increase with elevating temperature. The activation energy of diffusion can be calculated from the slope of the Arrhenius plots. **Table 2** shows the calculated activation energies for diffusion process. The activation energy of C. I. Disperse Red 13 is smaller than that of C. I. Disperse Blue 134. It shows that C. I. Disperse Red 13 would easily dye PE film compared with C. I. Disperse Blue 134. The activation energy of diffusion in water would be about three times larger than that in supercritical carbon dioxide.

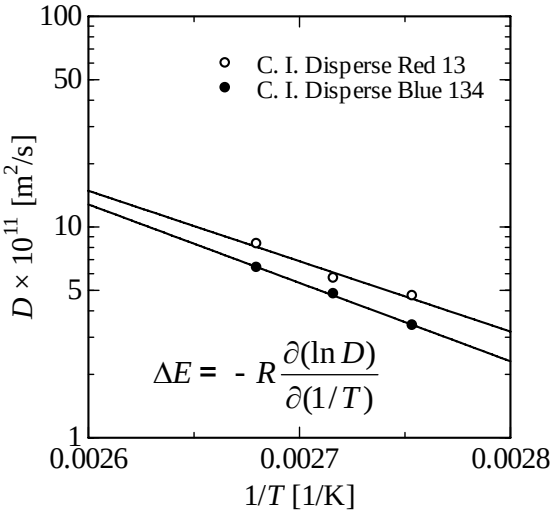

Figure 4 Influence of temperature for diffusion coefficients to PE at 25 MPa.

Influence of pressure

The experimental results of diffusion coefficients for disperse dyes to PE at 363.15 K and 373.15 K are shown in **Figure 5**. The measuring time was set to 10 min. The diffusion coefficients measured at the same temperature were increased with elevating pressure. However, the difference of the diffusion coefficients measured at the different pressures was very small and the pressure dependence of the diffusion coefficients is not remarkable.

Correlation by free volume of polymer

The relationship between mobility and volume rate is proposed by eq.(6) [8].

$$m_{\mathrm{d}} = A\exp(-B/f) \qquad (6)$$

where m_{d} is the mobility, A and B are the parameters for size and shape of solute. f is the volume rate and represented by following equation.

$$f = \frac{v_{\mathrm{f}}}{v} \qquad (7)$$

where v_{f} and v is the free volume and standard volume of polimer, respectively.

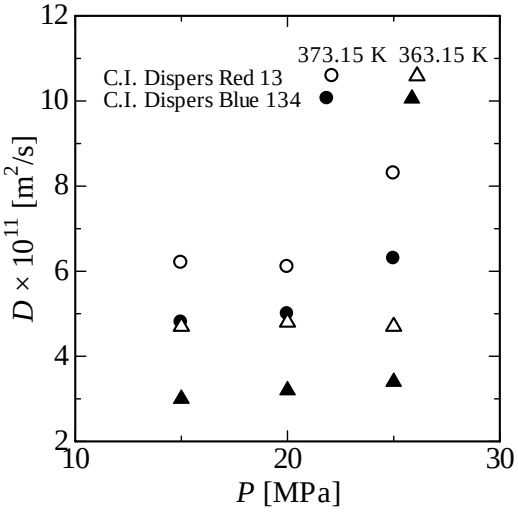

Figure 5 Influence of pressure for diffusion coefficient of disperse dyes to PE.

The relationship between mobility and diffusion coefficient is shown in eq.(8).

$$D \equiv RTm_{\mathrm{d}} \tag{8}$$

where R is the gas constant.

The following equation was derived from eqs.(6)-(8).

$$\ln(\frac{D}{T}) = -\frac{B}{f}\ln(AR) \tag{9}$$

Table 1 Experimental results of diffusion coefficients of disperse dyes in PE and PET films.

	Diffusion coefficient in PE		Diffusion coefficient in PET	
	$D\times10^{11}$ [m^2/s]		$D\times10^{14}$ [m^2/s]	
Experimental condition	5min	10min	30min	40 min
C. I. Disperse Red 13				
383.15K, 25MPa			2.89	2.82
378.15K, 25MPa				1.75
373.15K, 25MPa	8.3	8.3		1.08
373.15K, 20MPa		6.1		0.83
373.15K, 18MPa		6.2		
368.15K, 25MPa		5.7		
363.15K, 25MPa		4.7		
363.15K, 20MPa		4.8		
363.15K, 18MPa		4.7		
C. I. Disperse Blue 134				
373.15K, 25MPa	6.3	6.4		
373.15K, 20MPa		5.0		
373.15K, 15MPa		4.8		
368.15K, 25MPa		4.4		
363.15K, 25MPa		3.4		
363.15K, 20MPa		3.2		
363.15K, 15MPa		3.0		

Table 2 Activation energy for diffusion of disperse dyes to PE and PET

	ΔE [kJ/mol]	
	PE	PET
C.I. Disperse Red 13	64.0	112
C.I. Disperse Blue 134	71.2	

Figure 6 shows the relationship between diffusion coefficient to polymer and volume rate of polymer. The volume rates of polymer were calculated from the data for volume change of polyethylene terephthalate in supercritical carbon dioxide by Schnitzler et al. [9]. The logarithm of diffusion coefficients divided by the temperature shows a linear relationship to the inverse of the volume rate of polymer.

CONCLUSION

The diffusion coefficients of C. I. Disperse Red 13 and C. I. Disperse Blue 134 to PE and PET films in supercritical carbon dioxide were measured by film roll method. The diffusion coefficients of the disperse dyes to polyethylene and polyethylene terephthalate films in supercritical carbon dioxide increase with elevating temperature and pressure. The activation energy of diffusion indicated that C. I. Disperse Red 13 would easily dye PE film compared to C. I. Disperse Blue 134. The diffusion coefficients of disperse dyes to PE and PET films in supercritical carbon dioxide related to the volume rate of polymer.

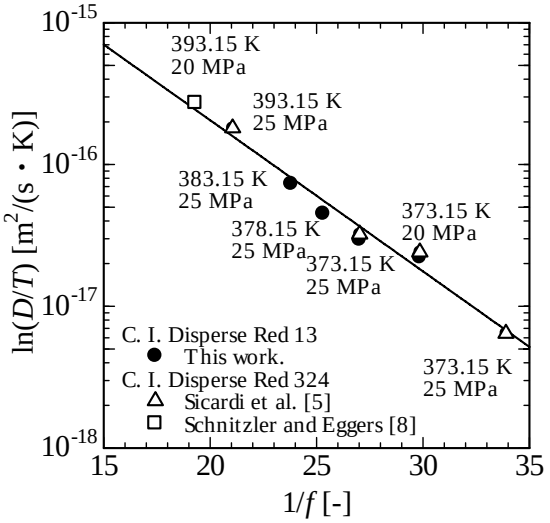

Figure 6 Relation between diffusion coefficients of disperse dyes to PET and volume rate of PET.

ACKNOWLEDGMENT

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