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ORIGINAL CONTRIBUTION

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Transport phenomena of sulfonated dyes into cellulose membrane: Effects of urea on parallel diffusion of mono azo dyes

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Abstract Effects of urea on transport phenomena of sulfonated azo dyes with different aggregation constants into water-swollen cellulose membrane have been studied at 25–55 °C. The results were analyzed on the basis of a parallel transport theory of surface and pore diffusion. Addition of urea decreased equilibrium adsorption of the dyes onto cellulose and increased the surface and pore diffusivities for the parallel diffusion model of the dye with high aggregation constant. Temperature dependence of the effects was also discussed.

Key words Sulfonated dye – cellulose membrane – urea – parallel transport theory – aggregation constant

Introduction

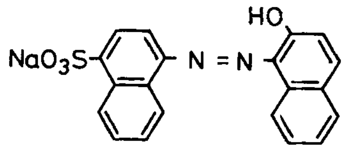
Urea is well known as a water structure breaker [1, 2] and may affect the transport of dyes from solution phase to fiber phase in equilibrium dyeing since the strength of hydrogen bond between urea and water is stronger than that between water and the hydroxyl group of cellulose [3]. However, there have been very few studies of the effects of urea on diffusion of dyes into substrates. In our previous papers [4–11], diffusion behavior of various sulfonated dyes into the water-swollen cellulose membrane has been investigated and analyzed on the basis of a parallel diffusion model consisting of surface and pore diffusion. It was revealed that diffusion of the dyes could be described by the parallel diffusion model, in which dye molecules diffuse in parallel both on the inner surface of the pores of cellulose in the adsorbed state (surface diffusion) and in the liquid phase of the waterfilled pores of cellulose (pore diffusion), in addition, the surface diffusivity of the model correlates with an affinity of the dyes and the pore diffusivity of the model correlates with molecular weight of the dyes with exceptions.

In the present paper, the effects of urea on parallel diffusion of dyes with different aggregation constant have been investigated on the basis of the parallel diffusion model. Furthermore, temperature dependence of the effects of urea is discussed.

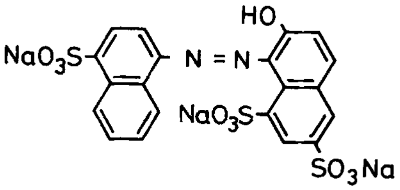
Experimental

Materials

Sulfonated mono azo dyes, C.I. Acid Red 88 (M.W. = 400.4) and C.I. Acid Red 18 (M.W. = 604.5) obtained from Tokyo Kasei Co. were purified by Robinson and Mills' method [12]. The structural formulae and code are shown in Fig. 1. Sodium chloride and urea were obtained from Nacalai Tesque Co. and Schwarg/Mann Division of ICN Biomedicals, respectively. The cellulose membrane (cellophane film) supplied by Rengo Co. was soaked in boiled



C. I. Acid Red 88 (AR88)



C. I. Acid Red 18 (AR18)

Fig. 1 The structural formulae of the dyes

deionized distilled water for 3 h (30 min × 6 times) and then washed with deionized distilled water. The thickness of the water-swollen membrane (l) was 38.6 μm as measured by a membrane thickness meter (Kohbunshi Keiki Co., Lit.). The void function (ε_p) and the volume per unit dry cellulose(V) in a water-swollen state were 0.733 and 2.38 $\mathrm{dm^3/kg}$, respectively, as measured by the pycnometric method [5].

Diffusion of the dye – adsorption isotherms

Equilibrium isotherms for adsorption of the dyes onto the cellulose membrane were measured by the batch method. Sodium chloride was added at 20 or 30 $\mathrm{mol/m^3}$ for C.I. Acid Red 88 (AR88) and 2 $\mathrm{mol/dm^3}$ for C.I. Acid Red 18 (AR18). One or five $\mathrm{mol/dm^3}$ of urea was added in the dye solution. The equilibrium for AR88 was attained in 2, 4, 8, and 16 h at 55, 45, 35, and 25 °C, respectively. The equilibrium for AR18 was attained in 3 h at 25 °C.

Adsorption rates and concentration profiles were measured using an ultrafiltration-type cell with a water jacket (Sartorius SM165 26). The membrane was placed on a plastic plate at the bottom of the cell to establish non-steady-state diffusion as described elsewhere [4]. Uptake curves were generated by the integral step method using one sheet of the membrane. The concentration profiles were measured by placing a stack of 10 membranes together during experiments and separating them for concentration analysis. The amount of the dye adsorbed over a given period was determined by the desorption of the dye from the membrane with 25% aqueous pyridine and measuring its concentration using a Hitachi U-3200 spectrophotometer with 25% pyridine as a reference. Experiments were carried out at 25–55 °C.

Theoretical

In the theoretical development of the diffusion equations, it is assumed that (1) surface and pore diffusion occur in parallel within a cellulose membrane, (2) pore and surface diffusivities are constant during the adsorption process, (3) the pore diameter and the void fraction of the membrane are constant during the adsorption process, (4) the concentration of the dye anions in the pores is in local equilibrium with the concentration of adsorbed dye anions on the surface of the pore wall, and (5) the diffusion of sodium chloride is complete before significant diffusion of the dye molecules. These assumptions lead to the following mass balance equation:

$$\varepsilon_P \frac{\partial C}{\partial t} + \frac{\partial q}{\partial t} = \varepsilon_P D_P \frac{\partial^2 C}{\partial z^2} + D_S \frac{\partial^2 q}{\partial z^2}\,, \tag{1}$$

where C and q are the concentrations of the dye in the pores and on the surface of the pore wall, respectively ($\mathrm{mol/m^3}$). $t(s)$ and $z(m)$ represent time and distance through membrane. ε_P is the void fraction of the membrane. D_P and D_S represent the pore and surface diffusivities, respectively ($\mathrm{m^2/s}$). Using the dimensionless variables defined in Eq. (2), Eq. (1) can be transformed to give Eq. (3).

$$\tau_P = \frac{D_P t}{l^2}\,, \quad \rho = \frac{z}{l}\,, \quad x = \frac{C}{C_0}\,,$$

$$y = \frac{q}{q_0}\,, \quad \alpha = \frac{q_0}{\varepsilon_P C_0}\,, \quad \beta = \alpha \frac{D_S}{D_P}\,, \tag{2}$$

$$\frac{\partial x}{\partial \tau_P} + \alpha \frac{\partial y}{\partial \tau_P} = \frac{\partial^2 x}{\partial \rho^2} + \beta \frac{\partial^2 y}{\partial \rho^2}\,, \tag{3}$$

where C_0 is the dye concentration in the bulk solution and q_0 is the adsorbed concentration of dye in equilibrium with $C_0(\mathrm{mol/m^3})$. There are two limiting cases: $\beta = 0$ (pore diffusion control) and $\beta = \infty$ (surface diffusion control). However, Eq. (3) cannot be solved for $\beta = \infty$, and hence Eq. (1) is transformed to

$$\frac{\partial x}{\partial \tau_S} + \alpha \frac{\partial y}{\partial \tau_S} = \alpha \frac{\partial^2 y}{\partial \rho^2} \quad \text{(surface diffusion control)}\,, \tag{4}$$

where $\tau_S = D_S t / l^2$. The relation between x and y is calculated according to the equilibrium isotherm (fourth assumption). Applying the Freundlich isotherm defined by

Eq. (5), we transformed Eqs. (3) and (4) into Eqs. (6) and (7), respectively.

$$y = x^{\gamma} \tag{5}$$

$$\left[\alpha + \frac{1}{\gamma}\, y^{(1-\gamma)/\gamma}\right]\frac{\partial y}{\partial \tau_{\mathrm{P}}} = \frac{1}{\gamma}\frac{\partial}{\partial \rho}\left[y^{(1-\gamma)/\gamma}\,\frac{\partial y}{\partial \rho}\right] + \beta\,\frac{\partial^2 y}{\partial \rho^2}\,, \tag{6}$$

$$\left[\alpha + \frac{1}{\gamma}\, y^{(1-\gamma)/\gamma}\right]\frac{\partial y}{\partial \tau_{\mathrm{S}}} = \alpha\,\frac{\partial^2 y}{\partial \rho^2}\ \text{(surface diffusion)}\ . \tag{7}$$

The initial and boundary conditions (I.C. and B.C.) are given by Eq. (8):

$$\begin{aligned}&\text{(I.C.)}\ y = 0 \quad \text{at } \tau_{\mathrm{P}} = 0 \text{ or } \tau_{\mathrm{S}} = 0\ ,\\ &\text{(B.C.)}\ y = 1 \quad \text{at } \rho = 0 \qquad \partial y/\partial \rho = 0 \quad \text{at } \rho = 1\ ,\end{aligned} \tag{8}$$

Eqs. (6) and (7) were transformed into finitie difference equations and solved numerically.

Results and discussion

Figure 2 shows the equilibrium isotherms for adsorption of C.I. Acid Red 88 (AR88) with high aggregation constant and C.I. Acid Red 18 (AR18) with low aggregation constant onto the cellulose membrane in the absence [8, 10] and presence of urea at 25 °C. Sodium chloride (20 mol/m^3 for AR88 and 2 mol/dm^3 for AR18) is also added to stimulate adsorption. The adsorption isotherms revealed Freundlich-type adsorption. Apparently, addition of urea decreased equilibrium adsorption for both dyes. Urea is known to increase the solubility of dyes in aqueous solution because urea breaks the structure of water around hydrophobic part of dye molecules and will consequently move the distribution of dyes in favor of the aqueous solution. Thus the chemical potential of dyes in urea aqueous solution is smaller than that in water without urea [3]. Freundlich constants (k and γ of $q_0 = kC_0{}^{\gamma}$) were determined from the intercepts and slopes of the lines and summarized in Tables 1 and 2. When an affinity of a dye on the substrate is high, k becomes large and γ becomes small. The value of α in Eq. (2) was determined and summarized in Tables 1 and 2.

Figure 3 shows the effects of urea on the experimental uptake curves for AR88 measured by using one sheet of cellulose membrane, which show the relation between the amount of the dye in one sheet of cellulose membrane [A′] (mol/kg) and time (min) at 25 °C. The bulk-phase concentration of the dye (C_0) and NaCl (C_{E}) were 0.1 and 30 mol/m^3, respectively. The amount of the dye in one sheet of cellulose membrane was decreased by addition of urea. The solid and broken lines show the theoretical lines for surface diffusion control (Eq. (7)) and pore diffusion control (Eq. (6)), respectively. The experimental data

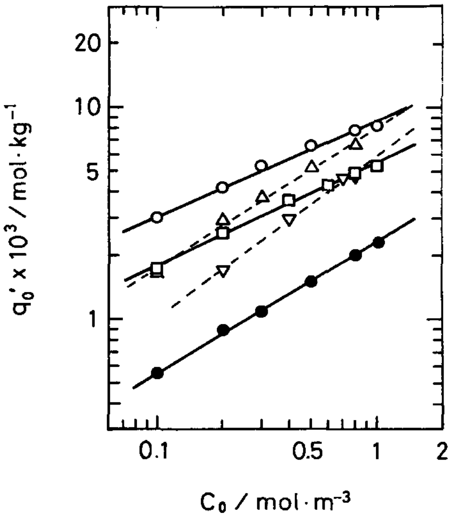


Fig. 2 Adsorption isotherms of C.I. Acid Red 88 (○, □ and ●) and C.I. Acid Red 18 (△ and ▽) on a cellulose membrane in the presence of different concentrations of urea at 25 °C. ○ and △: urea free, □ and ▽: urea 1 mol/dm^3, ●: urea 5 mol/dm^3. C_{E} = 20 mol/m^3 for AR88 and 2 mol/dm^3 for AR18

Table 1 Physical properties in the cellulose membrane – C.I. Acid Red 88 system in the presence of urea at 25 °C

Run No[a]	C_0 [mol/m^3]	C_{E} [mol/m^3]	α	k	γ	$D_{\mathrm{s}}' \times 10^{13}$ [m^2/s]	$D_{\mathrm{p}}' \times 10^{12}$ [m^2/s]
1 (1)	0.1	20	9.87	2.30	0.489	6.12	4.74
2 (1)	0.2	20	7.34	2.30	0.489	6.98	4.02
3 (10)	0.3	20	5.81	2.30	0.489	—	—
4 (1)	0.4	20	5.18	2.30	0.489	8.03	3.24
5 (1)	0.6	20	4.07	2.30	0.489	9.24	2.90
6 (1)	0.8	20	3.51	2.30	0.489	9.90	2.67
7 (1)	1.0	20	3.06	2.30	0.489	11.1	2.59
8 (1, 10)	0.1	30	13.1	3.15	0.501	6.07	6.36
9 (1)	0.2	30	10.0	3.15	0.501	6.38	5.04

[a] The number in parentheses corresponds to the number of sheets of the membrane superposed.

Table 2 Physical properties in the cellulose membrane – C.I. Acid Red 18 system in the presence of urea at 25 °C

Run No[a]	C_0 [mol/m^3]	C_E [mol/m^3]	α	k	γ	$D'_s \times 10^{12}$ [m^2/s]	$D'_p \times 10^{12}$ [m^2/s]
1 (1)	0.2	2	4.87	2.46	0.759	2.71	11.2
2 (1)	0.4	2	4.27	2.46	0.759	2.93	10.7
3 (1)	0.6	2	3.97	2.46	0.759	3.09	10.6
4 (1)	0.7	2	3.84	2.46	0.759	3.25	10.5
5 (1)	0.8	2	3.40	2.46	0.759	3.62	10.2

[a] The number in the parentheses corresponds to the number of sheets of the membrane superposed.

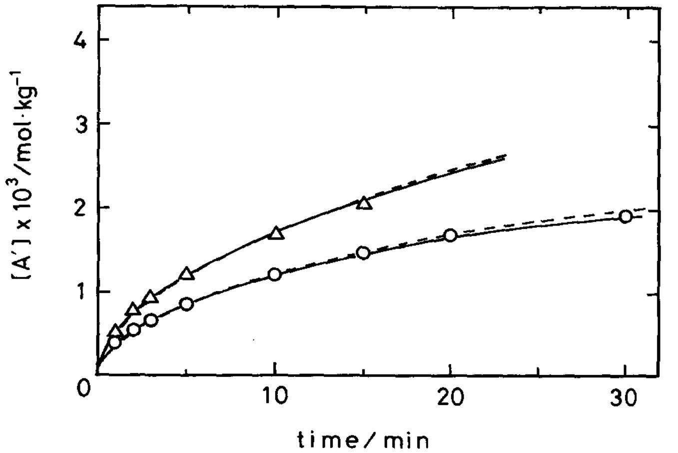


Fig. 3 Effects of urea on uptake curves of C.I. Acid Red 88 at 25 °C. △: urea free and ○: urea 1 mol/dm^3. $C_0 = 0.1$ mol/m^3. $C_E =$ 30 mol/m^3. (——): theoretical line for surface diffusion control [Eq. (7)], (– – –): theoretical line for pore diffusion control [Eq. (6)]

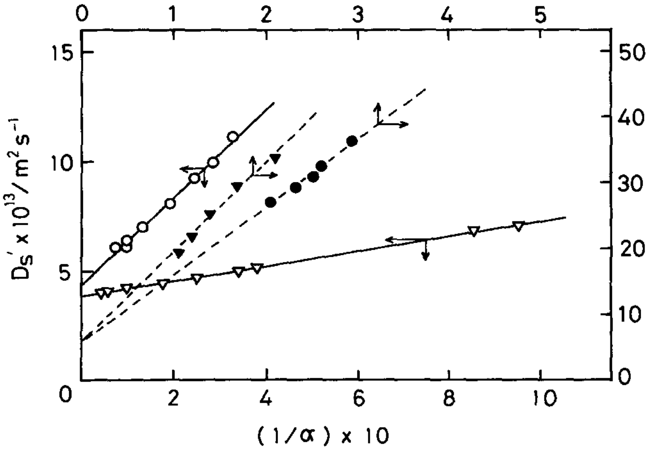


Fig. 4 The relation between the surface diffusivity based on surface diffusion control (D'_s) and 1/α at 25 °C. (○ and ▽): AR88, (● and ▼): AR18, (▽ and ▼): urea free and (○ and ●): urea 1 mol/dm^3

correlated well with both models. Then the surface diffusivity based on the surface diffusion control D'_s (m^2/s) and pore diffusivity based on pore diffusion control D'_p (m^2/s) were determined by matching the experimental values with the theoretical values calculated from Eqs. (7) and (6), respectively (see Tables 1 and 2).

As shown in our previous paper [9], the surface diffusivity of the parallel diffusion model (D_s) can be obtained by plotting D'_s vs. $1/\alpha$, as shown in Fig. 4. The kinetic experiments were carried out at a concentration of urea = 1 mol/dm^3, because the amount of adsorbed dye is very small when 5 mol/dm^3 urea is added as shown in Fig. 2, though the effects of urea on depression of adsorption increases with increasing urea concentration. The change of the degree of swelling by addition of urea was taken to be negligible at the concentration of 1 mol/dm^3 of urea. The plots of D'_s vs. $1/\alpha$ in the presence of urea were correlated by the lines. The increase of D'_s with increasing $1/\alpha$ indicates the increasing contribution of pore diffusion with decreasing α. The difference in slopes of the lines in the absence [8, 10] and presence of urea indicates the change of the pore diffusivity for the parallel diffusion model by addition of urea. The surface diffusivity for the parallel diffusion model D_s could be obtained from the intercept of the line. The intercept showed no significant change by addition of urea for the dyes. Obtained D_s was summarized in Table 3.

Figure 5 shows the relation between D'_p which was determined assuming pore diffusion control and α at 25 °C. It appears that the plots in the presence of urea were correlated by the lines as well as those in the absence of urea [8, 10]. Increasing D'_p with increasing α indicates the increasing contribution of surface diffusion with increasing α. There is little difference in the slopes in the absence and presence of urea. The pore diffusivity for the parallel diffusion model D_p was obtained from the intercept of the line [7] and summarized in Table 3. The values of D_p in the presence of urea is 7 times of that in the absence of urea for

Table 3 Physical properties of the dyes in the cellulose membrane at 25 °C

Dye (C.I. No.) (code)	Urea [mol/dm^3]	C_E [mol/m^3]	α	k	$D_s \times 10^{14}$ [m^2/s]	$D_p \times 10^{13}$ [m^2/s]	β
Acid Red 88[8]	Free	20–30	5.62–22.7	3.61–5.17	36.4	1.97	10.4–41.8
(AR88)	1	20–30	3.06–13.1	2.30–3.15	42.8	13.8	0.949–4.06
Acid Red 18[10]	Free	2000	4.75–9.46	3.46	54.3	91.4	0.282–0.562
(AR18)	1	2000	3.40–4.87	2.46	53.9	79.4	0.231–0.331

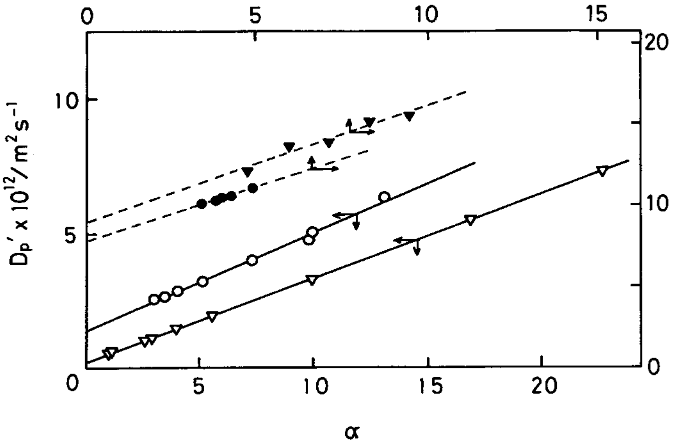


Fig. 5 Effects of α on the pore diffusivity based on pore diffusion control (D_p') at 25 °C. (○ and ▽): AR88, (● and ▼): AR18, (▽ and ▼): urea free and (○ and ●): urea 1 mol/dm^3

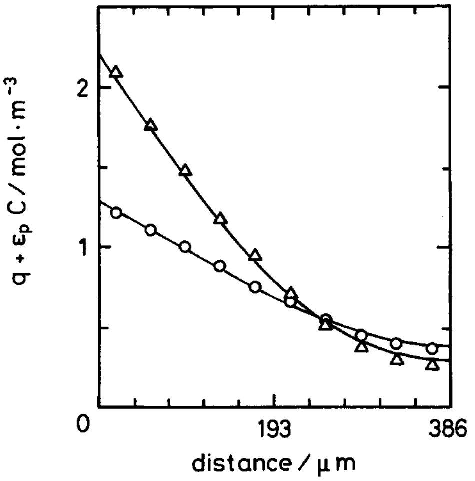


Fig. 6 The concentration–distance profiles in the stacked membrane for AR88 at 25 °C. The solid lines represent the theoretical lines for parallel diffusion calculated using D_s and D_p in Table 3. $C_0 = 0.3$ mol/m^3 and $C_E = 20$ mol/m^3. Diffusion time is 16 h. △: urea free and ○: urea 1 mol/dm^3

AR88. This result might be explained by the fact that urea breaks the regularity of the structure of water around hydrophobic parts of AR88 molecules and consequently increased entropy prevents aggregation of the dye. On the other hand, the value of D_p in the absence of urea is a little larger than that in the presence of urea for AR18. The reason for this is not clear, however, we speculate that the effect of urea as a structure breaker of water is little for AR18 with the low aggregation constant and on the contrary, the action of 2 mol/dm^3 of NaCl as a structure maker of water is enhanced by urea [14].

By the way, the parameter β defined in Eq. (2) is an indicator of the type of controlling diffusion. As described elsewhere [4], diffusion is controlled by surface diffusion for $\beta > 10$. On the other hand, diffusion is almost controlled by pore diffusion for $\beta < 0.1$. Parallel diffusion occurs for $0.1 \leq \beta \leq 10$. Therefore surface diffusion is dominant for AR88 in the absence of urea as seen in Table 3, due to small D_p caused by enhanced aggregation of the dye at 25 °C [8, 12]. Addition of urea increased the contribution of pore diffusion. On the other hand, the magnitude of β for AR18 in the absence of urea is smaller than 0.6. It indicates that the contribution of pore diffusion is larger than that of surface diffusion. Addition of urea made the contribution of pore diffusion larger in diffusion of AR18 due to smaller α.

Figure 6 shows the concentration–distance profiles for AR88 in the presence and absence of urea obtained by placing a stack of 10 membranes together for 16 h during uptake at 25 °C and separating them for concentration analysis. The lines are calculated from the parallel diffusion model using Eq. (6), D_s and D_p in Table 3. The theorectical concentration profiles agree well with the experimental profiles over the entire distance of the membrane. The dye concentration is higher inside the membrane in the presence of urea than that in the absence of urea in the profile at 25 °C as a result of increased D_p, although addition of urea decreased dye concentration near the outer surface of the membrane.

Figure 7 presents Arrehenius plots of D_s and D_p determined at 25, 35, 45, and 55 °C for AR88 in the absence [8]

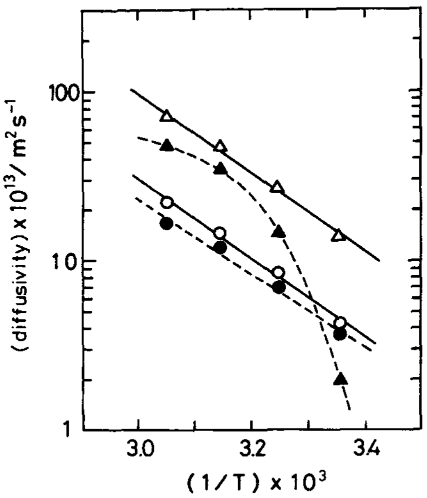


Fig. 7 Arrhenius plots of the surface diffusivity (○ and ●) and the pore diffusivity (△ and ▲) for the parallel diffusion model in the presence (○ and △) and absence (● and ▲) of urea for AR88

and presence of urea. The values of D_s in the presence of urea are higher than those in the absence of urea at any temperature, in which more enhanced effect of urea was observed to D_p in comparison to D_s. The plots of D_p in the absence of urea revealed a curved line with a steep slope at lower temperature and in contrast, the value of D_p in the presence of urea becomes large at lower temperature, and the resulting plots revealed a straight line. This result is consistent with the fact that the regularity of the structure of water is high at lower temperature. The activation energy of surface or pore diffusion in the presence of urea was 44.4 kJ/mol.

Conclusions

Uptake curves and concentration profiles of C.I. Acid Red 88 and C.I. Acid Red 18 on a cellulose membrane were measured at 25–55 °C and analyzed on the basis of the parallel diffusion model to investigate the effects of urea. The following conclusions were made. (1) Diffusion of the systems could be described by the parallel diffusion model. (2) Addition of urea decreased equilibrium dye adsorption for both dyes with different aggregation constants. (3) The surface diffusivity of the model for the dyes was little affected by addition of urea. (4) The pore diffusivity of the model for AR88 with high aggregation constant increased 7 times by addition of 1 mol/dm^3 of urea at 25 °C. (5) Addition of urea decreased dye concentration at the outer surface of the membrane and in contrast, increased dye concentration at inside of the membrane due to the enhanced pore diffusivity for AR88 at 25 °C. (6) Activation energy of surface or pore diffusion of AR88 in the presence of urea was 44.4 kJ/mol.

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