

# Effects of Sulfonated Surfactants on Parallel Diffusion of Mono Azo Dye with High Aggregation Constant into Cellulose Membranes

MASAKO MAEKAWA, CHIYO KAMADA, KIYOMI MIYATA

Division of Life Science and Human Technology, Nara Women's University, Nara 630-8506, Japan

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**ABSTRACT:** The effects of sulfonated surfactants on the adsorption and diffusion of mono azo dye into water-swollen cellulose membranes were studied at 25–55°C. The results were analyzed on the basis of the parallel diffusion theory of surface and pore diffusion. Addition of the surfactants increased the equilibrium adsorption of the dye onto cellulose and the pore diffusivity for the parallel diffusion model. The surface diffusivity for the model was not affected. The temperature dependence of the effects was also discussed. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 1781–1785, 2002

**Key words:** mono azo dye; sulfonated surfactant; cellulose membrane; parallel diffusion theory; aggregation of dye

## INTRODUCTION

A lot of surfactants are used as auxiliaries for textile processing. They are useful as dye solubilizers, dispersing agents, acceleration agents of dye uptake, dye fixing agents, retarding agents, and leveling agents in dyeing processes. It is known that anionic surfactants accelerate adsorption of anionic dyes onto cellulose; however, there are few studies that reveal the effects on the diffusion behavior of the dyes into the substrate immersed in the surfactant solution.

In our previous articles<sup>1–9</sup> we elucidated the diffusion behavior of sulfonated dyes into the water-swollen cellulose membranes on the basis of the parallel diffusion model, which consists of surface and pore diffusion. It was revealed that the dye molecules diffuse in parallel on the sur-

face of the pore wall and in the pores of the cellulose.

In the present article we elucidate the effects of sulfonated surfactants on the adsorption and diffusion of a dye with a high aggregation constant on the basis of the parallel diffusion model. The results are compared with those obtained in the aqueous solutions of sodium chloride or urea.

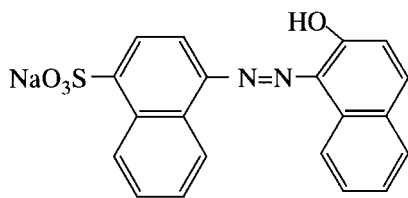
## EXPERIMENTAL

### Materials

The sulfonated mono azo dye CI Acid Red 88 (AR88, MW = 400.4, Tokyo Kasei Co.) was purified by the Robinson and Mills method.<sup>10</sup> The structural formula of the dye is shown in Figure 1. The sulfonated surfactants lauryl benzene sulfonic acid sodium salt (LAS, MW = 348.48) and sodium dodecyl sulfate (SDS, MW = 288.38) were obtained from Nacalai Tesque Co. and used after drying. The cellulose membrane (cellophane film, Rengo Co.) was soaked in boiled deionized dis-

Correspondence to: M. Maekawa (maekawa@cc.nara-wu.ac.jp).

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**Figure 1** The structural formula of CI Acid Red 88 used in the study.

tilled water for 3 h (30 min  $\times$  6 times) and then washed with deionized distilled water. The thickness of the water-swollen membrane ( $l$ ) was 38.6  $\mu\text{m}$  as measured by a membrane-thickness meter (Kohbunshi Keiki Co., Ltd.). The void fraction ( $\epsilon_P$ ) and the volume per unit dry cellulose ( $V$ ) in a water-swollen state were 0.733 and 2.38  $\text{dm}^3/\text{kg}$ , respectively, as measured by the pycnometric method.<sup>3</sup>

### Diffusion of Dye: Adsorption Isotherms

Equilibrium isotherms for adsorption of the dye onto the cellulose membrane were measured by the batch method. The concentration of SDS added in the dye solution was 8  $\text{mol}/\text{m}^3$  (ca. critical micelle concentration), and that for LAS was 3  $\text{mol}/\text{m}^3$  (ca. critical micelle concentration). The equilibrium adsorption for AR88 was attained in 2, 4, 8, and 16 h at 55, 45, 35, and 25°C, respectively.

The adsorption rates 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.<sup>2</sup> Uptake curves were generated by the integral step method using one sheet of the membrane. The amount of 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.

### THEORETICAL

The following mass balance equation described elsewhere<sup>1,2</sup> was adapted to the diffusion of the dye in the surfactant solution:

$$\epsilon_P \frac{\partial C}{\partial t} + \frac{\partial q}{\partial t} = \epsilon_P D_P \frac{\partial^2 C}{\partial z^2} + D_S \frac{\partial^2 q}{\partial z^2} \quad (1)$$

where  $C$  and  $q$  are the concentrations ( $\text{mol}/\text{m}^3$ ) of the dye dissolved in the pores and adsorbed on the inner surface of the pore wall, respectively;  $t$  (s) is the diffusion time through the membrane;  $z$  (m) is the distance through the membrane;  $\epsilon_P$  is the void fraction of the membrane; and  $D_P$  and  $D_S$  ( $\text{m}^2/\text{s}$ ) represent the pore and surface diffusivities, respectively. Equation (1) is transformed to eq. (2) using dimensionless variables.

$$\frac{\partial x}{\partial \tau_P} + \alpha \frac{\partial y}{\partial \tau_P} = \frac{\partial^2 x}{\partial \rho^2} + \beta \frac{\partial^2 y}{\partial \rho^2} \quad (2)$$

In the equation  $x = C/C_0$ ,  $y = q/q_0$ ,  $\tau_P = D_P t/l^2$ ,  $\rho = z/l$ ,  $\alpha = q_0/\epsilon_P C_0$ , and  $\beta = \alpha D_S/D_P$ , where  $C_0$  ( $\text{mol}/\text{m}^3$ ) is the concentration of the dye in the bulk solution;  $q_0$  ( $\text{mol}/\text{m}^3$ ) is the concentration of the dye adsorbed in equilibrium with  $C_0$ ;  $l$  (m) represents the thickness of the water-swollen membrane;  $\alpha$  indicates the degree of concentration of the dye from the liquid phase to the solid phase (membrane surface); and  $\beta$  is an indicator of the type of controlling diffusion. There are two limiting cases: when  $\beta = 0$  (pore diffusion control) and  $\beta = \infty$  (surface diffusion control). Because eq. (2) cannot be solved for  $\beta = \infty$ , eq. (1) is transformed to eq. (3):

$$\frac{\partial x}{\partial \tau_S} + \alpha \frac{\partial y}{\partial \tau_S} = \alpha \frac{\partial^2 y}{\partial \rho^2} \quad (3)$$

where  $\tau_S = D_S t/l^2$ .

When the relationship between  $x$  and  $y$  is calculated according to the equilibrium isotherm shown by eq. (4), eqs. (2) and (3) were transformed into eqs. (5) and (6), respectively.

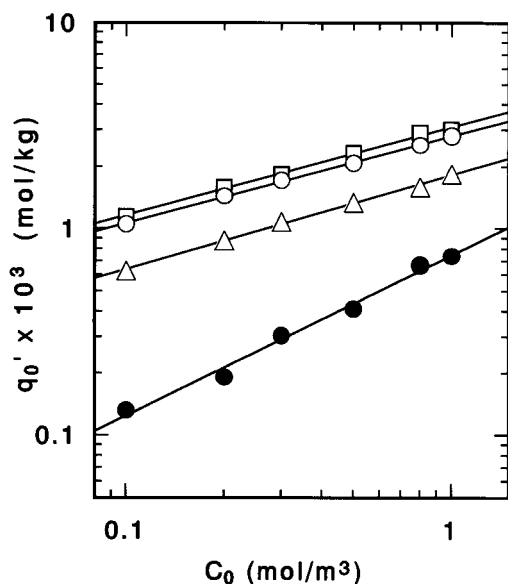
$$y = x^\gamma \quad (4)$$

$$\left[ \alpha + \frac{1}{\gamma} y^{(1-\gamma)/\gamma} \right] \frac{\partial y}{\partial \tau_P} = \frac{1}{\gamma} \frac{\partial}{\partial \rho} \left[ y^{(1-\gamma)/\gamma} \frac{\partial y}{\partial \rho} \right] + \beta \frac{\partial^2 y}{\partial \rho^2} \quad (5)$$

$$\left[ \alpha + \frac{1}{\gamma} y^{(1-\gamma)/\gamma} \right] \frac{\partial y}{\partial \tau_S} = \alpha \frac{\partial^2 y}{\partial \rho^2} \quad (6)$$

The initial and boundary conditions are given by the first and second lines of eq. (7), respectively:

$$y = 0 \quad \text{at} \quad \tau_P = 0 \quad \text{or} \quad \tau_S = 0$$



**Figure 2** The effects of the anionic surfactants on the adsorption isotherms of CI Acid Red 88 onto cellulose membranes at 25°C: (●) none, (△) LAS, (○) NaCl, and (□) SDS.

$$y = 1 \quad \text{at} \quad \rho = 0 \quad \partial y / \partial \rho = 0 \quad \text{at} \quad \rho = 1 \quad (7)$$

Equations (5) and (6) are transformed into finite difference equations and solved numerically.

## RESULTS AND DISCUSSION

Figure 2 shows the equilibrium isotherms at 25°C for the adsorption of AR88 onto the cellulose membrane in the presence of SDS or LAS. The data in the presence of NaCl (5 mol/dm<sup>3</sup>) and with no additives are also shown. The adsorption isotherms revealed Freundlich-type adsorption. Apparently the addition of surfactants, as well as

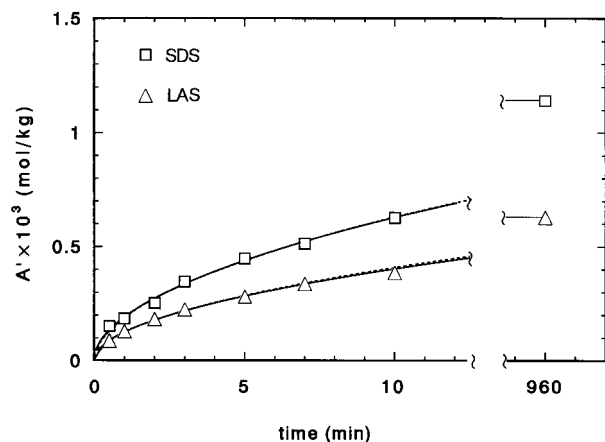
the addition of NaCl, increased the equilibrium adsorption for the dye. It is known that anionic surfactants and sodium chloride act as electrolytes in the adsorption of anionic dyes onto cellulose. This means that a diffuse layer of positive sodium ions forms at the fiber surface, neutralizing its negative charge. The dye anions are then able to approach sufficiently closely to the fiber for the inherent attractive forces between the dye and the fiber to operate. Because the concentration of the surfactants was about critical micelle concentration, there must be little micelle formation. This effect was confirmed by the fact that this increase was not observed when nonionic surfactant was added (unpublished data). Freundlich constants ( $k$  and  $\gamma$  of  $q_0 = kC_0^\gamma$ ) were determined from the intercepts and slopes of the lines and are summarized in Table I. When the affinity of a dye on the substrate is high,  $k$  becomes large and  $\gamma$  becomes small as described elsewhere.<sup>6</sup> The value of  $\alpha$  in eq. (2) was determined and is summarized in Table I.

Figure 3 shows the uptake curves for AR88 in the surfactant solution at 25°C ( $C_0 = 1 \times 10^{-4}$  mol/dm<sup>3</sup>). The theoretical lines for surface diffusion control and pore diffusion control are shown. The experimental data correlated well with both models. The surface diffusivity based on the surface diffusion model ( $D'_S$ ) and the pore diffusivity based on the pore diffusion model ( $D'_P$ ) were determined by matching the theoretical values with the experimental values (Table I).

As shown in our previous article,<sup>4</sup> the  $D'_S$  for the parallel diffusion model can be obtained by plotting  $D'_S$  versus  $1/\alpha$ ; therefore, it is represented in Figure 4. The plots of  $D'_S$  versus  $1/\alpha$  in the presence of the surfactants correlated with the lines. The increase of  $D'_S$  with increasing  $1/\alpha$  indicates the increasing contribution of pore diffu-

**Table I** Physical Properties in Cellulose Membrane–CI Acid Red 88 System at 25°C

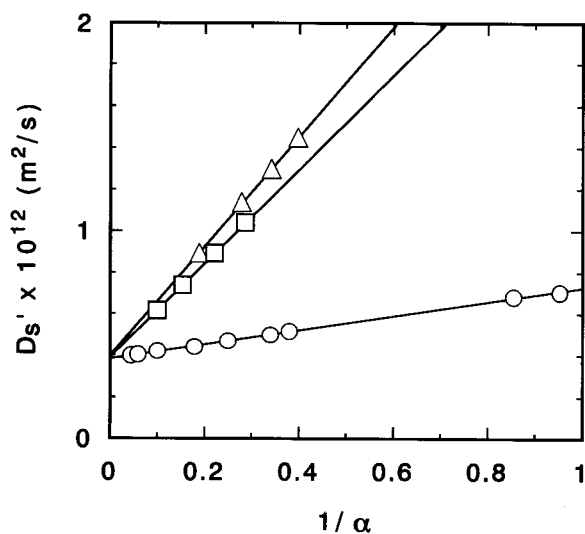
| Surfactant | $C_0$ (mol/m <sup>3</sup> ) | $\alpha$ | $k$   | $\gamma$ | $D'_S \times 10^{13}$<br>(m <sup>2</sup> /s) | $D'_P \times 10^{12}$<br>(m <sup>2</sup> /s) |
|------------|-----------------------------|----------|-------|----------|--|--|
| SDS        | 0.05                        | 10.0     | 1.30  | 0.426    | 6.17   | 4.81   |
|            | 0.10                        | 6.53     | 1.30  | 0.426    | 7.37   | 3.72   |
|            | 0.15                        | 4.53     | 1.30  | 0.426    | 8.92   | 3.04   |
|            | 0.20                        | 3.50     | 1.30  | 0.426    | 10.4   | 2.75   |
| LAS        | 0.05                        | 5.33     | 0.765 | 0.456    | 8.94   | 3.74   |
|            | 0.10                        | 3.60     | 0.765 | 0.456    | 11.4   | 3.91   |
|            | 0.05                        | 2.93     | 0.765 | 0.456    | 13.0   | 2.87   |
|            | 0.20                        | 2.52     | 0.765 | 0.456    | 14.5   | 2.74   |



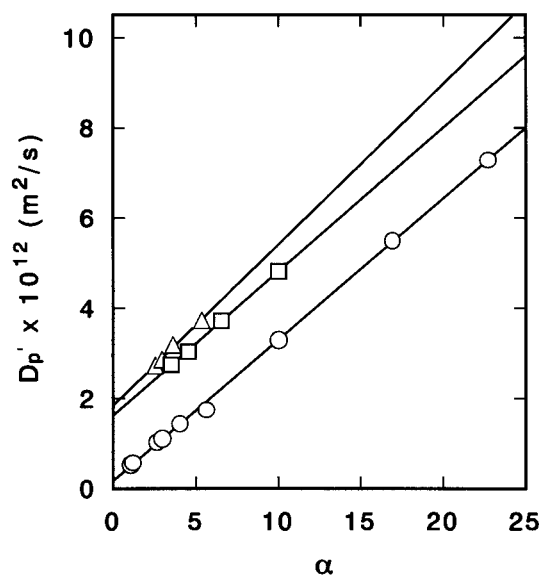
**Figure 3** The effects of the surfactants on the uptake curves of CI Acid Red 88 at 25°C;  $C_0 = 0.1 \text{ mol/m}^3$ . The theoretical lines for (—) surface diffusion control and (---) pore diffusion control are shown.

sion with decreasing  $\alpha$ . The difference in the slopes of the lines indicates the change of the  $D_P$  for the parallel diffusion model by the addition of the surfactants. The  $D_S$  for the parallel diffusion model could be obtained from the intercept of the line as  $3.89 \times 10^{-13} \text{ m}^2/\text{s}$  for SDS and  $3.99 \times 10^{-13} \text{ m}^2/\text{s}$  for LAS. The value of  $D_S$  showed no significant change with the addition of the surfactants.

Figure 5 shows the relation between  $D'_P$  and  $\alpha$  at 25°C. It appears that the plots in the presence of the surfactants correlated with the lines. Increasing  $D'_P$  with increasing  $\alpha$  indicates the in-



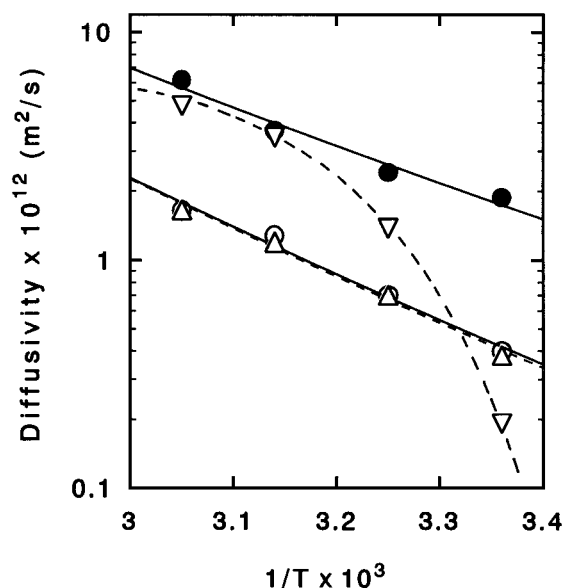
**Figure 4** Plots of  $D'_S$  versus  $1/\alpha$  to determine  $D_S$ : ( $\Delta$ ) LAS, ( $\circ$ ) NaCl, and (squ;) SDS.



**Figure 5** Plots of  $D'_P$  versus  $\alpha$  to determine  $D_P$ : ( $\Delta$ ) LAS, ( $\circ$ ) NaCl, and (squ;) SDS.

creasing contribution of surface diffusion with increasing  $\alpha$ .<sup>5</sup> There is no significant difference between the slopes in the absence and presence of the surfactants. The  $D_P$  was obtained from the intercepts of the lines as  $1.62 \times 10^{-12} \text{ m}^2/\text{s}$  for SDS and  $1.88 \times 10^{-12} \text{ m}^2/\text{s}$  for LAS. The addition of LAS ( $3 \text{ mol/m}^3$ ) or SDS ( $8 \text{ mol/m}^3$ ) increased the pore diffusivity 9.8 or 8.4 times, respectively, compared to that obtained in the presence of NaCl ( $1.92 \times 10^{-13} \text{ m}^2/\text{s}$ ). Such an increase was observed once when  $1 \text{ mol/dm}^3$  urea was added to this system,<sup>11</sup> in which the addition of urea reduced the aggregation of the dye and increased the pore diffusivity. Urea is known to break the water structure.<sup>12–15</sup> It has been reported that hydrating water molecules around the dye play an important role in the aggregation process of the dye.<sup>16</sup> Furthermore, Hori et al. reported that the addition of electrolytes with sulfonate groups increased the diffusivity of dyes in the solution and explained it as the action of the structure breaker of water for sulfonate groups.<sup>17</sup> Thus, the sulfonate groups of the surfactants in the present work also seemed to act as the water structure breaker and depressed aggregation for the dye. Consequently, the  $D_P$  for the dye might become small. The effects of the surfactants appeared at much lower concentration than that of urea.

The effects of temperature on the  $D_S$  and  $D_P$  values were examined in the presence of LAS ( $3 \text{ mol/m}^3$ ). Figure 6 represents Arrhenius plots of the  $D_S$  and  $D_P$  determined for the dye at 25, 35,



**Figure 6** The Arrhenius plots of the  $D_S$  and  $D_P$  in the presence of LAS or NaCl: (○)  $D_S$  for LAS, (△)  $D_S$  for NaCl, (●)  $D_P$  for LAS, and (▽)  $D_P$  for NaCl.

45, and 55°C. Those obtained in the NaCl solution<sup>6</sup> were also represented. The values of  $D_S$  in the presence of LAS were almost equal to those of NaCl at any temperature while the difference in the  $D_P$  between them was getting larger at lower temperature. The plots of  $D_P$  in the presence of NaCl revealed a curved line with a steep slope at lower temperature; however, the value of  $D_P$  in the presence of LAS becomes large at lower temperature, resulting in plots that revealed a straight line. This tendency coincides with the results obtained in the presence of urea.<sup>11</sup>

## CONCLUSIONS

The effects of SDS and LAS on the adsorption and diffusion of AR88 into cellulose membranes were measured at 25–55°C. The results were analyzed on the basis of the parallel diffusion model. The following conclusions were made:

1. The effects of surfactants as electrolytes were observed in equilibrium dyeing. Thus,

the addition of the anionic surfactants increased the equilibrium adsorption for the anionic dye.

2. The pore diffusivity for the model was increased almost 10 times by the addition of the surfactants at 25°C, and this effect decreased with increasing temperature. This phenomenon was explained by its effects as a water structure breaker for the sulfonate groups of the surfactants.

## REFERENCES

1. Sorensen, T. S., Ed. *Surfactant Science Series 79: Surface Chemistry and Electrochemistry of Membranes*; Marcel Dekker: New York, 1999; p 247.
2. Yoshida, H.; Kataoka, T.; Nango, M.; Ohta, S.; Kuroki, K.; Maekawa, M. *J Appl Polym Sci* 1986, 32, 4185.
3. Yoshida, H.; Kataoka, T.; Maekawa, M.; Nango, N. *Chem Eng J* 1989, 41, B1.
4. Yoshida, H.; Maekawa, M.; Nango, M. *Chem Eng Sci* 1991, 46, 429.
5. Maekawa, M.; Murakami, K.; Yoshida, H. *J Colloid Interface Sci* 1993, 155, 79.
6. Maekawa, M.; Tanaka, M.; Yoshida, H. *J Colloid Interface Sci* 1995, 170, 146.
7. Maekawa, M.; Murakami, M.; Yoshida, H. *Colloid Polym Sci* 1995, 273, 793.
8. Maekawa, M.; Kondo, M. *Colloid Polym Sci* 1996, 274, 1145.
9. Maekawa, M.; Kasai, K.; Nango, M. *Colloids Surf A* 1998, 132, 173.
10. Robinson, C.; Mills, H. *Proc R Soc Lond* 1931, A131, 576.
11. Maekawa, M.; Ohmori, M.; Yamashita, A.; Nango, M. *Colloids Surf A* 1997, 275, 784.
12. Katayama, A.; Matsuura, T.; Konishi, T.; Kuroki, N. *Kolloid Z Z Polym* 1956, 202, 157.
13. Takagishi, T.; Katayama, A.; Kuroki, N. *Sen-I Gakkaishi* 1969, 25, 381.
14. Rupley, J. A. *J Phys Chem* 1964, 68, 2002.
15. Walrafen, G. E. *J Phys Chem* 1966, 44, 3726.
16. Hamada, H.; Mitsuishi, M. *Dyes Pigment* 1991, 16, 111.
17. Hori, T.; Hayashi, T.; Sekiguchi, M.; Shimizu, T. *Sen-I Gakkaishi* 1979, 35, T-245.