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Disperse dyeing of nylon 6 fiber using gemini surfactants containing ammonium cations as auxiliaries

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Abstract

The dyeing behavior of the disperse dye, 1,4-diaminoanthraquinone (1,4-DAA), on nylon 6 fiber in the presence of the cationic gemini surfactants, propanediyl-α,ω-bis(dimethyldodecylammonium bromide) (DC3-12) and hexanediyl-α,ω-bis(dimethyldodecylammonium bromide) (DC6-12) as auxiliaries, was investigated, and compared with that obtained in the presence of the corresponding conventional surfactant, dodecyltrimethylammonium bromide (C12C1NBr). The dyeing rate increased in the order of C12C1NBr < DC3-12 < DC6-12, reflecting a difference in surfactant property. The extent of dye uptake altered slightly below the critical micelle concentration (CMC), but dye uptake decreased hyperbolically with an increase in surfactant concentration above the CMC. The decrease in the extent of dye uptake above the CMC is concerned with the solubilization capacity of 1,4-DAA into the micelles: the greater solubilization capacity reduced dye uptake. This result shows that the dye which is solubilized in the surfactant micelles rarely takes part in dyeing the fiber and the surfactant micelles act as a reservoir for the dye. A linear relationship was obtained between the amount of dye in the fiber and that in the dyebath, leading to the calculation of the apparent partition coefficients, *K*. The *K* values in the presence of the surfactants whose concentration was above the CMC increased in the order of C12C1NBr < DC6-12 < DC3-12 << water, indicating that they were also related to solubilization capacity. On the other hand, the *K* values increased in the order of water < C12C1NBr < DC6-12 < DC3-12 for the dyebath which contained a 1:1 molar ratio of dye:surfactant in which the surfactant concentrations were below the CMC. This result suggests that *K* is dependent not only on the solubilization capacity but also on the dispersing ability of the surfactant. The maximum extent of dye uptake on to nylon 6 fiber in the presence of surfactants whose concentration was above the CMC was 3.0×10^{-5}, 4.0×10^{-5}, and 3.3×10^{-5} mol g^{-1} for DC3-12, DC6-12, and C12C1NBr, respectively, at 100 °C, whereas those obtained in a dyebath containing a 1:1 molar ratio of dye:surfactant were 4.0×10^{-5}, 4.2×10^{-5}, and 3.3×10^{-5} mol g^{-1} for DC3-12, DC6-12, and C12C1NBr, respectively, at 100°C. This suggests that an improvement in dye uptake occurred in the presence of the gemini surfactants. Thus, it is concluded that gemini surfactants can be used to control dyeing kinetics or to improve dye uptake in the disperse dyeing of nylon. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Gemini surfactant; Disperse dyeing; Nylon 6; Cationic surfactant; Dyeing auxiliaries

1. Introduction

It is well known that surfactants added to the dyebath affect dyeing parameters such as the stability of the dyebath, levelness of dyeing, dyeing

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rate and dye uptake because of the dispersing, emulsifying and solubilizing ability of the surfactants. For this purpose, the dyeing of natural or synthetic fibers in the presence of surfactants with one head and one tail group has been studied extensively [1–10]. Recently, various compounds such as phosphatidylcholine liposome [11–18], double tailed surfactants [19–24] and bolaform electrolytes [25–30] have been used as dyeing auxiliaries [11–30]. The unilamellar and multilamellar liposome of egg phosphatidylcholine were used as vehicles for either dye or oxidative reagent in the dyeing and finishing of wool. The use of phosphatidylcholine liposome was found to be both practical and useful, and the phosphatidylcholine liposome could be used a modulator of dyeing kinetics [11–18]. Dialkyldimethylammonium bromide containing two tail groups was used in the disperse dyeing of polyester, nylon and acetate fibers [20–24]. The current authors have investigated the effects of bolaform electrolytes on the binding of acid dyes to poly(vinylpyrrolidone) [25–28] and the sorption of acid dyes on to a nylon 6 film and a silk fiber [29–30]. These studies suggest that the bolaform electrolytes could be used as dye association controllers or auxiliaries.

Although the properties of the micelles formed by gemini surfactants with two head and two tail groups have been studied extensively by Zana et al. [31–38], the effects of gemini surfactant on dye sorption have not been studied.

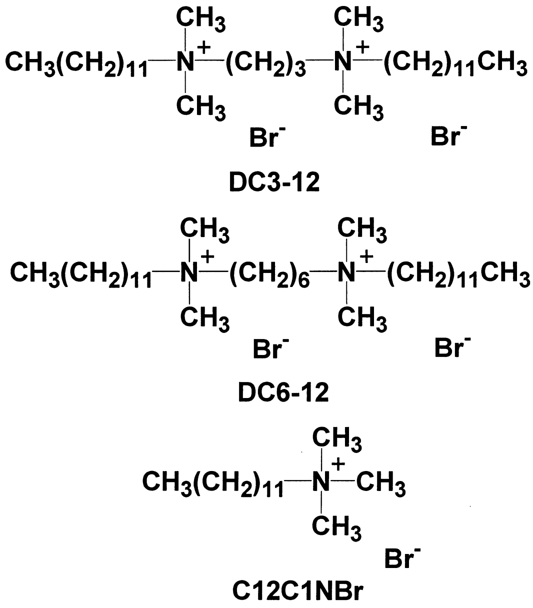
To investigate the use of the gemini surfactants as dyeing auxiliaries, the current authors considered the microenvironments of the gemini surfactant micelles by using a spin probe technique [39] and the solubilization behavior of disperse dyes in gemini surfactant micelles [40]. It was found that the microenvironments of the gemini surfactant micelles are quite different from those of conventional surfactant micelles and the solubilization capacity also differs between the gemini and conventional surfactants, which can be attributed to a difference in the adsorption of the disperse dye to the surfactant micelles.

In the present study, the application of 1,4-diaminoanthraquinone (1,4-DAA) to nylon 6 fiber in the presence of propanediyl-α,ω-bis(dimethyldodecylammonium bromide) (DC3-12) and hexanediyl-α,ω-bis(dimethyldodecylammonium bromide) (DC6-12) was investigated and compared with that secured in the presence of the corresponding conventional surfactant, dodecyltrimethylammonium bromide (C12C1NBr). The dependence of dye uptake on dyeing time and surfactant concentration and the difference in the sorption isotherms obtained using gemini and conventional surfactants are discussed.

2. Experimental

2.1. Materials

Two gemini surfactants and one conventional surfactant (Fig. 1) were used. Propanediyl-α,ω-bis-(dimethyldodecylammonium bromide) (DC3-12) and hexanediyl-α,ω-bis(dimethyldodecylammonium bromide) (DC6-12) were synthesized as described in a previous study [39,40]. The conventional surfactant, dodecyltrimethylammonium bromide (C12C1NBr) was purchased from the Tokyo Kasei Kogyo Co. (Tokyo, Japan) and was used without purification.



$CH_3(CH_2)_{11}-N^+(CH_3)_2-(CH_2)_3-N^+(CH_3)_2-(CH_2)_{11}CH_3 \; 2Br^-$

DC3-12

$CH_3(CH_2)_{11}-N^+(CH_3)_2-(CH_2)_6-N^+(CH_3)_2-(CH_2)_{11}CH_3 \; 2Br^-$

DC6-12

$CH_3(CH_2)_{11}-N^+(CH_3)_2-CH_3 \; Br^-$

C12C1NBr

Fig. 1. Surfactants used.

The disperse dye, 1,4-diaminoanthraquinone (1,4-DAA, C. I. Disperse Violet 1, Fig. 2) was purchased from the Tokyo Kasei Kogyo Co. (Tokyo, Japan) and was used without purification.

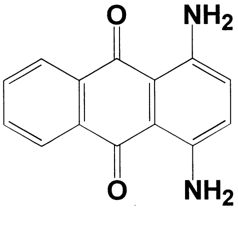
Multifilament nylon 6 fiber of 1890 denier/316 filaments, kindly supplied by Unitika Ltd., was used. The fiber was scoured four times in water at 95°C for 45 min using a liquor ratio of 50:1, immersed in pH 5.0 acetate buffer solution, which contains 0.05 mol dm^{-3} of anhydrous sodium acetate and 0.0275 mol dm^{-3} of acetic acid, for 1 day, blotted with Advantec No.2 filter paper, and then dried in a desiccator with silica gel at room temperature. *N*,*N*-dimethylformamide (DMF) was analytical grade.

2.2. Dye sorption on to nylon 6 fiber

2.2.1. Time dependence

A 50 cm^3 aqueous solution containing pH 5.0 acetate buffer, the surfactant and the disperse dye was prepared. Twenty milligrams of nylon 6 fiber was immersed in the dyebath using a sealed stainless steel pot of 200 cm^3 capacity housed in a laboratory scale dyeing machine Texam UR. MINI-COLOR MCUR-V5-6N (Nagoya, Japan). Dyeing was started at 20°C and the temperature raised by 4°C min^{-1} to 80°C. Dyeing was continued for a given time (1 min to 7 days) at its temperature and then the dyebath was cooled by 4°C min^{-1} to 60°C.

After dyeing, the fiber was washed with distilled water, soaped in 50 cm^3 of an aqueous solution of SUNMORL BK-90NM (0.75 g/l; Nicca Chemical Co., Ltd.; Fukui, Japan) in a Tokyo Rikakikai Thermistor Temppet T-80 water bath incubator (Tokyo, Japan) for 30 min at 25°C, rinsed thoroughly again, blotted with a filter paper, and dried in a desiccator with silica gel at room temperature. The amount of dye adsorbed by the nylon 6 fiber was determined by extraction with DMF at 95°C until the fiber became colorless. The absorbance of the stripped dyeing was determined spectrophotometrically using a Shimadzu UV-160A spectrophotometer (Kyoto, Japan). The molar extinction coefficient, ε, of 1,4-DAA in DMF at 553 nm and 25°C was 1407 m^2 mol^{-1}. The dye uptake of the nylon 6 fiber was determined using Eq. (1).



1,4-DAA

Fig. 2. Dye used.

$$r = \frac{A \cdot V_s}{10000 \cdot \varepsilon \cdot W_f} \tag{1}$$

where r is the amount of dye sorbed by the nylon 6 fiber (mol g^{-1}), A is the absorbance of the extracted dye solution at 553 nm, V_s is the volume of DMF solution, and W_f is the mass of the nylon 6 fiber.

2.2.2. Surfactant concentration dependence

Aqueous surfactant solutions of various concentrations both below and above the critical micelle concentration (CMC) were prepared using pH 5.0 acetate buffer solution. 1,4-DAA at a given, constant concentration was added to the solutions.

A 50 cm^3 aqueous dyebath was prepared and placed in a dyepot with 20 mg of nylon 6 fiber. Dyeing was accomplished and the amount of dye uptake on to the fiber was determined in the manner described in the previous section. In this experiment, dyeing was carried out at 80°C for 1 day.

2.2.3. Sorption isotherms

A 50 cm^3 aqueous dyebath containing pH 5.0 acetate buffer solution, the surfactants at a constant concentration, and the disperse dye at various concentrations (1×10^{-5} to 2×10^{-3} mol dm^{-3}) was placed in a pot with 20 mg of scoured nylon 6 fiber. Dyeing was carried out at 60–100°C for 1 day. The amount of dye adsorbed by the nylon 6 fiber was determined in the manner described in Section 2.2.1, leading to the determination of the sorption isotherms.

The sorption isotherms obtained for the dyebath containing a 1:1 and a 1:5 molar ratio of dye:surfactant were determined. In this experiment, the solid particles of surfactant and dye were ground at the same time with an agate mortar and added into pH 5.0 acetate buffer solution. After that, the solution was stirred by magnetic stirrer bar to form a stable, dispersed solution.

3. Results and Discussion

3.1. Time dependence

Plots of the amount of dye adsorbed by the nylon 6 fiber as a function of dyeing time at 80°C in the presence of the gemini and the conventional surfactants are shown in Fig. 3. The equilibrium sorption was established after dyeing for a period of 1 day in all cases. As described in the experimental section, the nylon 6 fiber was placed in the dyebath at ambient temperature and dyeing started before the dyebath reached the dyeing temperature (80°C) so that a significant amount of dye should have been adsorbed by the fiber prior to reaching 80°C. This shows that it is difficult to obtain accurate time dependence information during the initial stages of dyeing. In the present study, therefore, the apparent parameters for the dyeing kinetics were determined.

To estimate the apparent dyeing rate, the ratio of the dye uptake at time t, r_t, to that at equilibrium, r_{eq}, was plotted against dyeing time (Fig. 4).

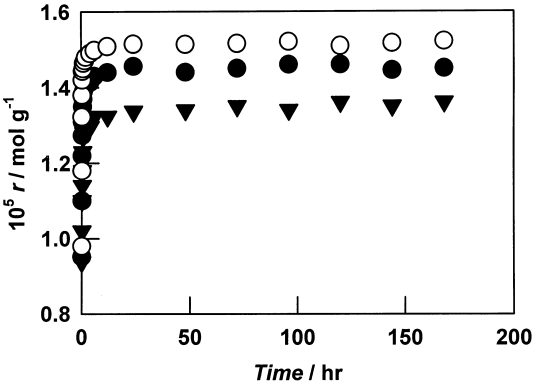


Fig. 3. Time dependence of the amount of 1,4-DAA sorbed by the nylon 6 fiber at 80°C. ●, DC3-12 (4×10^{-3} mol dm^{-3}); ▼, DC6-12 (4×10^{-3} mol dm^{-3}); ○, C12C1NBr (3×10^{-2} mol dm^{-3}). Initial dye concentration is 1.4×10^{-4}, 2.5×10^{-4}, and 2×10^{-4} mol dm^{-3} for DC3-12, DC6-12, and C12C1NBr.

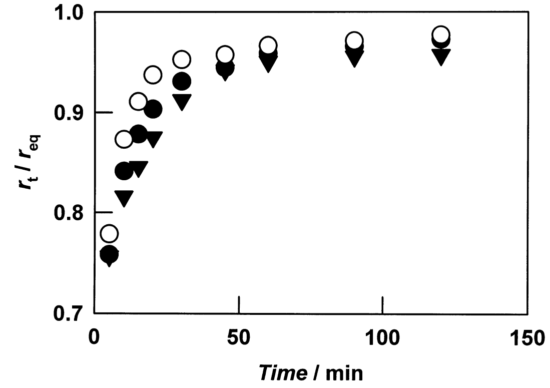


Fig. 4. Plots of r_r/r_{eq} against time at 80°C. ●, DC3-12 (4×10^{-3} mol dm^{-3}); ▼, DC6-12 (4×10^{-3} mol dm^{-3}); ○ C12C1NBr (3×10^{-2} mol dm^{-3}). Initial dye concentration is 1.4×10^{-4}, 2.5×10^{-4}, and 2×10^{-4} mol dm^{-3} for DC3-12, DC6-12, and C12C1NBr.

The ratio, r_t/r_{eq}, is related to time t using Eq. (2), which was derived for diffusion into an infinite long cylinder or filament with radius a by Hill [41].

$$\frac{r_t}{r_{eq}} = 1 - \sum \frac{4}{\alpha_n^2} \exp\left(-\frac{D\alpha_n^2 t}{a^2} \right) \qquad (2)$$

where α_n is the positive root of the Bessel function of the zero order and D is the diffusion coefficient, which here is calculated as the apparent diffusion coefficient. If the dyeing time is short, Eq. (2) is rewritten as follows:

$$\frac{r_t}{r_{eq}} = \frac{4}{\pi^{1/2}} \left(\frac{Dt}{a^2} \right)^{1/2} - \frac{Dt}{a^2} - \frac{1}{3\pi^{1/2}} \left(\frac{Dt}{a^2} \right)^{3/2} + \cdots \qquad (3)$$

$Dt/a^2 << 1$ leads to Eq. (4).

$$\frac{r_t}{r_{eq}} = \frac{4D^{\frac{1}{2}}}{\pi^{1/2} a} t^{1/2} \qquad (4)$$

The apparent diffusion coefficients of 1,4-DAA were calculated from the slope of the linear plot of r_t/r_{eq} against $t^{1/2}$ using Eq. (4) and are given in Table 1. The D values in the presence of the gemini surfactants were larger than that in the conventional surfactant: the apparent diffusion coefficients increased in the order of C12C1NBr < DC3-12 < DC6-12. Although the adsorption or condensation of the surfactants on the fiber sur-

Table 1
The diffusion coefficients of nylon 6 fiber in the presence of gemini and conventional surfactants

	DC3-12	DC6-12	C12C1NBr
D (10^{-11} cm^2 s^{-1})	3.8	6.7	1.5

face might affect the dye diffusion, the mechanism of increased dyeing rate in the presence of gemini surfactant is not clear.

3.2. Surfactant concentration dependence

The plots of dye uptake on to nylon 6 fiber, r, against surfactant concentration, C_{surf}, at 80°C in the presence of DC3-12, DC6-12, and C12C1NBr are shown in Figs. 5, 6 and 7, respectively. When surfactants were not added to the aqueous dyebath, the amount of dye adsorbed by the fiber increased with increasing dye concentration and reached a maximum at about 8×10^{-5} mol dm^{-3} dye concentration (see Figs. 5–7). This concentration is the solubility of 1,4-DAA in water at 80°C and is in good agreement with the values quoted in literature [42,43].

Below the CMC (the CMC values for DC3-12, DC6-12, and C12C1NBr are 1.2×10^{-3}, 1.2×10^{-3}, 1.5×10^{-2} mol dm^{-3}, respectively [39]), dye uptake in the case of dye concentrations below 8×10^{-5} mol dm^{-3} changed with surfactant concentration, while dye uptake in the case of dye concentrations above 8×10^{-5} mol dm^{-3}, hardly changed with changes in surfactant concentration. This result suggests that the surfactant monomer molecules and/or premicelles influence both the dye uptake and the dye solubility.

In the case of a dyebath with a surfactant concentration above the CMC and using dye concentrations below 8×10^{-5} mol dm^{-3}, dye uptake decreased hyperbolically with increasing surfactant concentration. This can be attributed to solubilization of the disperse dye into the micelles formed by the surfactants, leading to decreased dye which is accessible to the fiber. In the same surfactant concentration region, dye uptake in the case of solutions containing dye concentrations

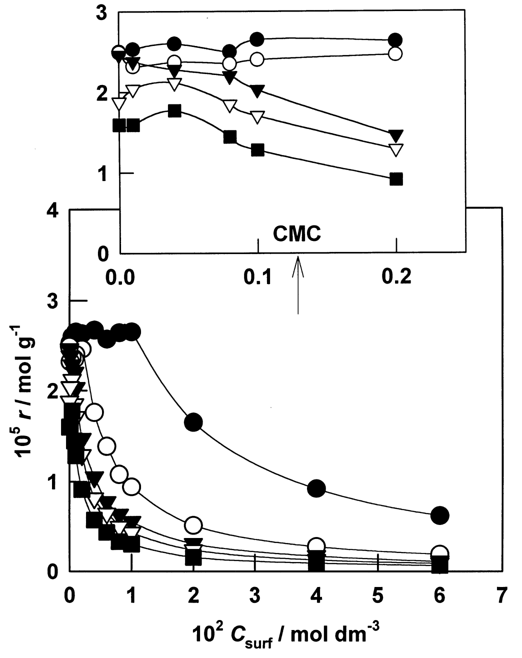


Fig. 5. Dependence of dye uptake on surfactant concentration for DC3-12 at 80°C. Initial dye concentration, ●, 6.4×10^{-4}; ○, 1.6×10^{-4}; ▼, 8×10^{-5}; ▽, 6×10^{-5}; ■, 4×10^{-5} mol dm^{-3}.

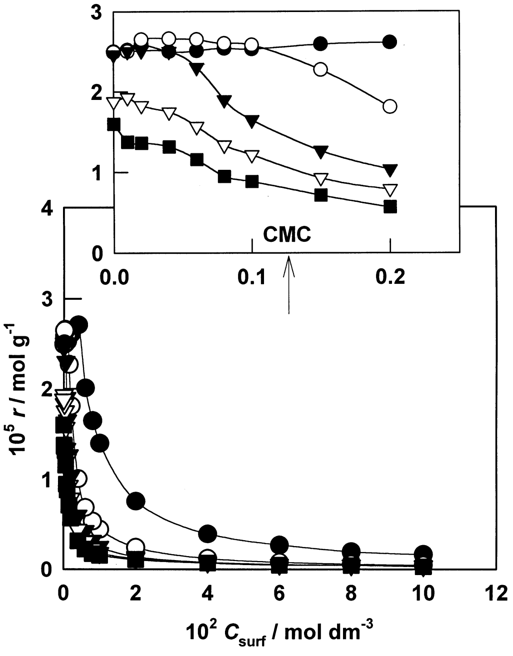


Fig. 6. Dependence of dye uptake on surfactant concentration for DC6-12 at 80°C. Initial dye concentration, ●, 6.4×10^{-4}; ○, 1.6×10^{-4}; ▼, 8×10^{-5}; ▽, 6×10^{-5}; ■, 4×10^{-5} mol dm^{-3}.

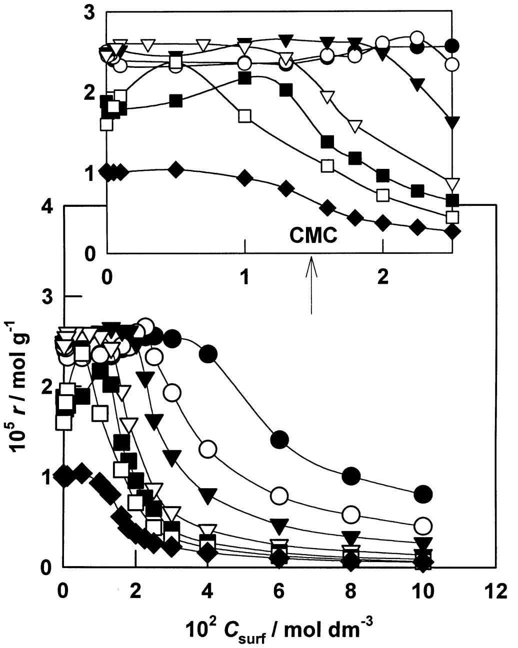


Fig. 7. Dependence of dye uptake on surfactant concentration for C12C1NBr at 80°C. Initial dye concentration, ●, 6.4×10^{-4}; ○, 3.2×10^{-4}; ▼, 1.6×10^{-4}; ▽, 8×10^{-5}; ■, 6×10^{-5}; □, 4×10^{-5}; ◆, 2×10^{-5} mol dm^{-3}.

above 8×10^{-5} mol dm^{-3} did not change even above the CMC; this can be explained as follows. Any present excess dye above its water solubility is precipitated at low surfactant concentrations. As the surfactant concentration is increased, more of the dye is solubilized into the micelles, resulting in dissolution of the precipitated dye. Until all the precipitated dye is dissolved, the saturated, free dye concentration outside the micelle is maintained, which contributes to constant dye uptake.

The manner of the reduction in dye uptake with increasing surfactant concentration was dependent on the kind of the surfactants and was of the order of DC6-12 > DC3-12 > C12C12NBr, which is inversely proportional to the square root of the solubilization capacity of 1,4-DAA into the micelles [40]. Thus, the higher solubilization capacity reduces dye uptake. From the above results, it can be concluded that dye which is solubilized in micelles rarely participates in sorption by the nylon 6 fiber and the surfactant micelles merely behave as a reservoir of the solubilized dye.

3.3. Sorption isotherms

The sorption isotherms of 1,4-DAA on nylon 6 fiber in the presence of both the gemini and conventional surfactants at 60–100°C are shown in Fig. 8, where C_{dye} represents the dye concentration in the dyebath at equilibrium. Dye uptake increased linearly with increasing dye concentration and attained a constant value above a certain dye concentration, which corresponded to the maximum extent of dye uptake at each temperature in the presence of the surfactant. Maximum dye uptake is given in Table 2. For all of the surfactants used, maximum dye uptake increased with increasing temperature and the values at 100°C were about twice as large as those at 60°C. The increase in dye uptake with increasing temperature is related to the increment in the amounts of the dye participating in the nylon dyeing: the amount of dye dissolved and/or dispersed should increase with increasing temperature. Maximum dye uptake at 60–90°C was of the order of DC3-12 < DC6-12 ≅C12C1NBr, whereas at 100°C maximum dye uptake in the presence of DC6-12 was 20–30% larger than that obtained in the presence of the other surfactants. This result suggests that DC6-12 increases the amount of dye participating in the nylon dyeing; the amount of dye dissolved and/or dispersed might therefore be enhanced by the addition of DC6-12 at 100°C.

The maximum total dye concentration, $C_{\text{dye}}^{\max}$, at equilibrium was determined from the crossover point of the two linear lines shown in Fig. 9 and is given in Table 3. The $C_{\text{dye}}^{\max}$ values increased with increasing temperature, indicating that more dye was present in the dyebath at higher temperature. If the maximum concentration of the dye dissolved, dispersed, or solubilized is designated as $C_{\text{dissolved}}^{\max}$, $C_{\text{dispersed}}^{\max}$, $C_{\text{solubilized}}^{\max}$, respectively, $C_{\text{dye}}^{\max}$ is represented as follows.

$$C_{\text{dye}}^{\max} = C_{\text{dissolved}}^{\max} + C_{\text{dispersed}}^{\max} + C_{\text{solubilized}}^{\max} \quad (5)$$

The concentration of the dye which is solubilized in the surfactant micelles was 4.17×10^{-5}, 6.27×10^{-5}, and 9.41×10^{-5} mol dm^{-3} for DC3-12 (4×10^{-3} mol dm^{-3}), DC6-12 (4×10^{-3} mol dm^{-3}), and C12C1NBr (4×10^{-2} mol dm^{-3}), respectively,

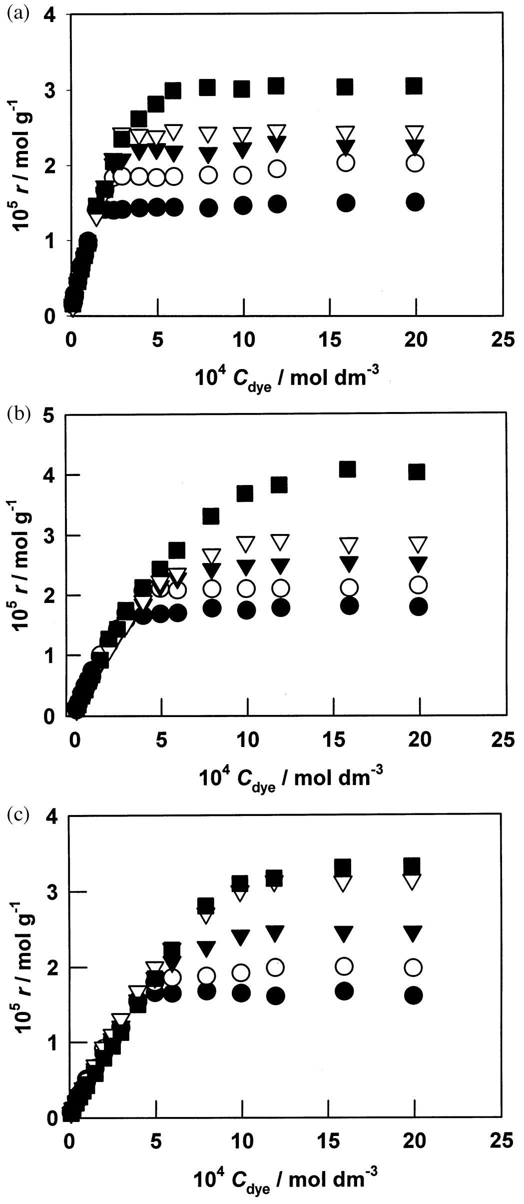


Fig. 8. Sorption isotherms of 1,4-DAA for the nylon 6. (a) DC3-12 (4×10^{-3} mol dm^{-3}); (b) DC6-12 (4×10^{-3} mol dm^{-3}); (c) C12C1NBr (4×10^{-2} mol dm^{-3}). ●, 60°C; ○, 70°C; ▼, 80°C; ▽, 90°C; ■, 100°C.

at 25°C [40]. If the order of solubilization capacity is assumed not to change with temperature, the $C_{\mathrm{dye}}^{\max}$ values are mainly affected by $C_{\mathrm{solubilized}}^{\max}$: the largest $C_{\mathrm{dye}}^{\max}$ value for C12C1NBr is due to the largest amount of dye solubilized in C12C1NBr micelle.

Table 2
The maximum dye uptake (10^{-5} mol g^{-1})

Temperature (°C)	DC3-12	DC6-12	C12C1NBr
60	1.5	1.8	1.7
70	2.0	2.1	2.0
80	2.3	2.5	2.5
90	2.5	2.9	3.1
100	3.0	4.0	3.3

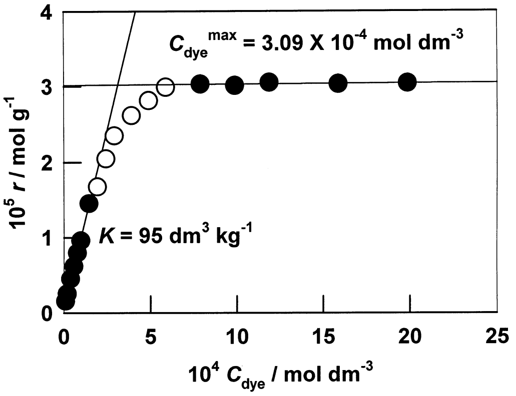


Fig. 9. Calculation of the maximum total dye concentration in the dyebath and the apparent partition coefficient.

Table 3
The maximum total dye concentration in the dyebath, $C_{\mathrm{dye}}^{\max}$ (10^{-4} mol dm^{-3})

Temperature (°C)	DC3-12	DC6-12	C12C1NBr
60	1.4	3.0	3.4
70	1.9	3.3	3.9
80	2.5	3.9	5.2
90	2.9	4.5	6.9
100	3.1	6.5	7.2

The apparent partition coefficients, *K*, were calculated from the slope of the linear part in the lower dye concentration region of Fig. 9 and are given in Table 4. These values were also influenced by the solubilization of the dye in the surfactant micelle: the *K* values became smaller in the presence of the surfactant micelles. This result also demonstrates that three phases of bulk water, micelle, and fiber are present in the dyebath and

Table 4
The apparent partition coefficients, K ($dm^3\ kg^{-1}$)

Temperature (°C)	DC3-12	DC6-12	C12C1NBr	Water
60	91	50	48	–
70	92	62	47	–
80	81	61	46	252
90	81	64	43	–
100	95	64	42	–

that the dye was distributed among these phases. Therefore, it is difficult to estimate the real partition coefficients of the dye between bulk water and fiber.

The sorption isotherms of 1,4-DAA on nylon 6 in a dyebath containing a 1:1 and a 1:5 molar ratio of dye:surfactant at 80–100°C are shown in Figs. 10 and 11, where the surfactant concentration was below CMC. Maximum dye uptake determined from Figs. 10 and 11 is given in Table 5. For each of the surfactants, maximum dye uptake increased with increasing temperature. The values obtained at 80–90°C were independent of the kind of the surfactant, while those at 100°C followed the order of C12C1NBr< <DC3-12<DC6-12. The values in the presence of the gemini surfactants were 10–30% larger than that in the presence of the conventional surfactant. Furthermore, maximum dye uptake in the presence of DC3-12 below the CMC was much larger than that above the CMC; thus, DC3-12 enhances the more amount of dye dispersed below the CMC.

The maximum total dye concentration, $C_{\mathrm{dye}}^{\mathrm{max}}$, at equilibrium was calculated as described previously and is given in Table 6. The $C_{\mathrm{dye}}^{\mathrm{max}}$ values increased with increasing temperature. As all the surfactant concentrations were below the CMC, the maximum dye concentration in the dyebath should be the sum of $C_{\mathrm{dissolved}}^{\mathrm{max}}$ and $C_{\mathrm{dispersed}}^{\mathrm{max}}$, because the dye solubilized in the micelle, $C_{\mathrm{solubilized}}^{\mathrm{max}}$, was not present. Nevertheless, in the case of the gemini surfactants, the $C_{\mathrm{dye}}^{\mathrm{max}}$ values in the dyebath containing a 1:5 molar ratio were much larger than those in the dyebath containing a 1:1 molar ratio, suggesting that any aggregates such as premicelles are formed in the dyebath containing a 1:5 molar ratio of dye and gemini surfactant.

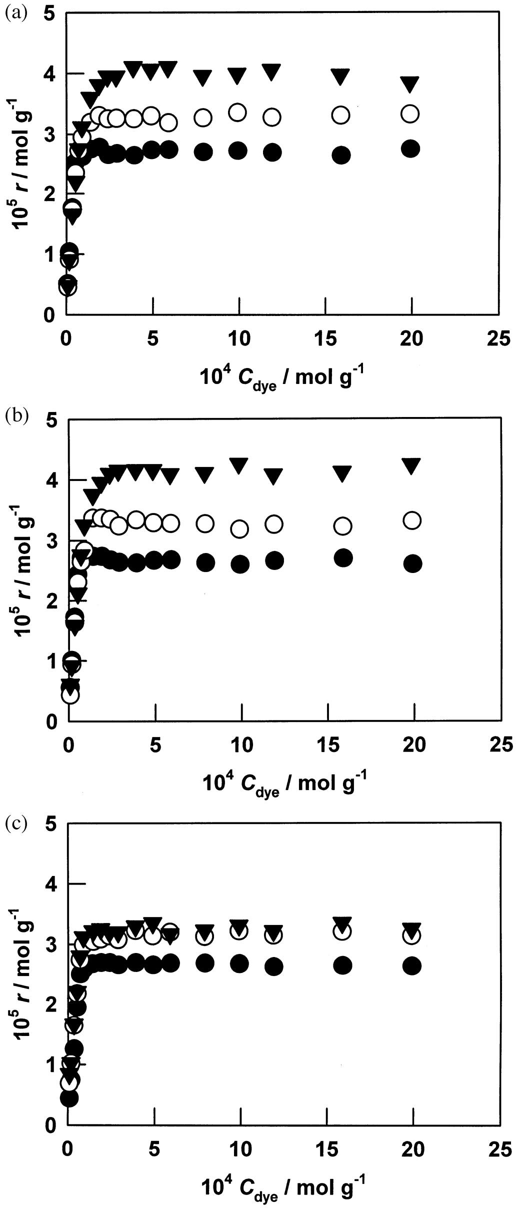


Fig. 10. Sorption isotherms of 1,4-DAA for the nylon 6 fiber in the dyebath containing the 1:1 molar ratio of dye and surfactant. (a) DC3-12; (b) DC6-12; (c) C12C1NBr. ●, 80°C; ○, 90°C; ▼, 100°C.

The apparent partition coefficients, K, are given in Table 7. The K values increased in the order of water<C12C1NBr<DC6-12<DC3-12 in the dyebath containing a 1:1 molar ratio. Considering this result together with the tendency of the $C_{\mathrm{dye}}^{\mathrm{max}}$

values, it follows that the gemini surfactants enhance the partition coefficients rather than the amount of dye dispersed. The mechanism of the enhancement of the partition coefficient is not clear. In a dyebath containing a 1:5 molar ratio, the K values increased in the order of DC6-12 < DC3-12 < < C12C1NBr. This result reflects the solubilization of 1,4-DAA into any aggregates such as premicelles as pointed out above.

Table 5
The maximum dye uptake (10^{-5} mol g^{-1}) in the dyebath containing the 1:1 and 1:5 molar ratio of dye and surfactant

Temperature (°C)	Molar ratio	DC3-12	DC6-12	C12C1NBr
80	1:1	2.7	2.7	2.7
90	1:1	3.3	3.3	3.2
100	1:1	4.0	4.2	3.3
100	1:5	4.1	4.2	3.6

Table 6
The maximum total dye concentration in the dyebath, $C_{\text{dye}}^{\text{max}}$ (10^{-5} mol dm^{-3}), in the dyebath containing the 1:1 and 1:5 molar ratio of dye and surfactant

Temperature (°C)	Molar ratio	DC3-12	DC6-12	C12C1NBr
80	1:1	4.7	5.6	7.6
90	1:1	7.0	7.4	8.2
100	1:1	9.6	10.8	8.3
100	1:5	14.2	18.7	9.2

Table 7
The apparent partition coefficients, K (dm^{-3} kg^{-1}), in the dyebath containing the 1:1 and 1:5 molar ratio of dye and surfactant

Temperature (°C)	Molar ratio	DC3-12	DC6-12	C12C1NBr
80	1:1	468	436	335
90	1:1	446	430	330
100	1:1	400	349	322
100	1:5	266	218	397

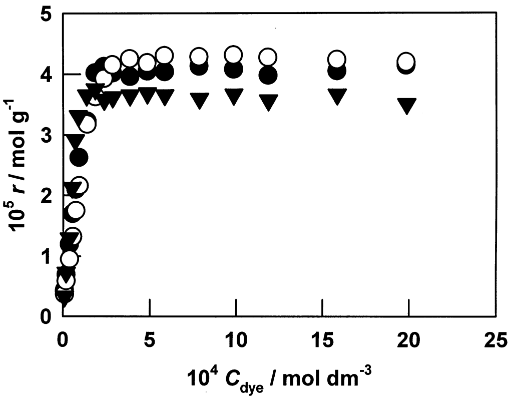


Fig. 11. Sorption isotherms of 1,4-DAA for the nylon 6 fiber in the dyebath containing the 1:5 molar ratio of dye and surfactant at 100°C. ●, DC3-12; ○, DC6-12; ▼, C12C1NBr.

4. Conclusions

For the disperse dyeing of nylon 6 fiber using gemini surfactants containing ammonium cations as auxiliaries investigated in the present study, the dyeing parameters were significantly dependent on the kind of surfactants.

The apparent diffusion coefficients of 1,4-DAA in the presence of the gemini surfactants were larger than that in the corresponding conventional surfactant. The manner of the reduction in dye uptake with increasing surfactant concentration was dependent on the kind of the surfactants and was of the order of DC6-12 > DC3-12 > C12C12NBr and the higher solubilization capacity reduces dye uptake. This suggests that dye which is solubilized in micelles rarely participates in sorption by the nylon 6 fiber and the surfactant micelles merely behave as a reservoir of the solubilized dye. The maximum total dye concentration, $C_{\text{dye}}^{\text{max}}$, at equilibrium was mainly affected by solubilization capacity in the presence of surfactant above the CMC, while it was dependent on the amount of dye dissolved and dispersed in the presence of surfactant below the CMC. The partition coefficient was dependent on the solubilization capacity in the presence of surfactant above the CMC, while below the CMC it was dependent on the dispersing ability of surfactant. This suggests that K is dependent not only on the solubilization capacity but also on the dispersing ability of surfactant. Maximum dye uptake in the presence of gemini surfactants both below and above the CMC was 10–30% larger than that obtained in the presence of corresponding conventional surfactant. It was attributed to the enhancement of either the amount of dye dissolved and/or dispersed or the partition coefficient.

From the above results, it is concluded that the gemini surfactants can be applied as a controller of dyeing kinetics or an improver of dye uptake in the disperse dyeing of the nylon 6 fiber.

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References

[1] Bird CL, Harris MP, Manchester F. J Soc Dyers Colour 1955;71:139.
[2] Bird CL, Manchester F. J Soc Dyers Colour 1955;71:604.
[3] Murray A, Mortimer K. J Soc Dyers Colour 1971;87:173.
[4] Derbyshire N, Mills WP, Shore J. J Soc Dyers Colour 1972;88:389.
[5] Savarino P, Barni E, Viscardi G, Carpignano R, Modica GD. J Soc Dyers Colour 1988;104:125.
[6] Yen PH, Chen KM. J Soc Dyers Colour 1998;114:160.
[7] Yen PH, Chen KM. J Soc Dyers Colour 1999;115:88.
[8] Choji N, Karasawa M, Sagae T, Sekido M. Sen'i Gakkaishi 1973;29:T301.
[9] Kuroiwa S. Sen'i Gakkaishi 1980;36:P27.
[10] Grancaric AM, Pusic T, Soljacic I. Text Chem Color 1997;29:33.
[11] de la Maza A, Parra JL, Manich A, Coderch L. J Soc Dyers Colour 1992;108:540.
[12] de la Maza A, Parra JL. J Soc Dyers Colour 1994;110:64.
[13] de la Maza A, Coderch L, Serra S, Parra JL. J Soc Dyers Colour 1997;113:165.
[14] de la Maza A, Parra JL, Bosch P. Text Res J 1991;61:357.
[15] de la Maza A, Parra JL, Bosch P, Coderch L. Text Res J 1992;62:406.
[16] de la Maza A, Parra JL. Text Res J 1993;63:44.
[17] de la Maza A, Parra JL. Text Res J 1994;64:255.
[18] de la Maza A, Manich AM, Coderch L, Parra JL. Text Res J 1995;65:163.
[19] Barni E, Carpignano R, Modica GD, Savarino P, Viscardi G. Disper Sci Technol 1988;9:75.
[20] Kim IS, Kono K, Takagishi T. Text Res J 1996;66:763.
[21] Kim IS, Kono K, Takagishi T. Text Res J 1997;67:555.
[22] Kim IS, Kono K, Takagishi T. Text Res J 1997;67:664.
[23] Kim IS, Kono K, Takagishi T. Text Res J 1997;67:767.
[24] Kim IS, Ishikawa Y, Kono K, Takagishi T. Text Res J 1998;68:422.
[25] Qian J, Hamada K, Mitsuishi M. Dyes Pigm 1994;25:167.
[26] Qian J, Hamada K, Mitsuishi M. Dyes Pigm 1994;26:217.
[27] Hamada K, Qian J, Hirata Y, Satomura K, Mitsuishi M. Dyes Pigm 1996;31:19.
[28] Hamada K, Satomura K, Mitsuishi M. Dyes Pigm 1996;31:205.
[29] Hamada K, Haizuka H, Yamazaki A. J Appl Polym Sci 1998;69:2247.
[30] Hamada K, Qian J, Mitsuishi M. J Soc Dyers Colour 1999;115:136.
[31] Zana R, Benrraou M, Rueff R. Langmuir 1991;7:1072.
[32] Alami E, Levy H, Zana R, Skoulios A. Langmuir 1993;9:940.
[33] Alami E, Beinert G, Marie P, Zana R. Langmuir 1993;9:1465.
[34] Frindi M, Michels B, Levy H, Zana R. Langmuir 1994;10:1140.
[35] Kern F, Lequeux F, Zana R, Candau SJ. Langmuir 1994;10:1714.
[36] Danino D, Talmon Y, Zana R. Langmuir 1995;11:1448.
[37] Danino D, Talmon Y, Levy H, Beinert G, Zana R. Science 1995;269:1420.
[38] Zana R, Levy H. Colloids Surf A: Physicochem Eng Asp 1997;127:229.
[39] Choi TS, Ichikawa H, Qian J, Shimizu Y, Shirai H, Hamada K. Sen'i Gakkaishi 1999;55:597.
[40] Choi TS, Shimizu Y, Shirai H, Hamada K. Dyes Pigm 2000;45:145.
[41] Hill AV. Proc Roy Soc 1928;104B:65.
[42] Bird CL, Manchester F, Harris P. Discuss Faraday Soc 1954;16:85.
[43] Bird CL. J Soc Dyers Colour 1954;70:68.