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Disperse dyeing of polyester 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 polyester fiber in the presence of two 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 in the presence of the gemini surfactants was larger than that for the conventional surfactant, reflecting a difference in surfactant property. Dye uptake decreased hyperbolically with increase in surfactant concentration above the critical micelle concentration (CMC). The observed decrease in the extent of the dye uptake above the CMC can be attributed to the solubilization capacity of 1,4-DAA into the micelles: the greater solubilization capacity reduced dye uptake. This result shows that dye which is solubilized within the surfactant micelles rarely takes part in the dyeing of the fiber and also that 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 values 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. In contrast, the *K* values hardly changed in the presence of surfactants whose concentration was below the CMC, suggesting that the *K* values cannot reflect the dispersing ability of the surfactants because the 1,4-DAA was dissolved in the dyebath under such conditions (120 °C). It was found that the affinity of the dye for the polyester fiber was unchanged by the addition of surfactant. Maximum dye uptake on to the polyester fiber in the presence of the surfactants whose concentration was below the CMC was 10.3×10^{-5}, 10.8×10^{-5}, and 9.1×10^{-5} mol g^{-1} for DC3-12, DC6-12, and C12C1NBr, respectively at 130 °C: the gemini surfactants slightly enhanced dye uptake. It is concluded that gemini surfactants can be used to control dyeing kinetics or to improve uptake of disperse dyes on to polyester. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Gemini surfactant; Disperse dyeing; Polyester; Cationic surfactant; Dyeing auxiliary

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1. Introduction

Polyester fiber has a highly compact and crystalline structure, and is markedly hydrophobic. For this reason, its aqueous dyeing is carried out at high temperature and high pressure using disperse dyes. The dyeing of polyester can be divided into several parallel processes such as dissolution and redissolution of disperse dye, transfer of dissolved dye from bulk solution to the fiber surface, diffusion and adsorption of dye at the fiber surface, and diffusion from the surface into the interior of the fiber [1–3]. It is well known that the additives in the dyebath affect the dyeing processes.

Solvent-assisted and carrier dyeing has been widely studied [4–9] as a means of accelerating dyeing rate, improving dye uptake and lowering dyeing temperature by means of changes in the physical properties of polyester, notably such as glass transition temperature (T_g). However, both solvents and carriers have serious problems, namely toxicity and unpleasant odor, poor light fastness, an adverse effect on the physical properties of the fiber, high costs of waste water treatment and environmental contamination and destruction [10]. Clearly, it seems sensible that efforts should be devoted toward the development of a new dyeing method to accelerate dyeing rate, improve dye uptake and lower dyeing temperature.

Surfactants added to a disperse dyebath affect the dyeing process because of their dispersing, emulsifying and solubilizing ability. Various surfactants have been studied in the dyeing of polyester from both scientific and commercial points of view. Recently, various compounds such as phosphatidylcholine liposome [11–21] and double tailed surfactants [22–26] have been examined as dyeing auxiliaries. When polyester fiber was dyed at 20–40 °C with disperse dyes using a microemulsion composing a small proportion of methylene chloride and phosphogliceride as the emulsifier, dye diffusion was uniform and the fastness of the dyeing to dry heat was excellent. Although this suggests the possibility of utilizing low temperature dyeing, the method suffers problems of organic solvents and usage at higher temperatures [20]. Dialkyldimethylammonium bromide containing two tail groups was used in the dyeing of polyester, nylon and acetate fibers with 1,4-diaminoanthraquinone [22–26]. The addition of the double tailed surfactants enabled the dyeing temperature to be reduced to 110, 50 and 60 °C, respectively for polyester, nylon and acetate fibers.

In contrast, the effects of a gemini surfactant with two head and two tail groups on dye sorption have not been studied, although the properties of the gemini surfactant micelles have been studied extensively by Zana et al. [27–34].

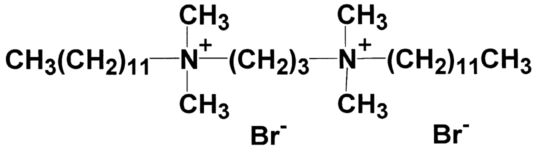
To investigate the use of gemini surfactants as dyeing auxiliaries, we considered both the microenvironments of the gemini surfactant micelles by using a spin probe technique [35] and the solubilization behavior of disperse dyes within gemini surfactant micelles [36]. A previous study concerned the effects of gemini surfactants on the disperse dyeing of nylon 6 fiber [37], and revealed that the dyeing rate in the presence of the gemini surfactants was larger than that for a corresponding conventional surfactant and also, that the maximum dye uptake was enhanced by some 10–30% using the gemini surfactant. Thus, gemini surfactants can be used to control the dyeing kinetics or to improve the uptake of disperse dyes on nylon 6 fiber.

The present study concerns the application of 1,4-diaminoanthraquinone (1,4-DAA) to polyester fiber in the presence of propanediyl-α,ω-bis(dimethyldodecylammonium bromide) (DC3-12) and hexanediyl-α,ω-bis(dimethyldodecylammonium bromide) (DC6-12). The results obtained were compared with those obtained 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 the gemini and conventional surfactants are discussed.

2. Experimental

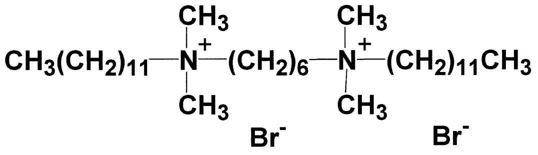
2.1. Materials

Two gemini surfactants and one conventional surfactant (Fig. 1) were used. Propanediyl-α,ω-bis(dimethyldodecylammonium bromide) (DC3-



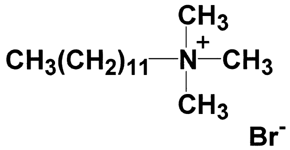
$CH_3(CH_2)_{11}-\overset{CH_3}{\underset{CH_3}{N^+}}-(CH_2)_3-\overset{CH_3}{\underset{CH_3}{N^+}}-(CH_2)_{11}CH_3 \quad Br^- \quad Br^-$

DC3-12



$CH_3(CH_2)_{11}-\overset{CH_3}{\underset{CH_3}{N^+}}-(CH_2)_6-\overset{CH_3}{\underset{CH_3}{N^+}}-(CH_2)_{11}CH_3 \quad Br^- \quad Br^-$

DC6-12



$CH_3(CH_2)_{11}-\overset{CH_3}{\underset{CH_3}{N^+}}-CH_3 \quad Br^-$

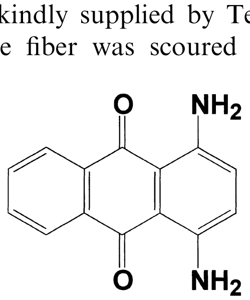
C12C1NBr

Fig. 1. Surfactants used.

12) and hexanediyl-α,ω-bis(dimethyldodecylammonium bromide) (DC6-12) were synthesized as described in a previous study [35,36]. The conventional surfactant, dodecyltrimethylammonium bromide (C12C1NBr) was purchased from Tokyo Kasei Kogyo Co. (Tokyo, Japan) and was used without purification.

The disperse dye, 1,4-diaminoanthraquinone (1,4-DAA, C. I. Disperse Violet 1, extra pure (98%), Fig. 2) was purchased from Tokyo Kasei Kogyo Co. (Tokyo, Japan) and used without further purification.

Multifilament polyester (PET) fiber of 75 denier/36 filaments, kindly supplied by Teijin Co. 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 contained 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 at room temperature.



1,4-DAA

Fig. 2. Dye used.

N, *N*-dimethylformamide (DMF) was analytical grade.

2.2. Dye sorption on to polyester 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 scoured polyester fiber was immersed in the dyebath in a sealed stainless steel pot of 200 cm^3 capacity housed in a Texam UR. MINI-COLOR MCUR-V5-6N (Nagoya, Japan) laboratory scale dyeing machine. Dyeing was started at 20 °C and the temperature raised by 4 °C min^{-1} to 100–130 °C. Dyeing was continued for a given time (1 min–2 days) at the final temperature and the dyebath was then cooled by 4 °C min^{-1} to 60 °C.

After dyeing, the fiber was rinsed in distilled water, washed in 50 cm^3 of an aqueous solution of SUNMORL BK-90NM (polyoxyethylene alkyl ether nonionic surfactant; 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 with distilled water, blotted with a filter paper, and dried in a desiccator at room temperature. The amount of dye sorbed by the polyester 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 polyester fiber was determined using Eq. (1).

$$r = \frac{A \cdot V_{\mathrm{s}}}{10{,}000 \cdot \varepsilon \cdot W_{\mathrm{f}}} \tag{1}$$

where r is the amount of dye sorbed by the polyester 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 the mass of the polyester fiber.

2.2.2. Surfactant concentration dependence

Aqueous surfactant solutions of various concentrations 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 pot with 20 mg of the scoured polyester fiber. Dyeing was accomplished and the amount of dye uptake on to the polyester fiber was determined in the manner described in the previous section. In this experiment, dyeing was carried out at 120 °C for 4 h.

2.2.3. Sorption isotherms

A 50 cm^3 aqueous dyebath containing pH 5.0 acetate buffer solution, surfactant at a constant concentration, and the disperse dye at various concentrations (1×10^{-5}–4×10^{-3} mol dm^{-3}) was placed in a dye pot together with 20 mg of the scoured polyester fiber. Dyeing was carried out at 110 °C for 12 h, 120 °C for 4 h and 130 °C for 1 h. The amount of dye adsorbed by the polyester 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 1:0.2 and a 1:5 molar ratio of dye:surfactant were determined. In this experiment, solid particles of surfactant and dye were ground together with an agate mortar and added to pH 5.0 acetate buffer solution. The solution was then stirred using a magnetic stirrer bar to form a stable dispersion.

2.2.4. Determination of dyeing transition temperature

A 50 ml aqueous solution containing pH 5.0 acetate buffer, surfactant and disperse dye at a constant concentration was placed in a dye pot together with 20 mg of the scoured polyester fiber. Dyeing was carried out at 70–130 °C for 30 min. The amount of dye sorbed by the polyester fiber was determined in the manner described in Section 2.2.1, and a plot of dye uptake as a function of dyeing temperature was constructed.

3. Results and discussion

3.1. Time dependence

Plots of the amounts of dye sorbed by the polyester fiber as a function of dyeing time at 120 °C in both the absence and presence of the gemini and conventional surfactants are shown in Fig. 3; similar plots were obtained at the other temperatures. From the time dependence of the dye uptake, the period for which equilibrium sorption was established was determined as 1 day at 100 °C, 8 h at 110 °C, 2 h at 120 °C, and 1 h at 130 °C. As described in the experimental section, the polyester fiber was placed in the dyebath at ambient temperature and dyeing began before the dyebath had reached the dyeing temperature (100–130 °C), so that a significant amount of dye should have been adsorbed by the polyester fiber prior to reaching 100–130 °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.

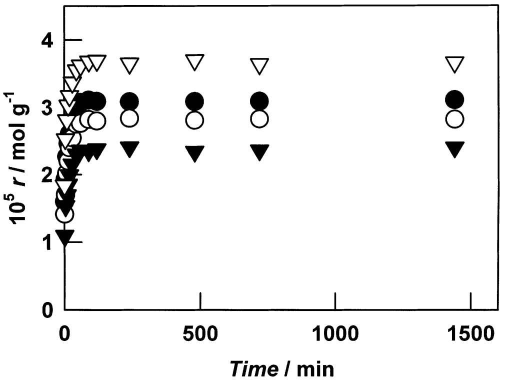


Fig. 3. Time dependence of the amount of 1,4-DAA sorbed by the polyester fiber at 120 °C. ●, DC3-12 (3×10^{-3} mol dm^{-3}); ○, DC6-12 (3×10^{-3} mol dm^{-3}); ▼, C12C1NBr (3×10^{-2} mol dm^{-3}); ▽, absence. Initial dye concentration is 5×10^{-4} mol dm^{-3}.

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 as a function of dyeing time (Fig. 4). As described previously [37], Eq. (2) was used to determine the apparent diffusion coefficient, D, where a is the radius of polyester fiber and $Dt/a^2 << 1$.

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

The apparent diffusion coefficients of 1,4-DAA were calculated from the slope of the linear plot of r_t / r_{eq} versus $t^{1/2}$ and are given in Table 1. The D values obtained in the presence of the gemini surfactants were larger than those using the conventional surfactant: the apparent diffusion coefficients increased in the order of water < C12C1NBr < DC3-12 < DC6-12. This result is similar to that obtained for the disperse dyeing of the nylon 6 fiber [37], suggesting that the addition of the gemini surfactants enhanced the apparent diffusion coefficients of the dye on both nylon 6 and polyester fibers. Although the adsorption of the surfactants on the fiber surface might have affected the dye diffusion, the mechanism of increased dyeing rate in the presence of the gemini surfactant is not clear.

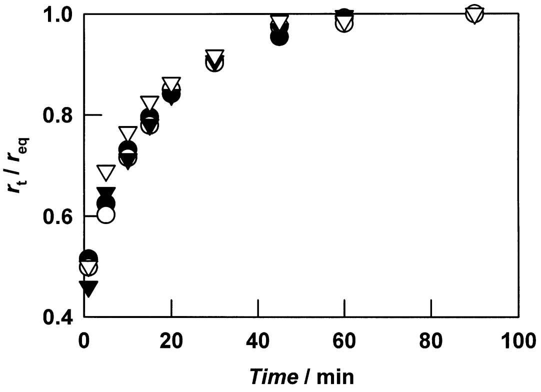


Fig. 4. Plots of r_t/r_{eq} versus time at 120 °C. ●, DC3-12 (3×10^{-3} mol dm^{-3}); ○, DC6-12 (3×10^{-3} mol dm^{-3}); ▼, C12C1NBr (3×10^{-2} mol dm^{-3}); ▽, absence. Initial dye concentration is 5×10^{-4} mol dm^{-3}.

Table 1
Diffusion coefficients in the presence of gemini and conventional surfactants, D (10^{-12} cm^2 s^{-1})

Temperature (°C)	DC3-12	DC6-12	C12C1NBr	Water
110	–	5.6	5.2	–
120	16.5	20.8	12.0	10.9

3.2. Surfactant concentration dependence

Plots of dye uptake on to polyester fiber, r, versus surfactant concentration, C_{surf}, at 120 °C in the presence of DC3-12, DC6-12, and C12C1NBr are shown in Figs. 5, 6 and 7, respectively. When surfactants were not present in the aqueous dyebath, the amount of dye adsorbed by the polyester fiber increased with increasing dye concentration and reached a maximum of about 1.6×10^{-3} mol dm^{-3} dye (see Figs. 5, 6 and 7). This particular concentration is the solubility of 1,4-DAA in water at 120 °C and is about 20 times as high as that at 80 °C [37].

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 [35]), dye uptake

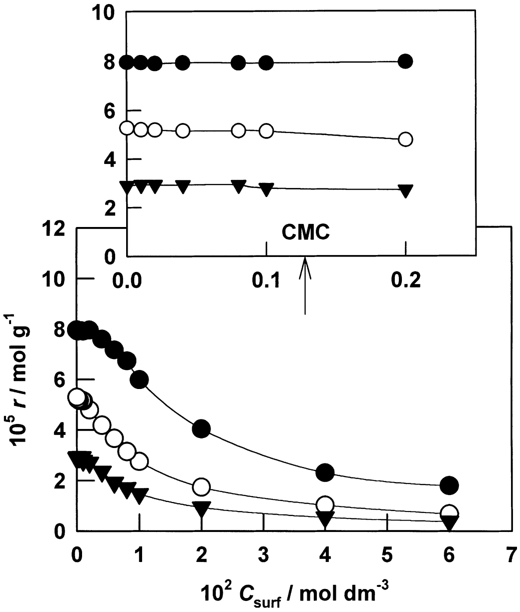


Fig. 5. Dependence of dye uptake on surfactant concentration for DC3-12 at 120 °C. Initial dye concentration, ●, 2×10^{-3}; ○, 8×10^{-4}; ▼, 4×10^{-4} mol dm^{-3}.

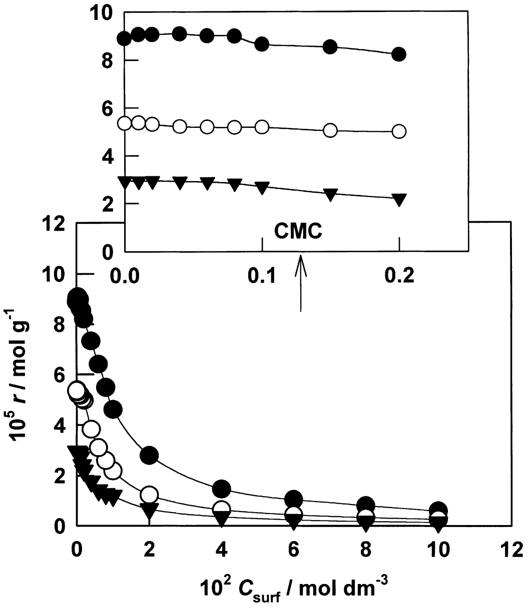


Fig. 6. Dependence of dye uptake on surfactant concentration for DC6-12 at 120 °C. Initial dye concentration, ■, 2×10^{-3}; ○, 8×10^{-4}; ▼, 4×10^{-4} mol dm^{-3}.

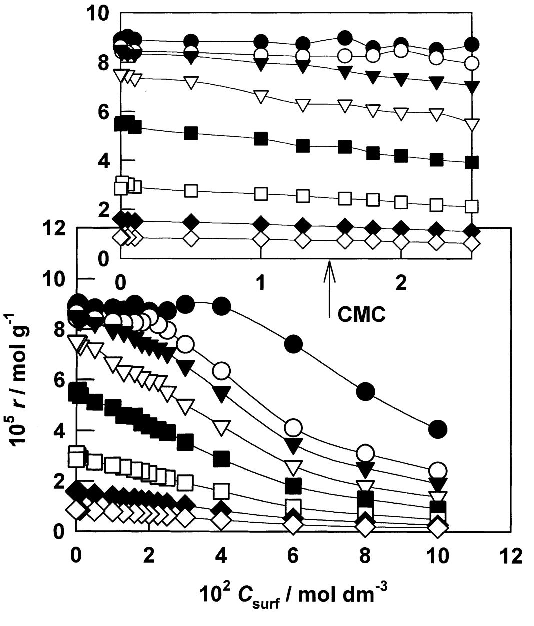


Fig. 7. Dependence of dye uptake on surfactant concentration for C12C1NBr at 120 °C. Initial dye concentration, ●, 4×10^{-3}; □, 2×10^{-3}; ▼, 1.6×10^{-3}; ▽, 1.2×10^{-3}; ■, 8×10^{-4} ; □, 4×10^{-4} ; ◆, 2×10^{-4} ; ◇, 1×10^{-4} mol dm^{-3}.

in the presence of C12C1NBr for dye concentrations below 1.6×10^{-3} mol dm^{-3} slightly decreased with increasing surfactant concentration, whereas for the gemini surfactants, dye uptake changed very little with surfactant concentration. This result is different to that obtained for nylon 6 fiber [37] for which dye uptake changed slightly as a function of surfactant concentration. On the other hand, in the case of the dyebath which contained surfactant at concentrations below the CMC and dye concentrations above 1.6×10^{-3} mol dm^{-3}, dye uptake was unaffected by changing surfactant concentration. This result suggests that surfactant monomer molecules and/or premicelles of C12C1NBr influenced both dye uptake and dye solubility, whereas those of the gemini surfactants did not influence dyeing.

In the case of a dyebath with a surfactant concentration above the CMC and dye concentrations below 1.6×10^{-3} mol dm^{-3}, dye uptake decreased hyperbolically with increasing surfactant concentration; this behavior was similar to that achieved for the nylon 6 fiber [37].

The nature of the observed decrease in dye uptake with increasing surfactant concentration was dependent on the kind of the surfactants and followed the order: DC6-12 > DC3-12 > C12C12NBr, which is inversely proportional to the square root of the solubilization capacity of 1,4-DAA into the micelles [36]; this finding is also similar to that for nylon 6 fiber [37]. Thus, the higher solubilization capacity reduced dye uptake. From the above results, it can be concluded that dye which is solubilized in surfactant micelles rarely participates in sorption by both polyester and nylon 6 fibers and that the surfactant micelles merely act as a reservoir of the solubilized dye.

3.3. Sorption isotherms

The sorption isotherms of 1,4-DAA on polyester fiber in both the absence and presence of the gemini and conventional surfactants at 110–130 °C are shown in Figs. 8 and 9, 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 corresponds to the maximum extent of dye

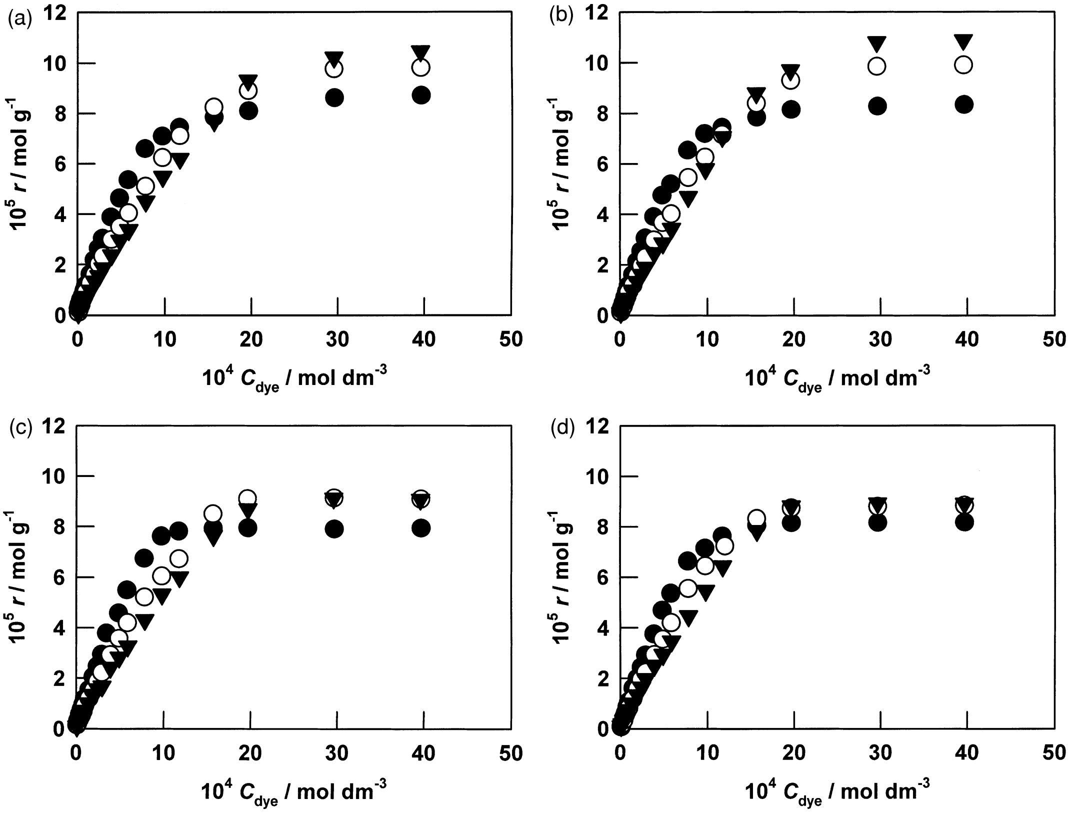


Fig. 8. Sorption isotherms of 1,4-DAA for the polyester fiber in both the absence and presence of the surfactants with concentrations below CMC. (a) DC3-12 (3×10^{-4} mol dm^{-3}); (b) DC6-12 (3×10^{-4} mol dm^{-3}); (c) C12C1NBr (3×10^{-3} mol dm^{-3}); (d) absence. ●, 110 °C; ○, 120 °C; ▼, 130 °C.

uptake at each temperature in the presence and absence of the surfactants. Maximum dye uptake values are given in Table 2. In all cases, maximum dye uptake increased with increasing temperature, which can be attributed to an increase in the amount of dye dissolved and/or dispersed should increase with increasing temperature. Although the order of maximum dye uptake changed with dyeing temperature, at 130 °C maximum dye uptake in the presence of the gemini surfactants was 13–19% greater than that obtained in the presence of the conventional surfactant. This suggests that the gemini surfactants increased the amount of dye participating in dyeing; thus, the amount of dye dissolved and/or dispersed might have been enhanced by the addition of the gemini surfactants at 130 °C.

In the presence of the surfactants at concentrations above the CMC, sorption isotherms were obtained and maximum dye uptake was determined (Table 2). Maximum dye uptake in the presence of DC3-12 was larger than that in its absence, whereas the addition of DC6-12 and C12C1NBr at concentrations above the CMC reduced maximum dye uptake at 120 and 130 °C. This result can be attributed to the amount of dye solubilized in micelles.

Maximum dye uptake in the dyebath which contained the 1:0.2 and the 1:5 molar ratio of dye:surfactant at 120 °C was determined from Fig. 9 and is presented in Table 2. Maximum dye uptake in the case of C12C1NBr hardly changed with increasing molar ratio of dye:surfactant, whereas dye uptake decreased in the cases of both

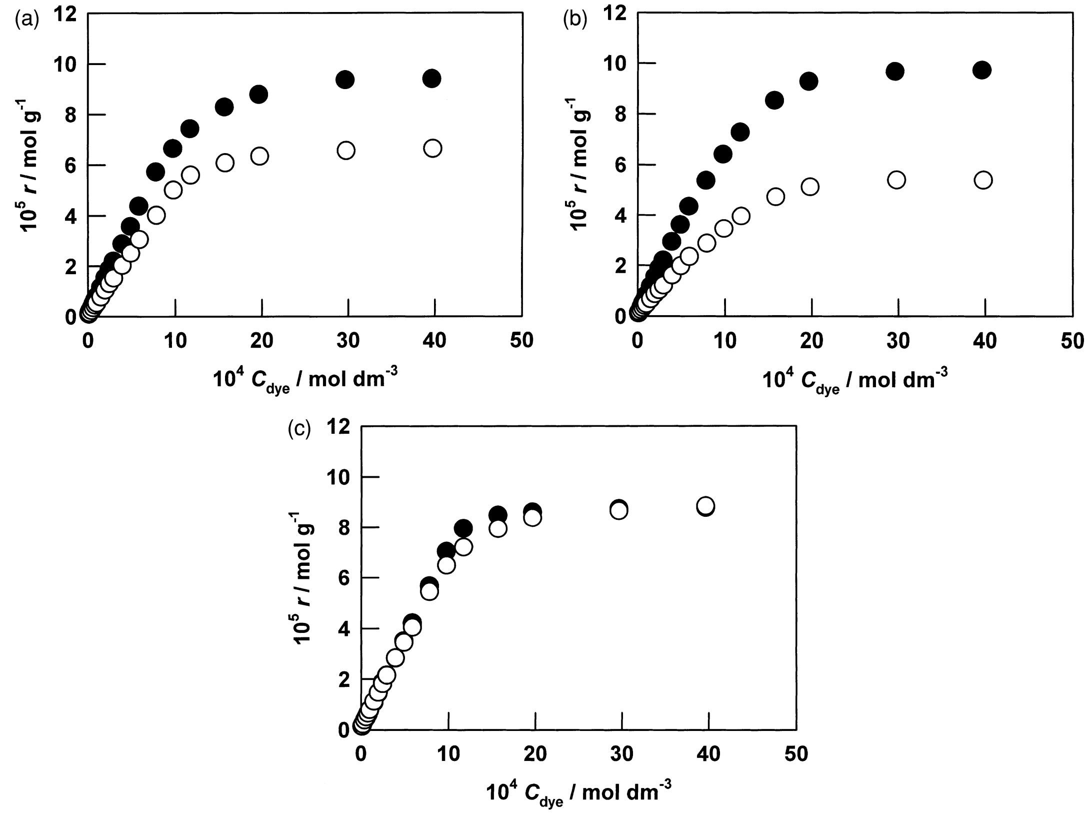


Fig. 9. Sorption isotherms of 1,4-DAA for the polyester fiber in dyebaths containing 1:0.2 and 1:5 molar ratios of dye and surfactant at 120 °C. (a) DC3-12; (b) DC6-12; (c) C12C1NBr. ●, D:S = 1:0.2 ; ○, D:S = 1:5.

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

	Temperature (°C)	DC3-12	DC6-12	C12C1 NBr	Water
Below CMC	110	8.7	8.3	7.9	8.2
	120	9.8	9.9	9.1	8.8
	130	10.3	10.8	9.1	8.9
Above CMC	110	9.6	9.1	8.2	
	120	9.8	8.5	7.6	
	130	9.9	8.2	7.4	
D:S = 1:0.2	120	9.4	9.7	8.8	
D:S = 1:5	120	6.6	5.4	8.8	

DC3-12 and DC6-12. Maximum dye uptake in the case of the dyebath which contained the 1:0.2 molar ratio of dye:surfactant (the surfactant concentrations were below the CMC) followed to the order: C12C1NBr < DC3-12 < DC6-12, compared to the order: DC6-12 < DC3-12 < C12C1NBr in the case of the 1:5 molar ratio. This finding is explained by the fact that micelles of the gemini surfactants were formed in the dyebath containing the 1:5 molar ratio of dye:surfactant. As the solubilization power (the amount of dye solubilized per mole of micellar surfactant) of 1,4-DAA at 25 °C was 0.0146, 0.0204 and 0.0040 for DC3-12, DC6-12 and C12C1NBr at a concentration below 1×10^{-1} mol dm^{-3}, respectively [36], this result shows that maximum dye uptake was dependent on the solubilization power of 1,4-DAA into micelles.

The maximum total dye concentration, $C_{\mathrm{dye}}^{\mathrm{max}}$, at equilibrium was determined from the crossover point of the two linear lines shown in Fig. 10 and is given in Table 3. The $C_{\mathrm{dye}}^{\mathrm{max}}$ values increased with increasing temperature, indicating that more dye

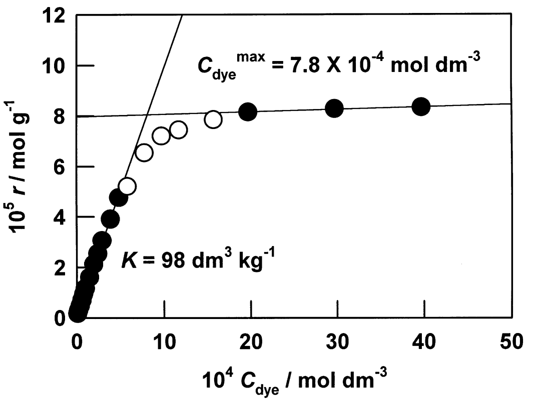


Fig. 10. Calculation of the maximum total dye concentration in the dyebath and the apparent partition coefficient. Example: the dyebath containing DC6-12 (3×10^{-4} mol dm^{-3}) at 110 °C.

Table 3
Maximum total dye concentration in the dyebath, C_{dye}^{max} (10^{-4} mol dm^{-3})

	Temperature (°C)	DC3-12	DC6-12	C12C1 NBr	Water
Below CMC	110	8.2	7.8	7.7	7.8
	120	12.6	13.3	12.0	10.7
	130	16.6	18.2	15.4	13.5
Above CMC	110	11.6	12.6	13.8	
	120	14.6	14.7	15.0	
	130	17.1	17.2	17.2	
D:S = 1:0.2	120	12.7	13.0	11.8	
D:S = 1:5	120	12.6	14.0	11.8	

was present in the dyebath at higher temperatures. When the surfactant concentration was below the CMC and the amount of dye solubilized in the micelles was negligible, C_{dye}^{max} was the sum of the maximum concentrations of the dye dissolved and dispersed. If the maximum concentrations of the dye dissolved and dispersed are designated as $C_{dissolved}^{max}$ and $C_{dispersed}^{max}$, C_{dye}^{max} is represented as follows

$$C_{dye}^{max} = C_{dissolved}^{max} + C_{dispersed}^{max} \tag{3}$$

The difference of C_{dye}^{max} in the absence and presence of the gemini and conventional surfactants at concentrations below the CMC is derived from the difference of $C_{dispersed}^{max}$ because the $C_{dissolved}^{max}$ value is affected only by temperature. This fact shows that the larger C_{dye}^{max} values obtained for the gemini surfactants are due to the larger dispersing ability of the gemini surfactants.

The maximum total dye concentration, C_{dye}^{max}, achieved in the presence of both the gemini and conventional surfactants at concentrations above the CMC followed the order: DC3-12 < DC6-12 < C12C1NBr. In this case, C_{dye}^{max} is represented by Eq. (4).

$$C_{dye}^{max} = C_{dissolved}^{max} + C_{dispersed}^{max} + C_{solubilized}^{max} \tag{4}$$

where $C_{solubilized}^{max}$ is the maximum concentration of dye solubilized. The amount of 1,4-DAA solubilized in the micelles at 25 °C was previously estimated to be 2.82×10^{-5} mol dm^{-3}, 4.32×10^{-5} mol dm^{-3}, and 5.49×10^{-5} mol dm^{-3} for DC3-12 (3×10^{-3} mol dm^{-3}), DC6-12 (3×10^{-3} mol dm^{-3}), and C12C1NBr (3×10^{-2} mol dm^{-3}), respectively [36]. If the order of solubilization capacity (DC3-12 < DC6-12 < C12C1NBr) is assumed not to change with the temperature, the observed difference of C_{dye}^{max} is determined by the amount of dye solubilized in the micelles: the largest C_{dye}^{max} value achieved for C12C1NBr is due to the largest amount of dye solubilized into C12C1NBr micelles.

The C_{dye}^{max} values obtained at 120 °C in the dyebath containing the 1:0.2 and 1:5 molar ratio of dye:surfactant increased in the order: C12C1NBr < DC6-12 < DC3-12. As described earlier, this is attributable to the larger $C_{dispersed}^{max}$ of the gemini surfactants.

The apparent partition coefficients, K, calculated from the slope of the linear part at the lower dye concentration region of Fig. 10 (Table 4) show that the K values decreased with increasing the dyeing temperature, suggesting that the partition process was exothermic. In the dyebath containing surfactants at concentrations below the CMC, the K values were quite similar to those in the absence of the surfactants at all temperatures. In the dyebath containing the surfactants with concentrations above the CMC and 1:5 molar ratio of dye:surfactant, K was diminished, which is due to the increase of C_{dye}^{max} through solubilization of the dye into the micelles. It is noteworthy that the apparent partition coefficients for the disperse dyeing of nylon 6 fiber were enhanced by the

Table 4
Apparent partition coefficients, K (dm^3 kg^{-1})

	Temperature (°C)	DC3-12	DC6-12	C12C1 NBr	Water
Below CMC	110	100	98	101	103
	120	75	74	76	81
	130	59	58	59	65
Above CMC	110	80	72	58	
	120	65	58	50	
	130	58	48	42	
D:S = 1:0.2	120	73	73	72	
D:S = 1:5	120	51	38	68	

addition of the gemini surfactants [37]. Although the difference observed between polyester and nylon 6 fiber with respect to the effects of the gemini surfactants on the partition coefficients might be attributed to their adsorption on the fiber surface, it is necessary to elucidate the partition mechanism.

3.4. Dyeing transition temperature

The plots of dye uptake, r, as a function of dyeing temperature in both the absence and presence of DC3-12, DC6-12, and C12C1NBr are shown in Fig. 11. The amount of dye sorbed by the polyester fiber suddenly increased around 90 °C and reached a maximum value around 120 °C, indicating that the dyeing transition temperature was about 90 °C. The addition of the surfactants did not change the dyeing transition temperature. This result shows that the change of the physical properties, such as the T_g observed when using carriers or solvents [4–9], does not occur in the used gemini and conventional surfactants.

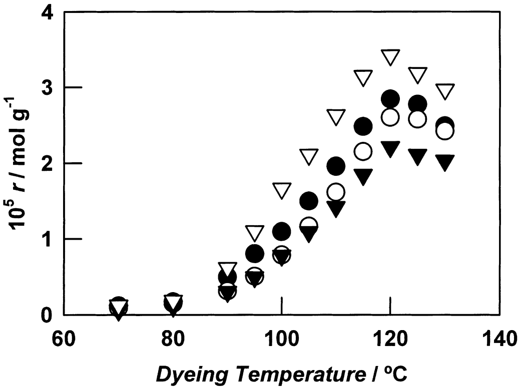


Fig. 11. Plots of dye uptake versus dyeing temperature; dyeing time was 30 min. ●, DC3-12; ○, DC6-12; ▼, C12C1NBr ; ▽, absence. Initial dye concentration 5×10^{-4} mol dm^{-3}.

4. Conclusions

In the disperse dyeing of polyester fiber using gemini surfactants containing ammonium cations as auxiliaries, dyeing parameters such as diffusion coefficient, maximum dye uptake and partition coefficient were influenced by the kind of surfactants used.

The apparent diffusion coefficients of 1,4-DAA in the presence of the gemini surfactants were larger than in the presence of the corresponding conventional surfactant. This result is in agreement with the finding obtained for the disperse dyeing of nylon 6 fiber [37], strongly suggesting that gemini surfactants can be used to control the kinetics at the dyeing of synthetic fibers.

Maximum dye uptake in the presence of the gemini surfactants at concentrations below the CMC at 130 °C was 13–19% larger than that obtained in the presence of the corresponding conventional surfactant. This was attributed to enhancement of the amount of dye dispersed. The difference in maximum total dye concentration, $C_{\mathrm{dye}}^{\mathrm{max}}$, achieved for the various surfactants can be attributed to their differing solubilization capacity at concentrations above the CMC, but appears to depend on the amount of dye dissolved and dispersed at concentrations below the CMC.

The addition of both the gemini and conventional surfactants did not alter the apparent partition coefficients at concentrations below the CMC. This result is quite different to that obtained for nylon 6 fiber; the observed difference between polyester and nylon 6 fiber in this particular behaviour might be attributed to their adsorption on the fiber surface.

From the above results, it is concluded that the gemini surfactants can be used to control dyeing kinetics or to improve dye uptake in the disperse dyeing of polyester.

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