

Application of Bolaform Electrolytes as Dyeing Auxiliaries for Acid Dyeing of Nylon 6

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Abstract:

The sorption behavior of sodium 1-phenylazo-2-hydroxy-6-naphthalene-sulfonate, sodium 1-phenylazo-2-hydroxy-7-naphthalenesulfonate, and sodium 1-phenylazo-2-hydroxy-8-naphthalenesulfonate by a nylon 6 film was investigated both in the presence and absence of various bolaform electrolytes. The addition of the bolaform electrolytes influenced the dye sorption and the manner of the influence was dependent on pH in the dye bath. In pure water, the dye uptake was significantly enhanced by the addition of some bolaform electrolytes. The sorption parameters determined from the sorption isotherms considering the dual sorption mechanism were affected by the addition of the bolaform electrolytes. Particularly the number of the binding sites for Langmuir type sorption was significantly changed in the presence of the bolaform electrolytes. This result is discussed on the basis of the complexation between the dyes and the bolaform electrolytes.

1. Introduction

The sorption and diffusion of acid dyes by nylon 6 fibers have been investigated from various points of view. In many cases for nylon 6, their sorption isotherms and diffusion processes are interpreted using a dual sorption mechanism, which consists of partition and Langmuir type sorption [1-7]. The effects of cosolutes, e.g. sodium chloride [8] and surfactants [9], on dye sorption by nylon have been also reported.

On the other hand, organic compounds possessing two cationic or anionic groups separated by relatively large distances are named 'bolaform electrolytes (bolytes)' or 'bolaform amphiphiles (bola-amphiphiles)' [10,11], whose physical properties, such as surface activity, solubilization, and micellization, have been studied extensively [12-14].

We have investigated the effects of bolaform electrolytes on the binding of monoazo sulfonated dyes with poly(vinylpyrrolidone) in aqueous solutions [15-18]. As a result, the aromatic bolaform electrolytes containing two quaternary ammonium and two phenyl groups lowered the first binding constants of the dyes with the polymer, while the aliphatic ones behaved oppositely. Recently, we reported the sorption behavior of acid dyes for a nylon 6 film and a silk fiber in the presence of aliphatic bolaform electrolytes and elucidated the effects of the bolaform electrolytes on the sorption [19,20].

In the present study, the effects of various bolaform electrolytes on the sorption of acid dyes by a nylon 6 film were investigated to elucidate the effects of the bolaform electrolytes as auxiliaries in dyeing process. Considering the sorption parameters determined by means of the dual sorption mechanism, we discuss the effects of the bolaform electrolytes on the acid dyeing of the nylon 6 film and the wool fiber.

2. Experimental

2.1. Acid dye

Three acid dyes, sodium 1-phenylazo-2-hydroxy-6-naphthalenesulfonate (A6S) sodium 1-phenylazo-2-hydroxy-7-naphthalenesulfonate (A7S), and sodium 1-phenylazo-2-hydroxy-8-naphthalenesulfonate (A8S) shown in Fig. 1 were used. A6S (Crocein Orange G) was purchased from Tokyo Kasei Kogyo Co. (Tokyo, Japan) and purified by repeated recrystallization from 80 % aqueous ethanol solution. A7S and A8S were synthesized by reacting diazotized aniline with 2-naphthol-7-sulfonic acid and 2-naphthol-8-sulfonic acid in an alkaline solution. After that, those dyes were purified by repeated recrystallization from 80 % aqueous ethanol solution. The purity of all the dyes was confirmed by elemental analysis

2.2. Bolaform electrolytes

Bolaform electrolytes containing two pyridine rings (DCPyn) shown in Fig. 2 were used. DCPyn was synthesized by making 1,*n*-dibromoalkane to react with pyridine in nitromethane. The products thus obtained were purified by repeated precipitation from methanol into acetone. Bolaform electrolytes having a xylene group as a spacer (DCXy2, DCXy4, DCXyBz, and DCXyPy, Fig. 2) were also used. These bolaform electrolytes were synthesized by making *p*-dibromoxylene with the corresponding *N,N*-dimethyl-*n*-alkylamine, *N,N*-dimethylbenzyl amine, and pyridine. The products were purified by repeated precipitation. The purity of all the bolaform electrolytes was confirmed by elemental analysis.

2.3. Nylon 6 film

Biaxially drawn nylon 6 film was kindly supplied by Unitika Co., whose thickness was 15 μm . The amino end group content was determined as 3.53×10^{-5} equivalent per g of nylon by the titration of *m*-cresol/methanol solution of the nylon 6 film with an aqueous methanol solution of hydrochloric acid. The nylon 6 film was pretreated in boiling water for 90 min, immersed in water for 1 day, and soaked in aqueous solutions having the same conditions as those used for the dye sorption, i.e. aqueous hydrochloric acid solutions (pH3 and pH4), acetate buffer solutions (pH4, pH5, and pH6), and

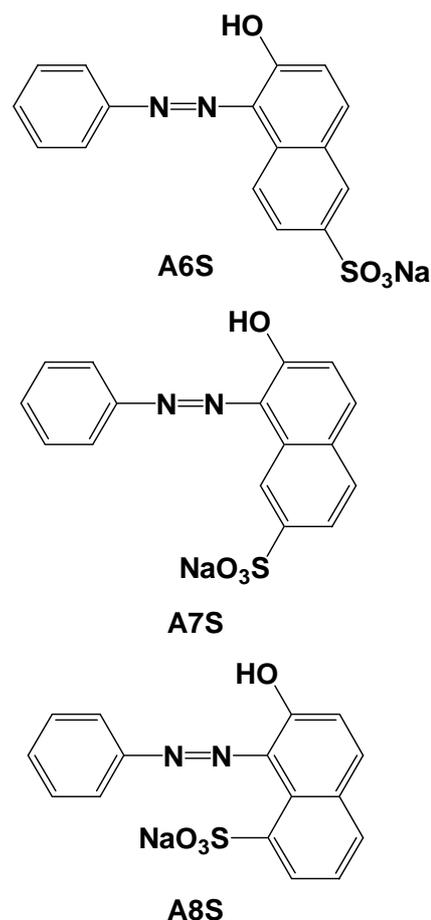


Fig. 1 Dyes used.

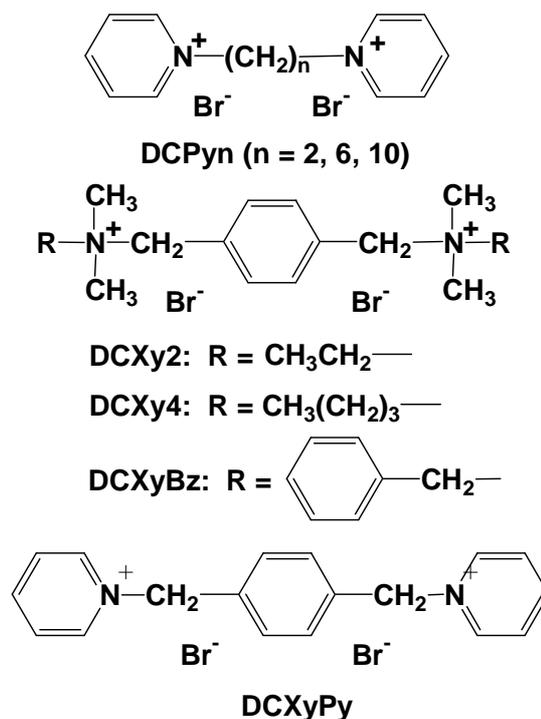


Fig. 2 Bolaform electrolytes used.

phosphate buffer solutions (pH6 and pH7) for another 1 day. After that, it was dried in a desiccator with silica gel.

2.4. Dye sorption

The dye was sorbed by soaking about 20 mg of the pretreated nylon 6 film in aqueous dye solutions. The dye sorption was carried out in both the absence and presence of the bolaform electrolytes at a given temperature for a desired time. After the sorption, the dyed film was removed from the dye bath, rinsed in cold water, blotted with filter paper to remove the remaining dye solution from the film surface, and dried in a desiccator with silica gel. The dye sorbed by the nylon 6 film was extracted with 25 mL of 25 % aqueous pyridine solution and its concentration was determined spectrophotometrically using a Shimadzu UV-160A spectrophotometer.

3. Results and Discussion

In the present study, the effect of the position at which a sulfonate group is attached in the dyes is discussed, but in the proceedings the results for A6S is argued. In the poster presentation, the results for A6S, A7S, and A8S will be compared.

3.1. Dependence of the dye uptake on bolaform electrolyte concentration

The change of the dye uptake with bolaform electrolyte concentration was investigated in various buffer solutions. In Figs. 3 and 4, the dye uptake, C_F , is plotted against bolaform electrolyte concentration, C_{BL} . At pH4, the dye uptake monotonously decreased with increasing bolaform electrolyte concentration. On the other hand, at pH5 and 6, the dye uptake slightly increased in the lower bolaform electrolyte concentration region and after that decreased or indicated a constant uptake. Furthermore, in pure water, the dye uptake was significantly enhanced by the addition of DCPy2. The dye uptake enhanced by the addition of DCPy2 was almost the same as those obtained at lower pH values in the absence of the bolaform electrolytes, indicating that these bolaform electrolytes make it possible to attain the enough amount of dye sorbed even in neutral pH region. This is due to the fact that the addition of DCPy2 diminished pH values in the dye bath: DCPy2 behaves as Lewis acid and hydroxide ions are bound to it, resulting in the increase of protons. The dye

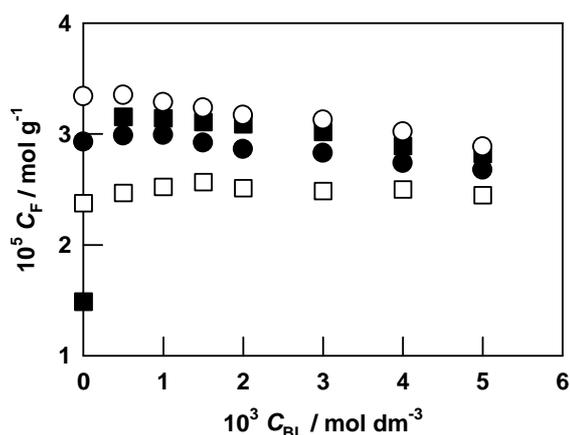


Fig. 3 Dependence of the dye uptake on bolaform electrolyte concentration in various buffer solutions containing DCPy2 at 80 °C, where dye concentration is $1 \times 10^{-4} \text{ mol dm}^{-3}$. ○, pH4; ●, pH5; □, pH6; ■, pure water.

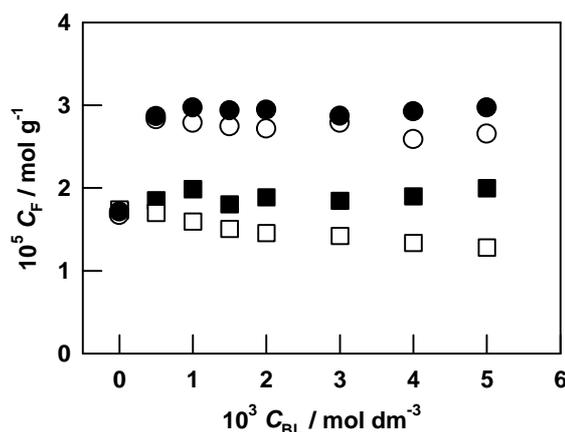


Fig. 4 Dependence of the dye uptake on bolaform electrolyte concentration in pure water at 80 °C, where dye concentration is $1 \times 10^{-4} \text{ mol dm}^{-3}$. ○, DCpXy2; ●, DCpXy4; □, DCpXyBz; ■, DCpXyPy.

uptake in pH7 phosphate buffer was significantly enhanced in the presence of DCPy2, too. The addition of DCPy10 also enhanced the dye uptake, whereas the addition of DCPy6 affected very little.

DCpXy2 and DCpXy4 also enhanced the dye uptake in pure water. In this case, the mechanism to enhance the dye uptake is different from that in the case of DCPy2. The reason why DCpXy2 and DCpXy4 enhanced the dye uptake is as follows. The bolaform electrolytes are bound with the acid dye, the complexes between the dye and the bolaform electrolytes are formed, and the complexes might be more easily sorbed by the nylon 6 film than the dye itself. On the other hand, the bolaform electrolytes containing aromatic rings as terminal groups, DCpXyBz and DCpXyPy, diminished and enhanced the dye uptake, respectively.

3.2. Sorption isotherms

The sorption isotherms of A6S for the nylon 6 film in various buffer solutions containing DCPy2 are shown in Figs. 5 and 6, where C_F is the amount of dye sorbed by the nylon 6 film and C_S is the dye concentration in the dye bath, which includes both the concentration of the free dyes and the complexes between the dyes and the bolaform electrolytes. The dye uptake decreased with increasing pH value, which is due to the decrease in the amount of the terminal amino end groups with increasing pH. The shapes of the sorption isotherms for all the other A6S / Nylon 6 / bolaform electrolyte systems were similar. The sorption isotherms were analyzed by means of the following bimodal sorption equation, where K_P is the partition coefficient, S the number of binding sites for the Langmuir type sorption, and K_L the intrinsic binding constant for the Langmuir type sorption.

$$C_F = K_P \cdot C_S + \frac{S \cdot K_L \cdot C_S}{1 + K_L \cdot C_S} \quad (1)$$

The first and second term in the right-hand side of eq. (1) express the dye uptake by the partition and Langmuir type sorption, respectively. These terms may contain an activity effect on the free dye in the higher concentration region.

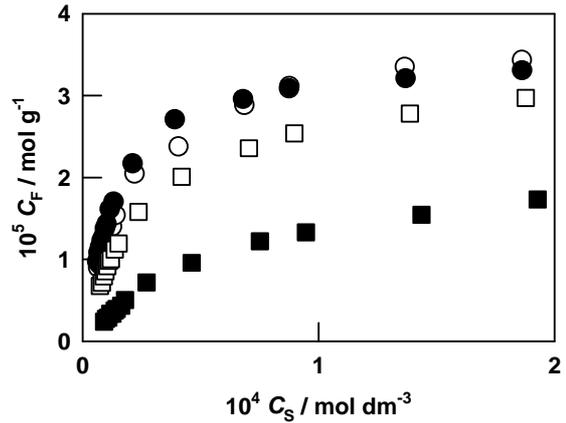


Fig. 5 Sorption isotherms of A6S for the nylon 6 film in various buffer solutions containing DCPy2 ($2 \times 10^{-3} \text{ mol dm}^{-3}$) at $80 \text{ }^\circ\text{C}$. \circ , pH4; \bullet , pH5; \square , pH6; \blacksquare , pH7.

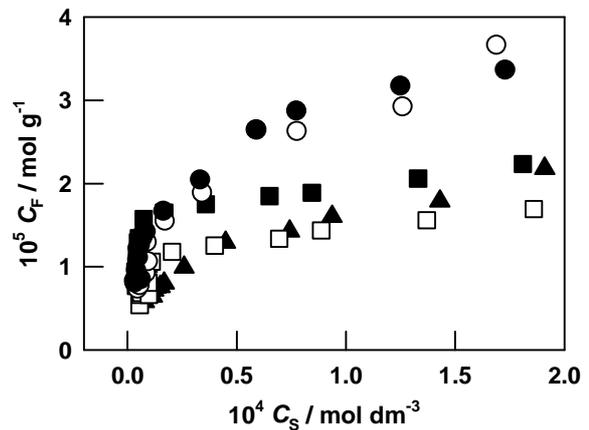


Fig. 6 Sorption isotherms of A6S for the nylon 6 film in pure water at $80 \text{ }^\circ\text{C}$, where bolaform electrolyte concentration is $2 \times 10^{-3} \text{ mol dm}^{-3}$. \circ , DCpXy2; \bullet , DCpXy4; \square , DCpXyBz; \blacksquare , DCpXyPy, \blacktriangle , absence.

The sorption parameters, K_P , S , and K_L were calculated using nonlinear regression of Sigma Plot (SPSS, U.S.A.). The S values thus obtained for DCPyn are shown in Fig. 7. In pH7 phosphate buffer solution and pure water, the S values in the presence of DCPy2 were two times as large as those in its absence, whereas in the case of DCPy10 the ratio of the presence to the absence was about 1.5. This result suggests that the bolaform electrolytes such as DCPy2 and DCPy10 can provide the binding sites of the acid dye. As was described above, this is due to the fact that the addition of DCPy2 diminished pH values in the dye bath: DCPy2 behaves as Lewis acid and hydroxide ions are bound to it, resulting in the increase of protons.

The sorption parameters for DCXy2, DCXy4, DCXyBz, and DCXyPy were also determined from the sorption isotherms using eq. (1). The number of binding sites for Langmuir sorption, S , for these bolaform electrolytes are shown in Fig. 8. In pure water, the addition of DCXy2, DCXy4, and DCXyPy enhanced the S values, while the presence of DCXyBz hardly affected them. In the other hand, in pH4 solutions, the addition of DCXy2, DCXy4, and DCXyPy enhanced the S values, whereas DCXyBz diminished the S values. DCXyBz blocks the binding sites and interrupt the binding of the acid dye with the binding sites of the nylon 6 film. This might be due to the fact that DCXyBz contains three benzene rings and these aromatic rings easily interrupt the interaction between the dye and the charged terminal groups of the nylon 6 film.

Thus the structure (terminal and spacer groups) of the bolaform electrolytes influences the number of binding sites for Langmuir sorption. The adequate design of the bolaform electrolytes makes it possible to develop excellent dyeing auxiliaries for acid dyeing of nylon 6.

Acknowledgement

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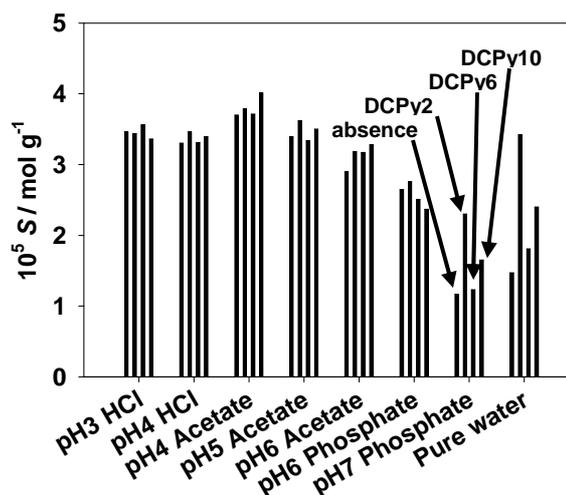


Fig. 7 Number of binding sites for Langmuir type sorption for the nylon 6 film in both the absence and presence of DCPyn at 80 °C.

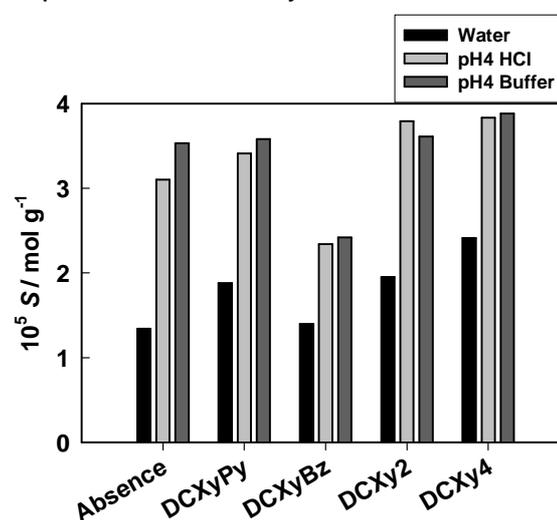


Fig. 8 Number of binding sites for Langmuir type sorption for the nylon 6 film in both the absence and presence of DCXy2, DCXy4, DCXyBz, and DCXyPy at 80 °C.

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