

Effects of a Bolaform Electrolyte on the Sorption of Acid Dyes by a Nylon 6 Film

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ABSTRACT: The sorption behavior of acid dyes by a nylon 6 film was investigated in the presence and absence of a bolaform electrolyte. The time dependence of the sorption changed with the pH values of the dye bath. At pH 3, equilibrium sorption was not established even after the immersion of the film in the aqueous dye solutions for 7 days, while at pH 4 and in pure water, equilibrium sorption was established after the immersion for 1 day. The sorption isotherms were determined and analyzed by means of the bimodal sorption equation. The sorption parameters thus determined were greatly affected by the dye structure and the pH values. The addition of the bolaform electrolyte reduced the amounts of dye sorbed by the nylon 6 film. This is believed to be due to the formation of the complexes between the dyes and the bolaform electrolyte in the dye bath. Thus, the bolaform electrolyte retards the sorption through the formation of the complexes. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 2247–2254, 1998

Key words: bolaform electrolyte; sorption; dyeing; acid dye; auxiliary

INTRODUCTION

The sorption and diffusion of acid dyes by nylon 6 have been investigated from various points of view. In many cases, their sorption isotherms and diffusion processes are interpreted using a dual sorption mechanism, which consists of partition and Langmuir-type sorption.^{1–6} The effects of co-solutes, for example, sodium chloride⁷ and surfactants,⁸ on dye sorption by nylon have been also reported.

On the other hand, bolaform electrolytes have been a matter of great interest for a long time.^{9,10} Recently bis(quaternary ammonium halide) surfactants have been exhaustively studied.^{11–15}

We have investigated the effects of bolaform electrolytes (bolytes) on the binding of monoazo sulfonated dyes with poly(vinylpyrrolidone) in aqueous solutions.^{16,17} As a result, the aromatic

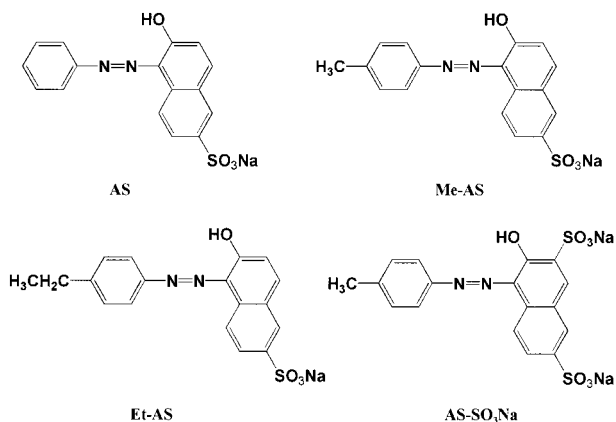
bolaform electrolytes containing 2 quaternary ammonium and 2 phenyl groups lowered the first binding constants of the dyes with the polymer, while the aliphatic ones behaved oppositely.

In the present study, the effects of an aliphatic bolaform electrolyte on the sorption of acid dyes by a nylon 6 film were investigated to apply as an auxiliary in dyeing process.

EXPERIMENTAL

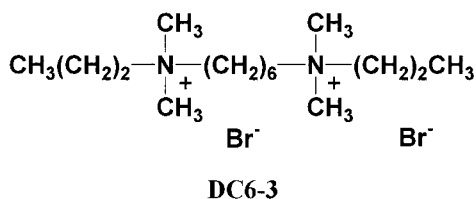
Four acid dyes, sodium 1-phenylazo-2-hydroxy-6-naphthalenesulfonate (AS), sodium 1-(4-methylphenylazo)-2-hydroxy-6-naphthalenesulfonate (Me-AS), sodium 1-(4-ethylphenylazo)-2-hydroxy-6-naphthalenesulfonate (Et-AS), and disodium 1-(4-methylphenylazo)-2-hydroxy-3,6-naphthalenedisulfonate (AS-SO₃Na) were used. The molecular structure of the dyes is as follows.

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AS (Crocein Orange G, C.I. Acid Orange 12, C.I. 15970) was purchased from Tokyo Kasei Co. (Tokyo, Japan) and purified by repeated recrystallization from aqueous ethanol. Me-AS was prepared as reported in our previous paper.¹⁸ Et-AS was synthesized by coupling of diazotized 4-ethylaniline with sodium salt of Schaeffer's acid (2-naphthol-6-sulfonic acid) in an alkaline condition. The dye obtained was purified by repeated washing with water and ethanol. The purity was confirmed by elemental analysis (Calcd. for Et-AS: C, 57.14; H, 4.00; N, 7.40; S, 8.5; Found: C, 57.44; H, 4.02; N, 7.59; S, 8.4). AS-SO₃Na was synthesized in the same procedure using *p*-toluidine and disodium salt of R acid (2-naphthol-3,6-disulfonic acid). The dye thus obtained was purified by repeated salting-out with NaCl and reprecipitating the aqueous solution with acetone. The purity was confirmed by elemental analysis (Calcd. for AS-SO₃Na at water content 8.33%: C, 40.13; H, 3.31; N, 5.51; Found: C, 40.47; H, 3.47; N, 5.46).

N,N'-bis(propyldimethyl)-1,6-hexanediammonium dibromide (DC6-3) was used as a bolaform electrolyte, which was prepared as follows. A mixed solution of 1-bromopropane and *N,N,N',N'*-tetramethyl-1,6-diaminohexane in nitromethane was stirred at room temperature for 4 days. The product was then filtered, purified by repeated precipitation from ethanol into ether, and dried. Purity was confirmed by elemental analysis. ANAL. calcd. for DC6-3: C, 45.94; H, 9.16; N, 6.70; Br, 38.2; Found: C, 45.47; H, 9.01; N, 6.66; Br, 39.8.



Biaxially drawn nylon 6 film whose thickness was 15 μm , was kindly supplied by Unitika Co. (Osaka, Japan). The amino end group content was determined as 3.53×10^{-5} equivalent per gram of nylon by the titration of a *m*-cresol-methanol solution of the nylon 6 film with an aqueous methanol solution of hydrochloric acid. This accurate titration showed that the amino end group content (4.65×10^{-5} eq/g) described in the previous article^{5,6} was not correct. 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, that is, aqueous hydrochloric acid solutions with pH 3 or pH 4 and pure water for another 1 day. After that, it was dried in a desiccator with silica gel.

The dyes were sorbed by soaking the pretreated nylon 6 film in the aqueous solutions containing a suitable amount of hydrochloric acid (1×10^{-3} , 1×10^{-4} , and 0 mol dm⁻³), which are designated as pH 3, pH 4, and H₂O, respectively. The dye sorption was carried out in the absence and presence of the bolaform electrolyte at a given temperature for a desired time. The amounts of dye sorbed by the film were determined in the same procedure as described in the previous article,⁵ using a Shimadzu UV-160A or UV-3100 spectrophotometer.

The pH values before and after the sorption experiments were measured by means of TOA HM-30V digital pH meter. In H₂O, pH was 5.5–5.9, which is because CO₂ and other probable pollutants were incorporated into the solutions. At all the pH values (pH 3, pH 4, and H₂O), the measured pH did not change before and after the sorption.

RESULTS AND DISCUSSION

Time Dependence of Dye Sorption

The time dependence of the amount of dye sorbed by the nylon 6 film, r , for AS is shown in Figure 1. In the case of pH 3, the amount of dye sorbed increased with time and equilibrium sorption was not established even after the immersion of the film in the aqueous dye solutions for a period of 7 days. This behavior was also observed for all the other dyes, as was pointed out in our previous articles.^{5,6} On the other hand, for pH 4 and H₂O, equilibrium sorption was established after the immersion for 8 h. This result is due to the change

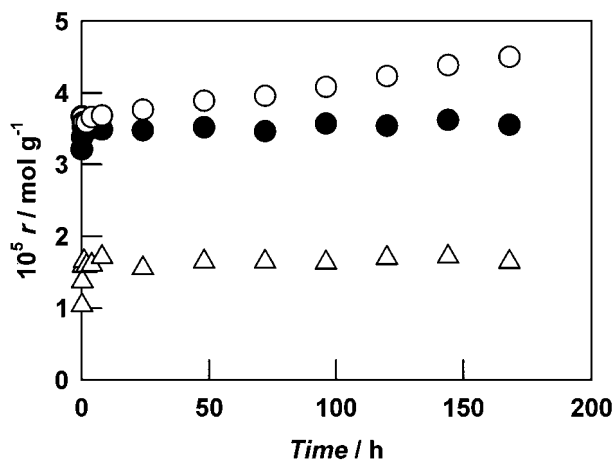


Figure 1 Time dependence of the amount of dye sorbed by the nylon 6 film at 353 K for AS (initial dye concentration is 1×10^{-4} mol dm $^{-3}$): (○) pH 3, (●) pH 4, and (△) H $_2$ O.

of the film structure with pH: the amount of the positively charged amino end group decreases with an increase of pH, which lowers swelling.

Sorption Isotherms

The previous reports^{5,6} demonstrate that the Langmuir-type sorption does not depend on time, even at pH 3, whereas the partition sorption does. Therefore, the sorption isotherms (Fig. 2) were determined on the basis of the data for the sorption at 1 day. Here, C_{free} is the concentration of free dyes in the bath.

The sorption isotherms were analyzed by means of the following bimodal sorption equation:^{1,3,5,6}

$$r = K_P \cdot C_{\text{free}} + \frac{n \cdot K_L \cdot C_{\text{free}}}{1 + K_L \cdot C_{\text{free}}} \quad (1)$$

where K_P is the partition coefficient, n is the number of binding sites for the Langmuir-type sorption, and K_L is the intrinsic binding constant for the Langmuir-type sorption. 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. The partition-type sorption term may contain an activity effect on the free dye in the higher concentration region.

The K_P , n , and K_L values were determined in the same manner as described in our previous

article⁵ and are given in Tables I, II, and III. The experimental data were exactly fitted by a curve drawn using the sorption parameters thus obtained (Fig. 2), suggesting the validity of the dual sorption mechanism.

The partition coefficients, K_P , for pH 3 are dependent on sorption time, as was pointed out in the previous reports,^{5,6} so that the values for each dye can not be simply compared. On the other hand, the values for pH 4 and H $_2$ O are those for equilibrium sorption and can be compared with each other. In all the cases, the K_P values for pH 4 were smaller than those for H $_2$ O. This refers to the hydrophobicity in the film; the decrease of the positively charged amino groups enhances the hydrophobicity, resulting in larger partition coefficients. The introduction of a methyl or ethyl group into the dyes had a little effect, while K_P for the dye containing 2 sulfonate groups, AS-SO $_3$ Na, was much smaller than those having 1 sulfonate group, AS, Me-AS, and Et-AS. This fact suggests that the hydrophobicity (hydrophilicity) of the dyes also influences the partition type sorption.

For all the dyes, the n values decreased with increasing pH, which is due to the decrease of the positively charged amino end groups with an increase of pH. As the titration of the amino end groups determined pKa as about 5.7, the fractions of the protonated amino end groups are 100, 98, and 39–61% at pH 3, pH 4, and H $_2$ O, respectively. The n values for the dyes, AS, Me-AS and Et-AS at pH 3 were 3.47 – 3.60×10^{-5} mol g $^{-1}$, coinciding with the content of the amino end groups (3.53

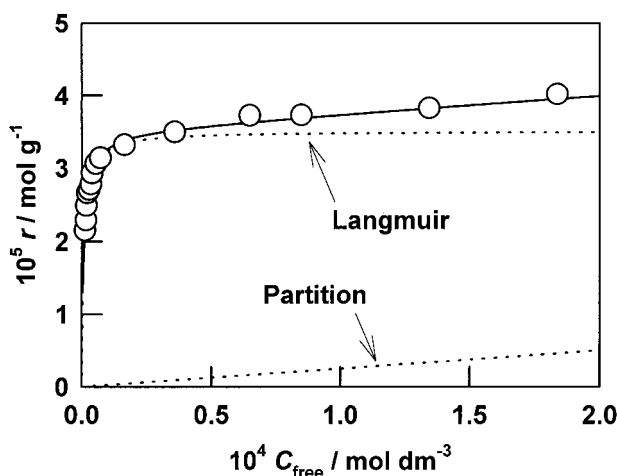


Figure 2 Sorption isotherm of AS for the nylon 6 film at 353 K and pH 3. The curve was calculated using the sorption parameters based on the dual sorption mechanism.

Table I Partition Coefficients $10^2 K_p$ ($\text{dm}^3 \text{g}^{-1}$)

Solution	333 K	343 K	353 K	363 K
AS				
pH 3	2.6 ± 0.2	2.5 ± 0.3	2.5 ± 0.5	3.7 ± 0.3
pH 4	0.6 ± 0.2	0.95 ± 0.15	1.1 ± 0.4	1.2 ± 0.2
H ₂ O	4.3 ± 0.2	4.1 ± 0.2	4.5 ± 1.2	4.4 ± 0.8
Me-AS				
pH 3	4.8 ± 0.6	4.8 ± 0.3	5.8 ± 0.5	6.5 ± 0.5
pH 4	2.1 ± 0.5	1.6 ± 0.6	2.4 ± 0.7	3.4 ± 0.7
H ₂ O	3.8 ± 0.9	4.7 ± 0.4	5.3 ± 0.6	3.2 ± 1.3
Et-AS				
pH 3	7.5 ± 0.8	7.3 ± 0.7	9.3 ± 0.4	12.2 ± 1.0
pH 4	1.2 ± 0.3	1.8 ± 0.6	2.2 ± 0.5	2.7 ± 0.2
H ₂ O	2.7 ± 0.5	2.5 ± 0.6	2.0 ± 0.4	1.3 ± 1.3
AS-SO ₃ Na				
pH 3	0.73 ± 0.08	1.08 ± 0.08	1.38 ± 0.14	2.2 ± 0.2
pH 4	0.29 ± 0.14	0.28 ± 0.20	0.79 ± 0.16	0.28 ± 0.11
H ₂ O	1.6 ± 0.2	1.2 ± 0.2	1.5 ± 0.3	0.5 ± 0.4

$\times 10^{-5} \text{ eq g}^{-1}$). From this, it is found that all the amino end groups in the nylon 6 film dissociate into cations at pH 3. The n values for AS-SO₃Na were almost half the values for the dyes containing 1 sulfonate group because 1 dye containing 2 negatively charged groups interacts with 2 positively charged amino end groups.³ Furthermore, at pH 4 and H₂O, all the protonated amino end groups seems to be accessible to the dyes.

The intrinsic binding constants for the Langmuir-type sorption, K_L , decreased in the order of pH 3 > pH 4 \gg H₂O. This also indicates that the

film structure changes with pH; the microenvironment around the positively charged amino end groups varies from pH to pH. Furthermore, the introduction of a methyl or ethyl group into the dyes enhanced the K_L values.

From the temperature dependence of the intrinsic binding constants, the thermodynamic parameters, the enthalpy change ΔH_L and the entropy change ΔS_L were calculated (Table IV). The binding processes for almost all the cases were endothermic ($\Delta H_L < 0$), whereas those for AS-SO₃Na at pH 3 and pH 4 were athermic ($\Delta H_L \approx 0$), showing the effects of the sulfonate groups.

Table II Number of Binding Sites for Langmuir-Type Sorption $10^5 n$ (mol g^{-1})

Solution	333 K	343 K	353 K	363 K
AS				
pH 3	3.51 ± 0.02	3.51 ± 0.02	3.50 ± 0.03	3.51 ± 0.02
pH 4	3.48 ± 0.02	3.37 ± 0.02	3.37 ± 0.03	3.33 ± 0.03
H ₂ O	1.73 ± 0.08	1.45 ± 0.05	1.31 ± 0.13	1.15 ± 0.10
Me-AS				
pH 3	3.57 ± 0.02	3.60 ± 0.04	3.47 ± 0.02	3.51 ± 0.04
pH 4	3.33 ± 0.02	3.37 ± 0.03	3.30 ± 0.02	3.14 ± 0.03
H ₂ O	2.33 ± 0.05	2.14 ± 0.04	1.64 ± 0.03	1.36 ± 0.08
Et-AS				
pH 3	3.49 ± 0.03	3.59 ± 0.03	3.47 ± 0.02	3.60 ± 0.02
pH 4	3.43 ± 0.02	3.37 ± 0.03	3.35 ± 0.03	3.360 ± 0.013
H ₂ O	2.48 ± 0.09	2.48 ± 0.06	2.18 ± 0.10	1.97 ± 0.09
AS-SO ₃ Na				
pH 3	1.770 ± 0.009	1.768 ± 0.008	1.741 ± 0.011	1.808 ± 0.011
pH 4	1.650 ± 0.006	1.602 ± 0.011	1.564 ± 0.006	1.586 ± 0.008
H ₂ O	0.65 ± 0.02	0.651 ± 0.012	0.54 ± 0.02	0.327 ± 0.012

Table III Intrinsic Binding Constants for Langmuir-Type Sorption $10^{-5} K_L$

Solution	333 K	343 K	353 K	363 K
AS				
pH 3	23.9 ± 0.7	16.6 ± 0.5	12.3 ± 0.5	9.0 ± 0.2
pH 4	21.2 ± 0.8	16.1 ± 0.9	10.8 ± 0.6	7.6 ± 0.3
H ₂ O	1.4 ± 0.2	1.05 ± 0.08	0.64 ± 0.12	0.46 ± 0.07
Me-AS				
pH 3	53 ± 3	42 ± 4	35.3 ± 1.2	26.0 ± 1.3
pH 4	46 ± 4	35 ± 2	27.0 ± 1.3	19.1 ± 1.7
H ₂ O	3.0 ± 0.3	1.81 ± 0.14	1.32 ± 0.07	0.80 ± 0.09
Et-AS				
pH 3	73 ± 4	50 ± 2	31.5 ± 1.2	20.3 ± 0.9
pH 4	61 ± 5	43 ± 5	24 ± 2	15.9 ± 0.8
H ₂ O	3.3 ± 0.4	1.81 ± 0.11	0.94 ± 0.09	0.46 ± 0.04
AS-SO ₃ Na				
pH 3	56 ± 11	52 ± 13	55 ± 14	54 ± 12
pH 4	29 ± 2	31 ± 6	33 ± 4	28 ± 4
H ₂ O	4.3 ± 0.8	2.9 ± 0.3	1.7 ± 0.3	1.24 ± 0.12

The influence of the alkyl groups, that is, the methyl and ethyl group was complicated and did not show any tendency. For all the dyes, the endothermic heat (the absolute values of ΔH_L) increased in the order of pH 3 \leq pH 4 < H₂O, and ΔS_L decreased in the same order. Particularly, the ΔS_L values for H₂O were negative. The above results might be explained by the release of hydrating water molecules around the dyes and the positively charged amino end groups. The negative entropy change indicates the smaller release of the hydrating water molecules, which is con-

nected with the swelling of the nylon 6 film. Thus, the binding processes in H₂O are quite different from those at pH 3 and pH 4.

Effects of the Bolaform Electrolyte on Dye Sorption

In this section, the amounts of dye sorbed by the nylon 6 film r were determined on the basis of the data for the sorption at 1 day. As shown in Figures 3 and 4, the amounts of dye sorbed by the film decreased monotonically with increasing bolaform electrolyte concentration C_{BL} . The smaller

Table IV Enthalpy Change ΔH_L and Entropy Change ΔS_L

Solution	ΔH_L (kJ mol ⁻¹)	ΔS_L (J mol ⁻¹) K ⁻¹
AS		
pH 3	-32.4 ± 0.6	24.9 ± 1.7
pH 4	-34.9 ± 0.2	17 ± 6
H ₂ O	-38.5 ± 0.3	-17 ± 9
Me-AS		
pH 3	-23 ± 2	59 ± 6
pH 4	-29 ± 2	40 ± 5
H ₂ O	-43 ± 3	-24 ± 8
Et-AS		
pH 3	-43 ± 2	2 ± 6
pH 4	-46 ± 3	-8 ± 10
H ₂ O	-66 ± 3	-92 ± 9
AS-SO ₃ Na		
pH 3	-0.6 ± 1.7	127 ± 5
pH 4	0 ± 4	123 ± 11
H ₂ O	-43 ± 3	-21 ± 7

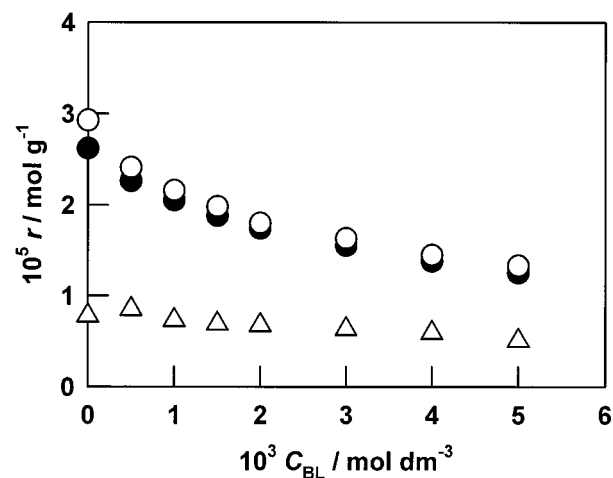


Figure 3 Dependence of dye sorbed by the nylon 6 film on bolaform electrolyte concentration at 353 K for AS (initial dye concentration is 1.5×10^{-5} mol dm⁻³): (○) pH 3, (●) pH 4, and (△) H₂O.

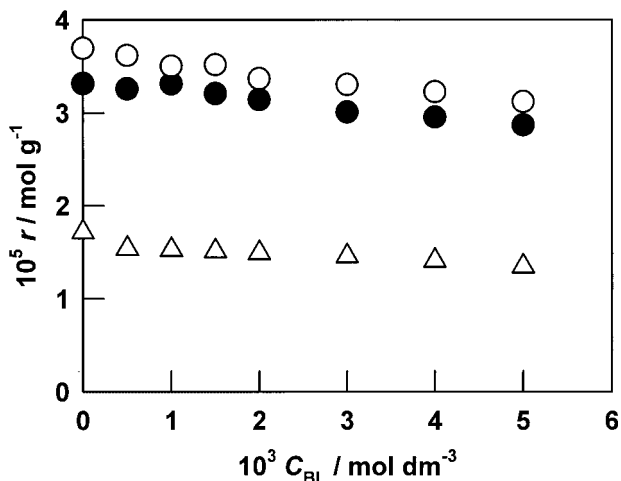


Figure 4 Dependence of dye sorbed by the nylon 6 film on bolaform electrolyte concentration at 353 K for AS (initial dye concentration is 1×10^{-4} mol dm $^{-3}$): (○) pH 3, (●) pH 4, and (△) H $_2$ O.

pH and the initial dye concentration were, the larger the extent of the decrease became. The extent of the decrease in H $_2$ O was very slight. The positively charged groups of the bolaform electrolyte is believed to bind with the negatively charged groups of the dyes^{15,16} so that the formation of their complexes may affect the dye sorption. The change of the ionic strength with increasing bolaform electrolyte concentration also influences the dye sorption. Although, in the present study, the effects of the ionic strength are not considered, the buffer systems will be investigated in the near future.

The sorption isotherm for AS at 353 K in the presence of the bolaform electrolyte with a constant concentration (2×10^{-3} mol dm $^{-3}$) is shown

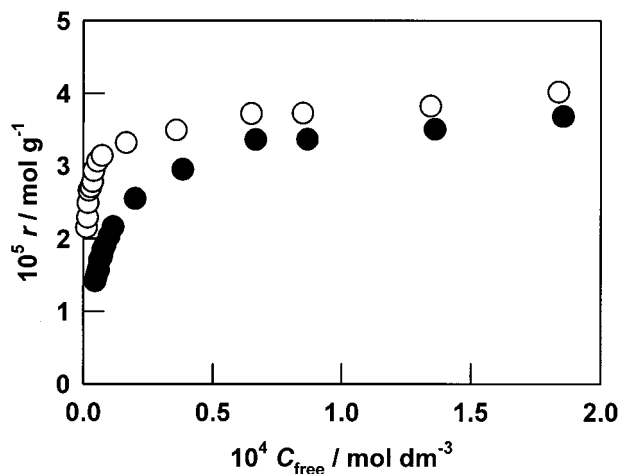


Figure 5 Sorption isotherms of AS by the nylon 6 film at 353 K and pH 3 in the presence (●) and absence (○) of the bolaform electrolyte.

in Figure 5, together with that in its absence. The other dyes showed the same tendency, as follows: the amounts of dye sorbed in the presence of the bolaform electrolyte were smaller than those in its absence in the concentration region examined.

The sorption isotherms were analyzed using the bimodal sorption equation, eq. (1), and the sorption parameters, K_P , n , and K_L , were determined (Table V). The K_P and n values in the presence of the bolaform electrolyte were similar to those in its absence; the binding sites in the nylon 6 film were not influenced by the addition of the bolaform electrolyte.

On the other hand, the K_L values at pH 3 and pH 4 were markedly reduced by the addition of the bolaform electrolyte. A schematic model of the interaction between the dyes and the nylon 6 film

Table V K_P , n , and K_L Values in the Presence of Bolaform Electrolyte at 353 K

Value	Solution	pH 3	pH 4	H $_2$ O
$10^2 K_P$ (dm 3 g $^{-1}$)	AS	2.8 ± 0.4	1.4 ± 0.6	4.4 ± 0.4
	Me-AS	6.9 ± 0.8	1.9 ± 0.2	4 ± 2
	Et-AS	9.6 ± 1.7	2.6 ± 0.4	1.1 ± 0.9
	AS-SO $_3$ Na	1.9 ± 0.4	0.5 ± 0.3	0.5 ± 0.5
$10^5 n$ (mol g $^{-1}$)	AS	3.32 ± 0.04	3.19 ± 0.04	1.25 ± 0.07
	Me-AS	3.43 ± 0.04	3.32 ± 0.05	1.65 ± 0.03
	Et-AS	3.39 ± 0.03	3.32 ± 0.03	2.27 ± 0.08
	AS-SO $_3$ Na	1.720 ± 0.005	1.54 ± 0.02	0.38 ± 0.04
$10^{-5} K_L$ (dm 3 mol $^{-1}$)	AS	1.59 ± 0.04	1.36 ± 0.04	0.60 ± 0.06
	Me-AS	3.55 ± 0.11	2.89 ± 0.13	1.49 ± 0.07
	Et-AS	5.21 ± 0.17	4.53 ± 0.17	0.84 ± 0.06
	AS-SO $_3$ Na	7.50 ± 0.18	2.90 ± 0.18	1.3 ± 0.4

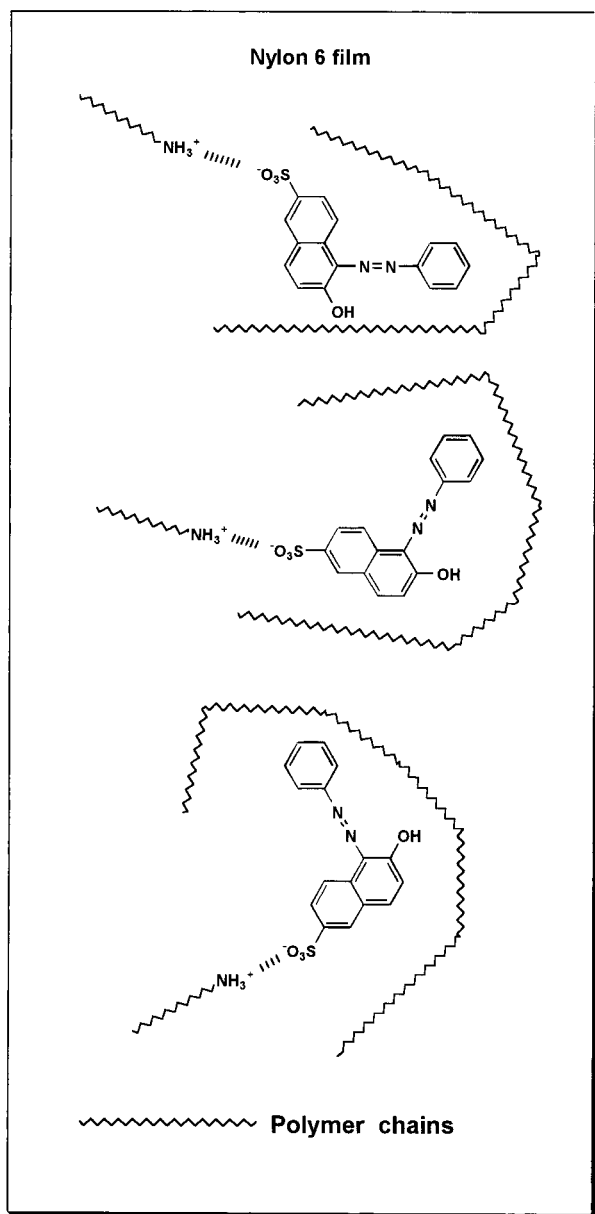


Figure 6 A schematic model on the interactions.

in the presence of the bolaform electrolyte is shown in Figure 6, where the free dyes and the complexes between the dye and the bolaform electrolyte exist in the dye bath. In this figure, the interaction between the nonionic parts of the dyes and the polymer chains is not clear, but actually the nonionic parts interact with the polymer chains through dispersion forces. Now we assume that only the free dye interact with the amino end group. When the concentration of the dye sorbed by the nylon 6 film, the dye bound with the bolaform electrolyte and the free dye are defined as

C_b , C_{comp} , and C_{free} ; the total dye concentration C_0 is represented by eq. (2).

$$C_0 = C_b + C_{comp} + C_{free} \quad (2)$$

The binding constant of the dye with the bolaform electrolyte, K_{comp} , is given as follows:

$$K_{comp} = \frac{C_{comp}}{C_{free} \cdot (C_{BL} - C_{comp})} \quad (3)$$

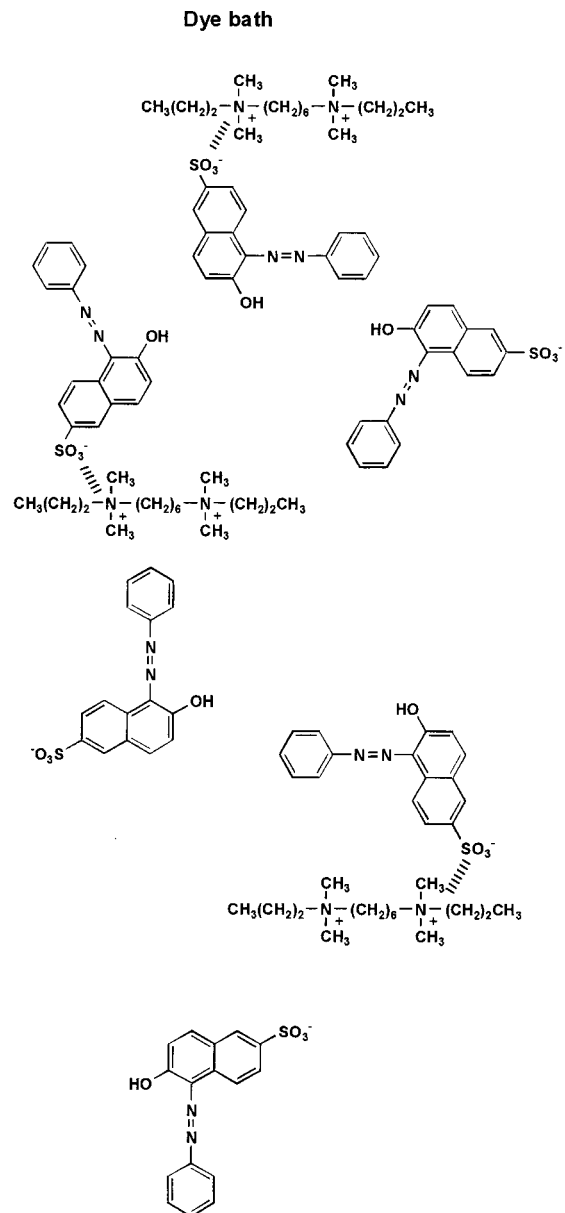


Table VI Binding Constants of the Dyes with the Bolaform Electrolyte K_{comp} ($\text{dm}^3 \text{mol}^{-1}$) at 353 K

Solution	pH 3	pH 4
AS	3370	3470
Me-AS	4470	4170
Et-AS	2520	2120
AS-SO ₃ Na	3170	5140

where C_{BL} is the initial concentration of the bolaform electrolyte. Since the bolaform electrolyte is added in large excess, that is, $C_{BL} \gg C_{\text{comp}}$,

$$K_{\text{comp}} = \frac{C_{\text{comp}}}{C_{\text{free}} \cdot C_{BL}} \quad (4)$$

Substituting eq. (4) into eq. (2), we obtain

$$C_{\text{free}} = \frac{C_0 - C_b}{1 + K_{\text{comp}} \cdot C_{BL}} \quad (5)$$

This equation indicates that the free dye concentration in the presence of the bolaform electrolyte is less than that in its absence by a factor of $1/(1 + K_{\text{comp}} \cdot C_{BL})$.

As the K_L value is approximately proportional to the C_{free} value, the relationship between the K_L values in the presence and absence of the bolaform electrolyte is given by the following equation:

$$\frac{K_L^{\text{pres}}}{K_L^{\text{abs}}} \approx \frac{1}{1 + K_{\text{comp}} \cdot C_{BL}} \quad (6)$$

where K_L^{pres} and K_L^{abs} are the K_L values in the presence and absence of the bolaform electrolyte, respectively.

Modifying eq. (6), we obtain

$$K_{\text{comp}} \approx \frac{1}{C_{BL}} \cdot \left(\frac{K_L^{\text{abs}}}{K_L^{\text{pres}}} - 1 \right) \quad (7)$$

The K_{comp} values determined using eq. (7) are given in Table VI. For all the dyes except AS-SO₃Na, K_{comp} was independent of pH. The large error contained in K_L are responsible for the difference between pH 3 and pH 4 in the K_{comp} values

for AS-SO₃Na. The binding constants of the dyes with the bolaform electrolyte were on the order of those determined in the different dye–bolaform electrolyte systems by means of visible absorption spectroscopy.^{16,17} This suggests that the assumption of the formation of the complexes between the dyes and the bolaform electrolyte in the bath is reasonable.

The K_L values in H₂O were similar both in the presence and absence of the bolaform electrolyte. The sorption of the bolaform electrolyte and the complex presumably leads to this result, but the mechanism is not clear.

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