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Effects of Bolaform Electrolytes on the Interaction Between a Water-soluble Polymer and Sulphonated Monoazo Dyes. Part 4: Dyes Containing two Sulphonate Groups and Aromatic Bolaform Electrolytes with Different Chain Length of the Spacer Groups

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ABSTRACT

The effects of aromatic bolaform electrolytes containing two quaternized amino groups, two phenyl groups and different chain lengths of the spacer groups on the interaction between poly(vinylpyrrolidone) and sulphonated monoazo dyes containing two sulphonate groups were investigated using visible absorption spectrum measurements. Several kinds of complexes between the dye containing two sulphonate groups and aromatic bolaform electrolytes could be formed, with dye:bolyte ratios of 1:1 or 1:2. The 1:2 complex is, however, not likely to be formed due to steric hindrance and its low solubility, so that the preferential formation of the 1:1 complexes is assumed. The binding constants of the dye with the aromatic bolaform electrolytes calculated, under this assumption, were found to be dependent on the chain length of the spacer groups. Furthermore, the thermodynamic parameters for the binding were smallest when the number of carbon atoms in the spacer groups was six. This result can be explained by the structure of the complexes. An equation based on the equilibria in the ternary system containing the dyes, the bolaform electrolytes and poly(vinylpyrrolidone) was used to estimate the first binding constants of the dye/bolaform electrolyte complexes with the polymer. In all cases of the aromatic bolaform electrolytes, their addition reduced the binding constants of the dye with the polymer, but the manner of the reduction was dependent on the length of the spacer methylene chains. Copyright © 1996 Elsevier Science Ltd

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INTRODUCTION

Substituents in dye molecules play an important role in their binding processes with substrates such as polymers, surfactant micelles, cyclodextrins, etc. In particular, the effects of substituents on the binding of dyes with poly(vinylpyrrolidone) (PVP) have been extensively studied.[1–7] Takagishi *et al.* discussed the effects of alkyl chains in Methyl Orange homologues using thermodynamic parameters for the binding.[1,2] Maruthamuthu & Subramanian investigated the interaction between PVP and a series of disazo dyes (Evans Blue, Trypan Blue and Benzopurpurin 4B).[3,4] We have studied the effects of fluorine atoms and sulphonate groups on the binding of monoazo sulphonated dyes with PVP.[5–7] As a result, it was found that these substituents affect the binding process.

The effects of bolaform electrolytes (bolytes) containing two cationic groups (bisquaternary ammonium) on the interaction between sulphonated monoazo dyes and PVP have also been investigated.[8–10] As a result of these studies, not only the bolyte structure, but also the dye structure, is involved with the way in which the bolytes affect the interaction: aromatic bolaform electrolytes lowered the binding constants, while aliphatic ones enhanced them, and the degree of the enhancement was influenced by the size of the dye molecules.

In this study, a monoazo sulphonated dye containing two sulphonate groups, and a series of aromatic bolaform electrolytes with different chain lengths of the spacer group were used. The reason for using a dye having two anionic groups was the high water solubility of its complexes with the bolaform electrolytes carrying the longer spacer groups, although a more complicated binding process is predicted, as described in a previous paper.[10] The first binding constants of the dye/bolaform electrolyte complexes with PVP were calculated from visible absorption spectra. The effects of the sulphonate groups in the dye and of the spacer groups in the bolaform electrolytes are discussed.

EXPERIMENTAL

Materials

A monoazo sulphonated dye, namely disodium 1-(4-methylphenylazo)-2-hydroxy-3,6-naphthlene-disulphonate (p-TR), was used.

This dye (p-TR), was synthesized by coupling diazotized 4-toluidine with the disodium salt of R acid (2-naphthol-3,6-disulphonic acid). The dye thus obtained was purified by repeated salting-out with NaCl and reprecipitating the aqueous solution with acetone; purity was confirmed by elemental analysis. (Calculated for p-TR at water content 8.33%: C, 40.13; H, 3.31; N, 5.51%. Found: C, 40.47; H, 3.47; N, 5.46%.)

Six bolaform electrolytes, namely *N*,*N*′-bis(benzyldimethyl)-1,3-propanediammonium dibromide (DCBz3), *N*,*N*′-bis(benzyldimethyl)-1,4-butanediammonium dibromide (DCBz4), *N*,*N*′-bis(benzyldimethyl)-1,6-hexanediammonium dibromide (DCBz6), *N*,*N*′-bis(benzyldimethyl)-1,8-octanediammonium dibromide (DCBz8), *N*,*N*′-bis(benzyldimethyl)-1,10-decanediammonium dibromide (DCBz10), and *N*,*N*′-bis(benzyldimethyl)-1,12-dodecanediammonium dibromide (DCBz12), were used.

DCBz3 was prepared as described in a previous paper.[9] The other bolaform electrolytes were synthesized as follows: a mixed solution of the appropriate 1,*n*-dibromoalkane and *N*,*N*′-dimethylbenzylamine (molar ratio 1:4), in nitromethane was stirred at room temperature or at 323 K for 3 days. The products were then filtered, purified by repeated precipitation from ethanol into ether and dried. The purity was confirmed by elemental analysis; results are given in Table 1.

Poly(vinylpyrrolidone) (mol. wt 360 000) was purchased from Tokyo Kasei Kogyo Co. (Tokyo, Japan) and was used without further purification.

Visible absorption spectrum measurements

The visible absorption spectra of the binary systems containing the dye (3.00×10^{-5} mol dm^{-3}) and PVP or the bolaform electrolytes (various concentrations) were recorded using a Shimadzu UV-3100 or UV-160A spectrophotometer, as described in previous papers.[8–10]

The visible absorption spectra of the ternary systems including the dye, the bolaform electrolytes and PVP were similarly measured using a constant dye concentration (3.00×10^{-5} mol dm^{-3}), a constant bolyte concentration (6.00×10^{-5} mol dm^{-3}) and various polymer concentrations.

TABLE 1
Elemental Analysis Data

	Water content (%)	Calculated (%)				Found (%)			
		C	H	N	Br	C	H	N	Br
DCBz3	2.07	52.30	6.92	5.81	33.1	52.47	6.78	5.79	33.9
DCBz4	0.79	53.90	7.08	5.71	32.6	53.85	7.20	5.72	31.6
DCBz6	1.53	55.18	7.50	5.36	30.6	55.52	7.57	5.33	31.3
DCBz8	1.37	56.78	7.85	5.09	29.1	57.05	7.90	5.07	29.3
DCBz10	1.43	58.11	8.17	4.84	27.6	58.23	8.23	4.83	29.1
DCBz12	0.0	60.20	8.42	4.68	26.7	60.42	8.57	4.47	26.2

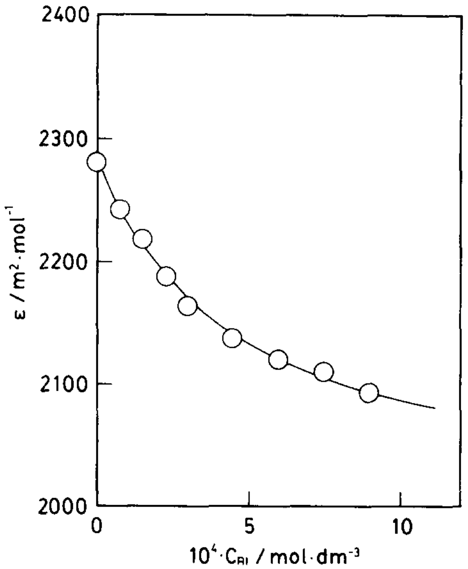


Fig. 1. Relationship between the extinction coefficients and the bolyte concentration for p-TR/DCBz6 system at 298 K and 517 nm.

RESULTS AND DISCUSSION

Interaction between the dye and the bolaform electrolytes

The UV absorption spectra of the aqueous bolyte solutions changed with bolyte concentration, as was pointed out in a previous paper.[9] The extinction coefficients at maximum absorption wavelength abruptly decreased at a specific concentration, owing to aggregation. The concentration region below this was therefore employed in the following study. The visible absorption spectra of aqueous solutions containing the dye (constant concentration) and the bolaform electrolytes changed with bolyte concentration. Figure 1 shows the plot of the extinction coefficients (ϵ) against the bolyte concentration for the p-TR/DCBz6 system. The addition of DCBz12 to the aqueous dye solution produced a precipitate, so that the spectral change for this system could not be investigated. The interaction between p-TR and the bolaform electrolytes except DCBz12 is now discussed.

As was pointed out in a previous paper,[10] a 1:1 or 1:2 (dye:bolyte ratio) complex is formed under the conditions used (bolyte concentration > > dye concentration), because p-TR has two negatively charged groups. If the 1:2 complex is hardly generated owing to steric hindrance and its low solubility, the following two equilibria can be assumed, namely

$$ {}^{-}_{(1)}\mathrm{O_3S-D-SO_3^-}_{(2)} + \mathrm{BL} \rightleftarrows \mathrm{BL}\cdot {}^{-}_{(1)}\mathrm{O_3S-D-SO_3^-}_{(2)} \tag{1} $$

$$ {}^{-}_{(1)}\mathrm{O_3S-D-SO_3^-}_{(2)} + \mathrm{BL} \rightleftarrows {}^{-}_{(1)}\mathrm{O_3S-D-SO_3^-}_{(2)}\cdot \mathrm{BL} \tag{2} $$

where ${}^{-}_{(1)}\mathrm{O_3S-D-SO_3^-}_{(2)}$ and BL express the dye and the bolaform electrolyte, respectively. $\mathrm{BL}\cdot {}^{-}_{(1)}\mathrm{O_3S-D-SO_3^-}_{(2)}$ and ${}^{-}_{(1)}\mathrm{O_3S-D-SO_3^-}_{(2)}\cdot\mathrm{BL}$ are two kinds of 1:1 dye/bolyte complexes. When the concentrations of the total dye, the total bolaform electrolyte, the complex $\mathrm{BL}\cdot {}^{-}_{(1)}\mathrm{O_3S-D-SO_3^-}_{(2)}$, the complex ${}^{-}_{(1)}\mathrm{O_3S-D-SO_3^-}_{(2)}\cdot\mathrm{BL}$ and the free dye are defined as C_O, C_BL, C^1_Comp,C^2_Comp and C_f, respectively, the binding constants of the sulphonate groups $\mathrm{SO_3^-}_{(1)}$ and $\mathrm{SO_3^-}_{(2)}$ with the bolaform electrolytes, K^1_Comp and K^2_Comp, are represented by eqns (3) and (4).

$$ K^1_\mathrm{Comp} = \frac{C^1_\mathrm{Comp}}{(C_\mathrm{BL} - C^1_\mathrm{Comp} - C^2_\mathrm{Comp})C_\mathrm{f}} \tag{3} $$

$$ K^2_\mathrm{Comp} = \frac{C^2_\mathrm{Comp}}{(C_\mathrm{BL} - C^1_\mathrm{Comp} - C^2_\mathrm{Comp})C_\mathrm{f}} \tag{4} $$

If $K_\mathrm{Comp} = K^1_\mathrm{Comp} + K^2_\mathrm{Comp}$ and $C_\mathrm{Comp} = C^1_\mathrm{Comp} + C^2_\mathrm{Comp}$ are defined, the following equation is derived from eqns (3) and (4).

$$ K_\mathrm{Comp} = \frac{C_\mathrm{Comp}}{(C_\mathrm{BL} - C_\mathrm{Comp})C_\mathrm{f}} \tag{5} $$

This equation is the same as that derived by assuming the formation of a single 1:1 complex.[8,9,10] Since $C_0 = C_\mathrm{f} + C_\mathrm{Comp}(C_0 = C_\mathrm{f} + C^1_\mathrm{Comp} + C^2_\mathrm{Comp})$, eqn (5) can then be rewritten as eqn (6):

$$ C_\mathrm{Comp} = 0.5\left\{A - \left(A^2 - 4C_0C_\mathrm{BL}\right)^{1/2}\right\} \tag{6} $$

where $A = C_0 + C_\mathrm{BL} + 1/K_\mathrm{Comp}$ $(A = C_0 + C_\mathrm{BL} + 1/(K^1_\mathrm{Comp} + K^2_\mathrm{Comp}))$.

On the other hand, if ϵ_f, ϵ^1_Comp and ϵ^2_Comp are the extinction coefficients of the free dye and the complex $\mathrm{BL}\cdot {}^{-}_{(1)}\mathrm{O_3S-D-SO_3^-}_{(2)}$ and ${}^{-}_{(1)}\mathrm{O_3S-D-SO_3^-}_{(2)}\cdot\mathrm{BL}$, respectively, then the observed extinction coefficient (ϵ) can be expressed as follows:

$$ \varepsilon = \frac{C_\mathrm{f}}{C_0}\varepsilon_\mathrm{f} + \frac{C^1_\mathrm{Comp}}{C_0}\varepsilon^1_\mathrm{Comp} + \frac{C^2_\mathrm{Comp}}{C_0}\varepsilon^2_\mathrm{Comp} \tag{7} $$

The following relationship is derived from eqns (3) and (4).

$$\frac{C^1_{\mathrm{Comp}}}{K^1_{\mathrm{Comp}}} = \frac{C^2_{\mathrm{Comp}}}{K^2_{\mathrm{Comp}}} \tag{8}$$

By considering $C_{\mathrm{Comp}} = C^1_{\mathrm{Comp}} + C^2_{\mathrm{Comp}}$, we obtain

$$C^1_{\mathrm{Comp}} = \frac{K^1_{\mathrm{Comp}}}{K^1_{\mathrm{Comp}} + K^2_{\mathrm{Comp}}} C_{\mathrm{Comp}} \tag{9}$$

$$C^2_{\mathrm{Comp}} = \frac{K^2_{\mathrm{Comp}}}{K^1_{\mathrm{Comp}} + K^2_{\mathrm{Comp}}} C_{\mathrm{Comp}} \tag{10}$$

By substituting eqns (6), (9), (10) and $C_{\mathrm{f}} = C_0 - C_{\mathrm{Comp}}$ into eqn (7), we then obtain

$$\varepsilon = \varepsilon_{\mathrm{f}} + \frac{\left(K^1_{\mathrm{Comp}}\varepsilon^1_{\mathrm{Comp}} + K^2_{\mathrm{Comp}}\varepsilon^2_{\mathrm{Comp}}\right)/\left(K^1_{\mathrm{Comp}} + K^2_{\mathrm{Comp}}\right) - \varepsilon_{\mathrm{f}}}{2C_0} \left\{A - \left(A^2 - 4C_0C_{\mathrm{BL}}\right)^{1/2}\right\} \tag{11}$$

If the two 1:1 complexes are indistinguishable spectrophotometrically, i.e. $\epsilon^1_{\mathrm{Comp}} = \epsilon^2_{\mathrm{Comp}}$ $(= \epsilon_{\mathrm{Comp}})$, eqn (11) becomes the same equation as that derived by assuming the formation of a single 1:1 complex except that K_{Comp} is an apparent binding constant: $K_{\mathrm{Comp}} = K^1_{\mathrm{Comp}} + K^2_{\mathrm{Comp}}$. Whether the two 1:1 complexes are distinguishable spectrophotometrically or not, the apparent binding constant, K_{Comp}, and a constant, $(K^1_{\mathrm{Comp}}\epsilon^1_{\mathrm{Comp}} + K^2_{\mathrm{Comp}}\epsilon^2_{\mathrm{Comp}})/(K^1_{\mathrm{Comp}} + K^2_{\mathrm{Comp}})$, can be calculated on the basis of eqn (11) by using the nonlinear least-squares method.[8] The solid line in Fig. 1 expresses the fitting curve calculated using the parameters obtained above, showing good agreement with the experimental values. Similar results were obtained for all the bolaform electrolytes at all the temperature used in this study.

The binding constants calculated for p-TR/DCBz6 at several wavelengths were almost the same (Table 2). This indicates that complexes other than the 1:1 complexes do not exist in the system, i.e. the 1:2 complex is not formed. In the binding of 1-(4-sulphonaphthylazo)-2-hydroxy-6-naphthalenesulphonic acid, disodium salt (C.I. Acid Red 13, R-2) with DCBz6, a different result was obtained:[10] the binding constants at several wavelengths were

TABLE 2

Binding Constants, K_{Comp} ($\mathrm{dm^3\ mol^{-1}}$) for p-TR/DCBz6 System at 298 K

500 nm	517 nm	550 nm
1778	2420	2422

TABLE 3

Binding Constants, K_{Comp} ($\mathrm{dm^3\ mol^{-1}}$)

	288 K	298 K	308 K	318K
DCBz3	2300	2360	2420	2480
DCBz4	3050	2710	2420	2180
DCBz6	3050	2420	1950	1600
DCBz8	3810	3250	2800	2430
DCBz10	4490	3790	3230	2780

quite different. The discrepancy between p-TR and R-2 could be explained by the positions of two sulphonate groups. For R-2, two sulphonate groups are attached to different aromatic rings, whereas for p-TR, they are in the same ring. The difference of the positions could affect the formation of the complexes.

The binding constants, K_{Comp}, determined for several bolaform electrolytes are given in Table 3. At 288 K, the K_{Comp} values increased with increasing spacer chain length, whereas, at 318 K, the minimum value was shown for DCBz6. The thermodynamic parameters (the enthalpy change, ΔH_{Comp}, and the entropy change, ΔS_{Comp}) were then calculated (Table 3 and Fig. 2). The thermodynamic parameters were smallest when the number of carbon atoms in the spacer groups was six. This might be explained as follows, namely when one of the positively charged groups in the bolaform electrolytes interacts with either of the sulphonate groups in the dye, the phenyl ring of the dye could interact with the other cationic group or the phenyl ring of the bolytes. The possibility of the interaction depends on the length of the spacer groups. The distance between the sulphonate groups and the phenyl ring in the dye was calculated as 0.76–1.02 nm (Fig. 3). For the bolaform electrolytes, two kinds of distance between the groups were also estimated as shown in Fig. 3. The distance between two cationic groups (A) for DCBz6 is in fair agreement with the distance between the sulphonate groups and the phenyl ring in the dye, indicating that the positively charged ammonium group is located above the phenyl ring of the dye. For the cation-π interaction of tetramethylammonium cation with benzene, the enthalpy and free energy change were calculated as −40 and −17 kJ $\mathrm{mol^{-1}}$, respectively,[11] leading to −77 J $\mathrm{mol^{-1}\ K^{-1}}$ entropy change. These large negative

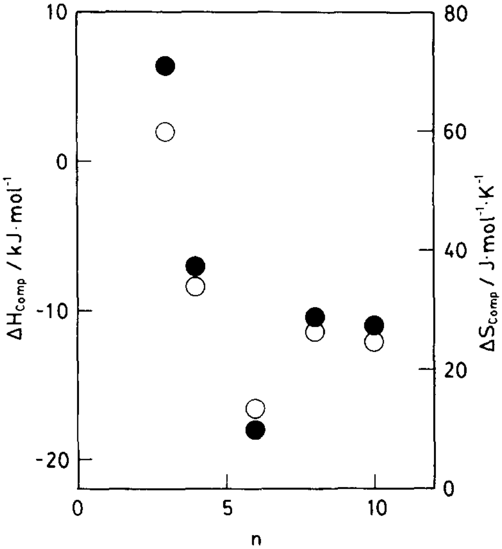
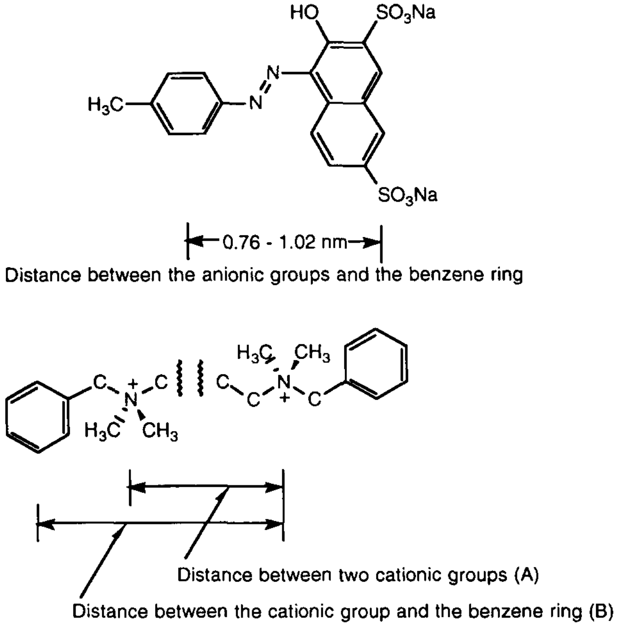


Fig. 2. Dependence of thermodynamic parameters for the binding of the dye with the bolaform electrolytes on the number of carbon atoms in the spacer groups of the bolytes, *n*. ○, ΔH_{Comp}; ●, ΔS_{Comp}.

values might contribute to the smallest enthalpy and entropy change for DCBz6 (Table 4). Furthermore, the distance between the cationic group and the phenyl ring (B) for DCBz3 fits in with the distance between the sulphonate groups and the phenyl ring in the dye, suggesting overlap of the two phenyl rings. This overlapping results in hydrophobic interaction, giving a less negative (more positive) enthalpy change and a more positive (less negative) entropy change. Thus the largest enthalpy and entropy change must be observed for DCBz3. In the case of DCBz4, DCBz8 and DCBz10, the methylene group, $-CH_2-$, is located above the phenyl ring. Consequently, the enthalpy and entropy change is of intermediate value. From the above results, it is concluded that the thermodynamic parameters are strongly related to the structure of the complexes.

TABLE 4
Thermodynamic Parameters for the Binding of p-TR with the Bolaform Electrolytes

	ΔH_{Comp} (kJ mol^{-1})	ΔS_{Comp} (J mol^{-1} K^{-1})
DCBz3	1.91 ± 0.03	71.00 ± 0.09
DCBz4	−8.54 ± 0.03	37.06 ± 0.09
DCBz6	−16.40 ± 0.07	9.8 ± 0.2
DCBz8	−11.42 ± 0.03	28.92 ± 0.11
DCBz10	−12.18 ± 0.03	27.64 ± 0.09



Number of carbon atoms in the spacer groups, n	Distance A (nm)	Distance B (nm)
3	0.53	0.79 - 1.03
4	0.66	0.92 - 1.16
6	0.92	1.18 - 1.42
8	1.19	1.45 - 1.69
10	1.45	1.71 - 1.95

Fig. 3. Distances between the groups in the dye and the bolaform electrolytes.

Interaction between p-TR and PVP

A similar spectral change to those reported in previous papers[5–10] were observed with increasing polymer concentration. To analyze the spectral change, the extinction coefficients (ϵ) at three wavelengths (493, 500 and 548 nm) were used. To calculate the first binding constants (K_{Bind}), the same equation as used in previous investigations[5–10] was employed:

$$\varepsilon = \frac{\varepsilon_{\mathrm{f}} - \varepsilon}{C_{\mathrm{p}}} \cdot \frac{1}{K_{\mathrm{Bind}}} + \varepsilon_{\mathrm{b}} \tag{12}$$

where ϵ_{f} and ϵ_{b} are the extinction coefficients of the free and bound dye, respectively, and C_{P} is the polymer concentration based on the monomer unit. This equation includes the assumption that the bound dye concentration is much smaller than C_{P}, which is fulfilled in all the systems investigated.

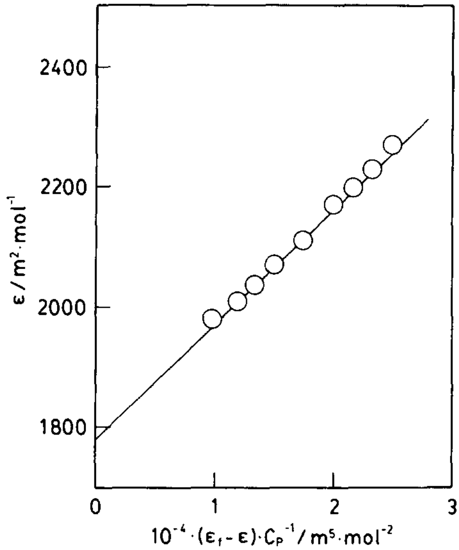


Fig. 4. Plot of ϵ against $(\epsilon_f - \epsilon)/Cp$ for p-TR at 298 K and 500 nm.

TABLE 5

Binding Constants, K_{Bind}, and Thermodynamic Parameters of p-TR with PVP

	K_{Bind} (dm^3 mol^{-1}) 288 K	298 K	308 K	318 K	ΔH_{Bind} (kJ mol^{-1})	ΔS_{Bind} (J mol^{-1} K^{-1})
493 nm	67.8	49.9	42.9	34.0	−17.0 ± 1.4	−24 ± 5
500 nm	69.3	52.1	44.9	34.1	−17.3 ± 1.4	−25 ± 5
548 nm	59.8	50.4	48.8	35.6	−12 ± 3	−8 ± 10

The plot of ϵ against $(\epsilon_f - \epsilon)/C_p$ gave good linearity, as shown in Fig. 4. The first binding constants (K_{Bind}), were calculated from the slopes and are given in Table 5. The values at 493 and 500 nm showed good agreement, whereas those at 548 nm deviated from them. This is due to the small spectral change at 548 nm. The binding constants for p-TR were much smaller than those for 1-(4-methylphenylazo)-2-hydroxy-6-naphthalenesulphonate (p-TS), which contains a single sulphonate group.[7] Furthermore, the enthalpy change, ΔH_{Bind}, both for p-TS and p-TR was the same, while the entropy change, ΔS_{Bind}, for p-TR was more negative than that for p-TS.[7] This is probably relatable to the hydrophilicity of the dyes.

Interaction between p-TR/bolaform electrolyte complexes and PVP

The change of the extinction coefficients with increasing polymer concentration in the presence and absence of the bolaform electrolyte (DCBz6) is

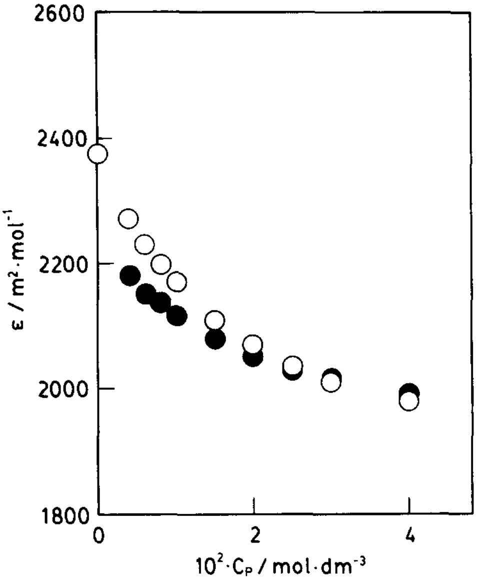


Fig. 5. Relationship between the extinction coefficients and the polymer concentration for p-TR in the absence (○) and presence (●) of DCBz6 (6×10^{-4} mol dm^{-3}) at 298 K and 500 nm.

shown in Fig. 5. Similar results were observed for all the bolytes. Assuming that 1:1 dye/bolyte complexes are indistinguishable, the following equilibria exist in the systems:

$$\begin{array}{ccc} \text{Dye} + \text{BL} & \overset{K_{\text{Comp}}}{\rightleftarrows} & \text{Dye}\cdot\text{BL} \\ + & & + \\ \text{PVP} & & \text{PVP} \\ \downarrow\uparrow K_{\text{Bind}} & & \downarrow\uparrow K_{\text{Bind}}^{\text{Comp}} \\ \text{Dye}\cdot\text{PVP} + \text{BL} & \overset{K^{\text{P}}_{\text{Comp}}}{\rightleftarrows} & \text{Dye}\cdot\text{BL}\cdot\text{PVP} \end{array} \tag{13}$$

where Dye · BL, Dye · PVP and Dye · BL · PVP represent the dye/bolyte, dye/PVP and dye/bolyte/PVP complexes, respectively; K_{Comp} and K_{Bind} are the binding constants of the dye with the bolyte and the dye with PVP, as described in the preceding section, while $K^{\text{P}}_{\text{Comp}}andK^{\text{Comp}}_{\text{Bind}}$ are the binding constants of the dye/PVP complex with the bolyte and the dye/bolyte complex with PVP, respectively. On the basis of the above four equilibria, the following equation can be derived, in the manner described previously.[8]

$$\varepsilon = \frac{\varepsilon_f + K_{\text{Comp}}C_{\text{BL}}\varepsilon_{\text{Comp}} - (1 + K_{\text{Comp}}C_{\text{BL}})\varepsilon}{K_{\text{Bind}}\left(1 + K^{\text{P}}_{\text{Comp}}C_{\text{BL}}\right)} \cdot \frac{1}{C_{\text{P}}} + \frac{\varepsilon_b + K^{\text{P}}_{\text{Comp}}C_{\text{BL}}\varepsilon_{\text{bComp}}}{1 + K^{\text{P}}_{\text{Comp}}C_{\text{BL}}} \qquad (14)$$

where ϵ_f, ϵ_b and ϵ_{Comp} are as defined in the previous sections: ϵ_{bComp} represents the extinction coefficient of the dye/bolyte/PVP complex. The initial bolaform electrolyte concentration used is C_{BL}.

Using the values of ϵ_f, ϵ_b, ϵ_{Comp}, K_{Comp} and K_{Bind} determined in the previous sections, the plots of the observed extinction coefficients, against $\{\epsilon_f + K_{\text{Comp}}C_{\text{BL}}\epsilon_{\text{Comp}} - (1 + K_{\text{Comp}}C_{\text{BL}})\epsilon\}/C_{\text{P}}$ would give $K^{\text{P}}_{\text{Comp}}$ and ϵ_{bComp}. The binding constant of the dye/bolyte complex with PVP, $K^{\text{Comp}}_{\text{Bind}}$ can be determined from the following relationship:

$$K_{\text{Comp}}K^{\text{Comp}}_{\text{Bind}} = K_{\text{Bind}}K^{\text{P}}_{\text{Comp}} \qquad (15)$$

The $K^{\text{Comp}}_{\text{Bind}}$ values calculated here are apparent ones, because it contains the assumption that the 1:1 dye/bolyte complexes are indistinguishable.

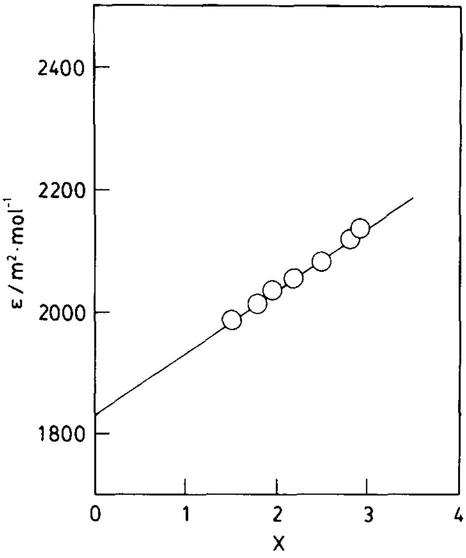


Fig. 6. Plot of ϵ against X for p-TR in the presence of DCBz6 at 298 K and 500 nm. $X = 10^{-4} \cdot \epsilon_f + K_{\text{Comp}}C_{\text{BL}}\epsilon_{\text{Comp}} - (1 + K_{\text{Comp}}C_{\text{BL}})\epsilon/C_{\text{P}}, C_{\text{BL}} = 6 \times 10^{-4}$ mol dm^{-3}.

TABLE 6
Binding Constants, $K_{\mathrm{Bind}}^{\mathrm{Comp}}$ ($\mathrm{dm^3\,mol^{-1}}$)

	288 K	298 K	308 K	318 K
DCBz3	49.7	47.8	23.7	14.9
DCBz4	55.0	35.0	39.4	27.5
DCBz6	34.8	30.9	29.2	11.4
DCBz8	27.7	24.2	9.7	3.2
DCBz10	10.4	17.2	22.5	18.0

In all the cases investigated, the plots of ϵ against $\{\epsilon_{\mathrm{f}} + K_{\mathrm{Comp}} C_{\mathrm{BL}}\epsilon_{\mathrm{Comp}} - (1 + K_{\mathrm{Comp}}C_{\mathrm{BL}})\epsilon\}/C_{\mathrm{P}}$ were almost linear, as shown in Fig. 6. The $K_{\mathrm{Bind}}^{\mathrm{Comp}}$ values were smaller than the binding constants of the dye itself with PVP for all the bolaform electrolytes. This suggests that the aromatic bolaform electrolytes reduce the binding constants for the dye containing two sulphonate groups, as well as for the dye carrying one sulphonate group.[9] Furthermore, the longer the spacer groups, the smaller the $K_{\mathrm{Bind}}^{\mathrm{Comp}}$ values at 288 and 298 K.

The thermodynamic parameters for the binding of the dye/bolyte complexes with PVP could not be determined with high accuracy. However, for DCBz3, DCBz4, DCBz6 and DCBz8, the $K_{\mathrm{Bind}}^{\mathrm{Comp}}$ values had a tendency to decrease with increasing temperature, whereas for DCBz10, the opposite tendency was found (Table 6).

From the above results, it is concluded that the aromatic bolaform electrolytes reduce the binding constants and that the manner of the reduction is dependent on the length of the spacer methylene chain.

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