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Effects of Bolaform Electrolytes on the Interaction between a Water-Soluble Polymer and Sulphonated Monoazo Dyes. Part 3: Dyes Containing Two Naphthalene Rings

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ABSTRACT

The effects of bolaform electrolytes containing two quaternized amino groups on the interaction between poly(vinylpyrrolidone) and sulphonated monoazo dyes containing two naphthalene rings were investigated using visible absorption spectrum measurements. Several kinds of complex between the dye containing two sulphonate groups and an aromatic bolaform electrolyte were formed. The first binding constants of the dyes containing two naphthalene rings with the polymer were much larger than those of the dyes containing one benzene and one naphthalene ring. An equation based on the equilibria in the ternary systems 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 the case of the dyes containing two naphthalene rings, aliphatic bolaform electrolytes enhanced the first binding constants just as in the case of the dyes having one benzene and one naphthalene ring. However, the degree of the enhancement for the former was much larger than that for the latter. The influence of the bolaform electrolytes on the thermodynamic parameters for the binding was dependent on the number of the sulphonate groups in the dyes. This is explained by the difference in the structure of the dye/bolaform electrolyte complexes formed.

1 INTRODUCTION

The size of dye molecules is one of the most important factors which determine their binding constants with several substrates such as polymers, surfactant

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micelles, cyclodextrins, etc. For example, when benzene rings were replaced by naphthalene rings, the affinity of the dye molecule with gelatin greatly increased.[1] Thus the replacement of benzene rings by naphthalene rings is expected to increase the binding constants of dyes with polymers.

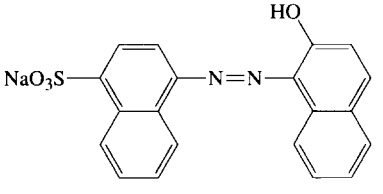
On the other hand, we have studied the effects of bolaform electrolytes (bolytes) containing two cationic groups (bisquaternary ammonium) on the interaction between sulphonated monoazo dyes and poly(vinylpyrrolidone) (PVP).[2,3] The aromatic bolaform electrolytes containing two phenyl rings lowered the first binding constants of the sulphonated azo dyes with PVP through the formation of complexes between the dyes and the bolaform electrolytes, while the aliphatic ones behaved oppositely.

In the present study, the effects of aliphatic and aromatic bolaform electrolytes on the interaction between PVP and sulphonated monoazo dyes containing two naphthalene rings in aqueous solutions were investigated using visible absorption spectroscopy. An equation based on the equilibria in the ternary systems containing the dyes, the bolaform electrolytes, and PVP, as described in previous papers,[2,3] was used to determine the first binding constants of the dye/bolaform electrolyte complexes with PVP. The first binding constants obtained are discussed and compared with those of the dyes containing one benzene and one naphthalene ring.

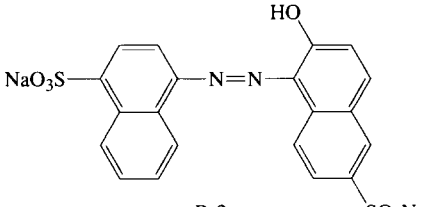
2 EXPERIMENTAL

2.1 Materials

Two monoazo sulphonated dyes, viz. 1-(4-sulphonaphthylazo)-2-hydroxynaphthalene, sodium salt (CI Acid Red 88, R-1) and 1-(4-sulphonaphthylazo)-2-hydroxy-6-naphthalenesulphonic acid, disodium salt (CI Acid Red 13, R-2) were used.



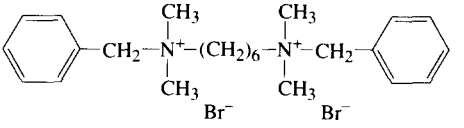
R-1



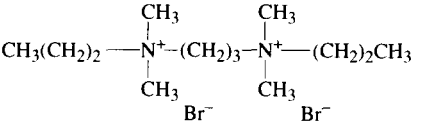
R-2

R-1 was commercially purchased from Tokyo Kasei Kogyo Co. (Tokyo, Japan) and purified by repeated salting-out with NaCl and reprecipitating the aqueous solution with acetone. R-2 was prepared as described in a previous paper.[4]

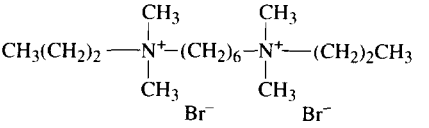
Three bolaform electrolytes, viz. *N,N'*-bis(benzyldimethyl)-1,6-hexanediammonium dibromide (DCBz6), *N,N'*-bis(propyldimethyl)-1,3-propanediammonium dibromide (DC3-3) and *N,N'*-bis(propyldimethyl)-1,6-propanediammonium dibromide (DC6-3) were used.



DCBz6



DC3-3



DC6-3

DCBz6 was prepared as described in a previous paper.[3] DC3-3 and DC6-3 were synthesized by the reaction of 1-bromopropane with the corresponding diamine (*N,N,N',N'*-tetramethyl-1,3-propanediamine or *N,N,N',N'*-tetramethyl-1,6-propanediamine) in nitromethane at room temperature for three days. The products were then filtered, purified by repeated precipitation from methanol into acetone and dried. Purity was confirmed by elemental analysis. (Calculated for DC3-3 at water content 1·2 %: C, 41·01; H, 8·60; N, 7·36; Br, 42·0 %. Found: C, 40·97; H, 9·47; N, 7·36; Br, 41·3%. Calculated 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 %.)

Poly(vinylpyrrolidone) (mol. wt 360000) was purchased from Tokyo Kasei Kogyo Co., and used without further purification.

2.2 Visible absorption spectrum measurements

In the absence and presence of the bolaform electrolytes ($6{\cdot}00 \times 10^{-4}$ or $1{\cdot}20 \times 10^{-3}$ mol dm^{-3}), the visible absorption spectra of aqueous solutions with various polymer concentrations and a constant dye concentration ($3{\cdot}00 \times 10^{-5}$ mol dm^{-3}) were recorded using a Shimadzu UV-3100 spectrophotometer together with a Shimadzu SPR-5 temperature controller.

The visible absorption spectra of the aqueous solutions with various bolyte concentrations and a constant dye concentration ($3{\cdot}00 \times 10^{-5}$ mol dm^{-3}) were similarly measured.

3 RESULTS AND DISCUSSION

3.1 Interaction between the dyes and the bolaform electrolytes

Spectral change of the aqueous dye solutions was observed with increasing bolyte concentration. The result is shown in Fig. 1 as the plot of the extinction coefficient against the bolyte concentration. In the case of R-1, the addition of DCBz6 and DC3-3 to the aqueous dye solutions produced precipitates of the complexes between the dye and the bolaform electrolytes, so that the visible absorption spectra for these systems could not be measured. Therefore, the results for R-1/DC6-3, R-2/DCBz6, R-2/DC3-3 and R-2/DC6-3 system are discussed below.

In the present study, the bolaform electrolyte concentration is much greater than the dye concentration, resulting in the formation of a 1 : 1 or 1 : 2 (dye : bolyte ratio) complex. Because R-2 has two negatively charged groups, it can bind with one or two positively charged groups. Furthermore, two kinds of 1 : 1 complex are thought to be formed, as the sulphonate groups of R-2 are distinguishable (the two quaternary ammonium groups

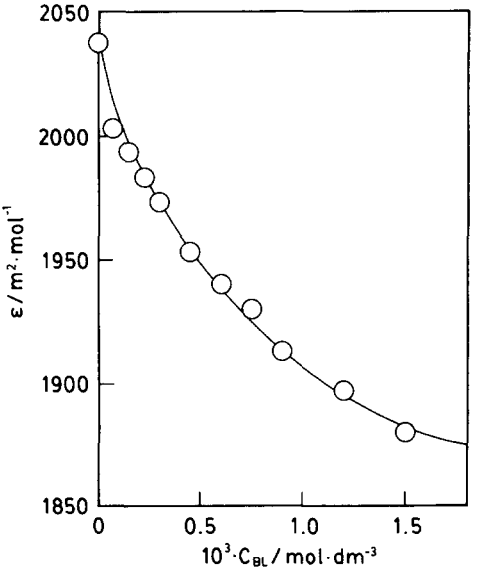


Fig. 1. Relationship between the extinction coefficients and the bolyte concentration for R-2/DC3-3 system at 298 K and 530 nm.

of the bolaform electrolyte are indistinguishable). It is difficult to determine which kinds of complex are formed owing to the small spectral change. However, formation of the 1 : 2 complex would be expected to be greatly inhibited, because of steric hindrance and its low solubility in water. Therefore, the following single equilibrium is assumed; to simplify the analysis, the two kinds of 1 : 1 complexes are assumed to be indistinguishable spectrophotometrically.

$$\mathrm{D} + \mathrm{BL} \rightleftarrows \mathrm{D{\cdot}BL} \tag{1}$$

where D, BL and D·BL express the dye, the bolyte and the dye/bolyte complex, respectively. When the concentrations of the total dye, the total bolaform electrolyte, the bound dye (the complex) and the free dye are defined as C_0, C_{BL}, C_{comp} and C_f, respectively, the binding constant of the dye with the bolaform electrolyte (K_{Comp}) is represented by eqn (2). K_{Comp} for R-2 should be defined as the apparent binding constant including the above assumption.

$$K_{Comp} = \frac{C_{Comp}}{(C_{BL} - C_{Comp})C_f} \tag{2}$$

Since $C_0 = C_f + C_{Comp}$, eqn (2) can be rewritten as expressed in eqn (3):

$$C_{Comp} = 0{\cdot}5\{A - (A^2 - 4C_0C_{BL})^{1/2}\} \tag{3}$$

where $A = C_0 + C_{BL} + 1/K_{comp.}$ On the other hand, if ϵ_f and ϵ_{Comp} are the extinction coefficients of the free and bound dye, respectively, then the observed extinction coefficient can be expressed as follows, by considering eqn (3) and $C_f = C_0 - C_{Comp}$:[2,3]

$$\epsilon = \epsilon_f + \frac{\epsilon_{Comp} - \epsilon_f}{2C_0}\left\{A - (A^2 - 4C_0C_{BL})^{1/2}\right\} \tag{4}$$

On the basis of eqn (4), the binding constant, K_{Comp}, and the extinction coefficient of the bound dye, ϵ_{Comp}, can be calculated by using the nonlinear least-squares method.[2] The solid line in Fig. 1 expresses the fitting curve calculated using K_{Comp} and ϵ_{Comp} obtained above, showing good agreement with the experimental values. The agreement for R-2 might demonstrate the formation of the 1 : 1 complexes.

However, the binding constants calculated for the R-2/DCBz6 system at several wavelengths were quite different (Table 1). This suggests that more than one equilibrium exists in this system: more than one complex is formed. This result, therefore, cannot define what kinds of complex are formed.

The binding constants for the other systems, R-1/DC6-3, R-2/DC3-3 and R-2/DC6-3, are given in Table 2. The K_{Comp} value for R-1/DC6-3 at 318 K could not be determined owing to large experimental errors. In the case of

TABLE 1
Binding Constants, K_{Comp} (dm^3 mol^{-1}), for R-2/DCBz6 System at 298 K

495 nm	*509 nm*	*522 nm*	*530 nm*	*575 nm*
4390	6670	9060	10340	4790

TABLE 2
Binding Constants, K_{Comp} (dm^3 mol^{-1})

		288 K	*298 K*	*308 K*	*318 K*
R-1					
	DC6-3	2270	1590	2540	
R-2					
	DC3-3	1550	1410	1490	1470
	DC6-3	3100	2960	2690	2430

the aliphatic bolaform electrolytes, the extent of the spectral change was smaller, so that only the binding constants at the wavelength where the largest difference was observed could be calculated. Therefore, the dependence of the binding constants on the wavelength, i.e. whether more than one complex is formed or not, cannot be determined.

The K_{Comp} values for R-1/DC6-3 were greater than those (1130, 930 and 1180 dm^3 mol^{-1} at 288, 298 and 308 K, respectively) for sodium 1-phenylazo-2-hydroxy-6-naphthalenesulphonate (AS)/*N*,*N*'-bis(butyldimethyl)-1,6-hexanediammonium dibromide (DC6-4). Although the bolaform electrolyte investigated is different, the replacement of the benzene ring by a naphthalene ring influences the binding constants.

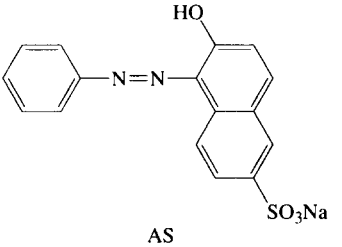
3.2 Interaction between the dyes and PVP

Similar spectral changes to those reported in previous papers[5–8] were observed with increasing polymer concentration. To analyze the spectral change, the extinction coefficients at two wavelengths (495 and 575 nm) were used. At the former wavelength, the extinction coefficients decreased with increasing polymer concentration (C_P) based on monomer units, whereas at the latter wavelength they increased. To estimate the first binding constant (K_{Bind}) the same equation as used in previous investigations[2,3,5–8] was employed:

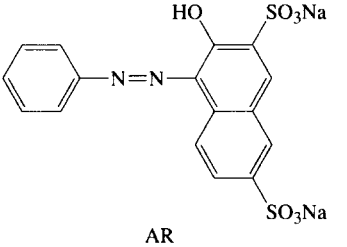
$$\epsilon = \frac{\epsilon_f - \epsilon}{C_p} \cdot \frac{1}{K_{Bind}} + \epsilon_b \tag{5}$$

where ϵ_f and ϵ_b are the extinction coefficients of the free and bound dye, respectively. This equation includes the assumption that the bound dye concentration is much smaller than C_P, which is fulfilled in all the systems investigated.

The plots of ϵ against $(\epsilon_f - \epsilon)/C_P$ gave good linearity for two dyes at two wavelengths, as shown in Fig. 2. The first binding constants (K_{Bind}) calculated from the slopes and the thermodynamic parameters (the enthalpy change, ΔH_{Bind}, and the entropy change, ΔS_{Bind}), as determined from the temperature dependence of K_{Bind} are given in Table 3 together with those for sodium 1-phenyl-2-hydroxy-6-naphthalenesulphonate (AS) and disodium 1-phenyl-2-hydroxy-3,6-naphthalenedisulphonate (AR).



AS



AR

For two of the dyes used in the present study (R-1 and R-2) the K_{Bind} values and the thermodynamic parameters at 495 and 575 nm showed good agreement, confirming that only a single equilibrium exists in the dye and polymer system.

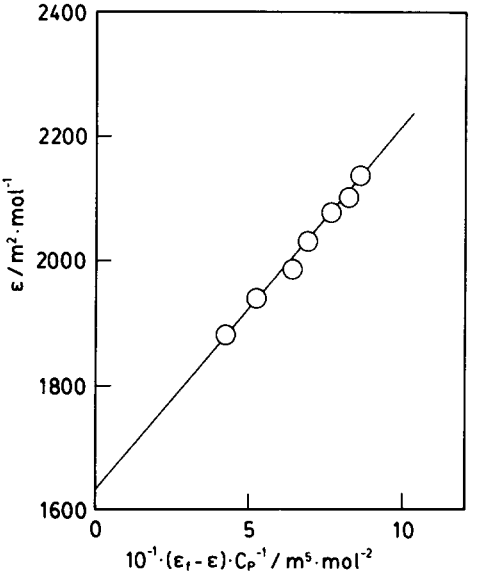


Fig. 2. Plot of ϵ against $(\epsilon_f - \epsilon)/C_p$ for R-2 at 298 K and 495 nm.

TABLE 3
Binding Constants. K_{Bind} and Thermodynamic Parameters

		K_{Bind} (dm^3 mol^{-1})				ΔH_{Bind}	ΔS_{Bind}
		288 K	*298 K*	*308 K*	*318 K*	(*kJ mol*$^{-1}$)	(*J mol*$^{-1}$ *K*$^{-1}$)
R-1	495 nm	1330	880	600	410	−29·8 ± 0·3	−43·7 ± 0·9
	575 nm	1200	820	528	380	−29·7 ± 0·9	−44 ± 3
R-2	495 nm	232	174	144	107	−19·1 ± 1·2	−21 ± 4
	575 nm	240	176	146	100	−21 ± 2	−29 ± 7
AS[a]	480 nm	73·1	59	52	39	−15·3 ± 1·8	−17 ± 6
AR[b]	485 nm	44	41	37·6	35·4	−10·7 ± 0·5	−5·6 ± 1·5

[a]Ref. 2.
[b]Ref. 7.

The replacement of a benzene ring by a naphthalene ring made the binding constants much larger, although the position of the sulphonate groups should be considered. This indicates that the hydrophobic moiety of the dyes is a relevant factor in the interaction between the dyes and PVP. Furthermore, the number of the sulphonate groups affected the binding constants: the K_{Bind} values for the dyes carrying two sulphonate groups were much smaller than those for the dyes having one such group. This result shows that the hydrophilic moiety of the dyes also affects the interaction. Thus both the hydrophobic and hydrophilic moieties need to be considered to explain the binding constants.

The enthalpy and entropy changes for the dyes having two naphthalene rings were more exothermic and more negative, respectively, than those for the dyes containing one benzene and one naphthalene ring. If the replacement of a benzene ring by a naphthalene ring influences the hydrophobic interaction, the enthalpy and entropy changes would be less exothermic (more endothermic) and less negative (more positive), respectively. However, results obtained in this present study are not in accord with this. It is worthwhile to point out that the thermodynamic parameters were determined on the basis of the first binding constants. The first binding constant is the product of the intrinsic binding constant and the number of binding sites. The number of binding sites is thought to vary from dye to dye, so that the entropy change is apparent, as Reeves *et al.* have noted.[9] As several kinds of interaction such as electrostatic, dipole–dipole, hydrophobic and hydrogen bonding are effective in the dye/PVP systems, the reason why the thermodynamic parameters are affected by the dye structure is not clear.

3.3 Interaction between dye/bolaform electrolyte complexes and PVP

The change of extinction coefficients with increasing polymer concentration in the presence and absence of the bolaform electrolyte is shown in Fig. 3. A similar change was observed for all the systems: the addition of the bolaform electrolytes reduced the extinction coefficients. This suggests that the bolaform electrolytes have an influence in the interaction between the dyes and PVP. Since the interaction between the dyes and the bolaform electrolytes has been established, we assume the following equilibria:

$$\begin{array}{ccc} & \overset{K_{\mathrm{Comp}}}{\rightleftarrows} & \\ \mathrm{Dye} + \mathrm{BL} & & \mathrm{Dye} \cdot \mathrm{BL} \\ + & & + \\ \mathrm{PVP} & & \mathrm{PVP} \\ \downarrow\uparrow K_{\mathrm{Bind}} & & \downarrow\uparrow K_{\mathrm{Bind}}{}^{\mathrm{Comp}} \\ & \overset{K_{\mathrm{Comp}}{}^{\mathrm{P}}}{\rightleftarrows} & \\ \mathrm{Dye} \cdot \mathrm{PVP} + \mathrm{BL} & & \mathrm{Dye} \cdot \mathrm{BL} \cdot \mathrm{PVP} \end{array} \qquad (6)$$

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 $K_{\mathrm{Comp}}{}^{\mathrm{P}}$ and $K_{\mathrm{Bind}}{}^{\mathrm{Comp}}$ 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,

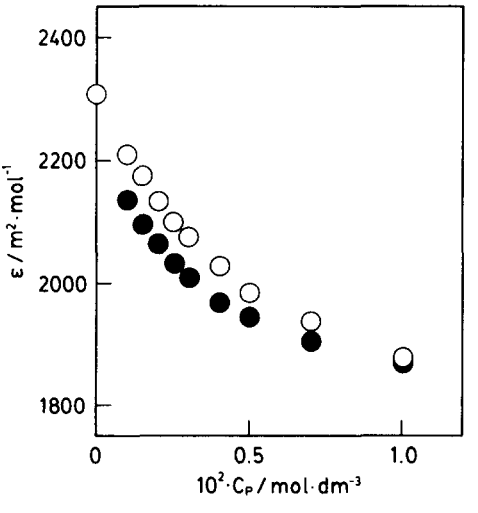


Fig. 3. Relationship between the extinction coefficients and the polymer concentration for R-2 in the (○) absence and (●) presence of DC6-3 (6×10^{-4} mol dm ^{3}) at 298 K and 495 nm.

the following equation can be derived, in the same manner as described in a previous paper,[2]

$$\epsilon = \frac{\epsilon_f + K_{Comp}C_{BL}\epsilon_{Comp} - (1 + K_{Comp}C_{BL})\epsilon}{K_{Bind}(1 + K_{Comp}{}^{P}C_{BL})} \cdot \frac{1}{C_P} + \frac{\epsilon_b + K_{Comp}{}^{P}C_{BL}\epsilon_{bComp}}{1 + K_{Comp}{}^{P}C_{BL}} \quad (7)$$

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 is used as 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, ϵ, against $\{\epsilon_f + K_{Comp}C_{BL}\epsilon_{Comp} - (1 + K_{Comp}C_{BL})\epsilon\}/C_P$ would give $K_{Comp}{}^{P}$ and ϵ_{bComp}. The binding constant of the dye/bolyte complex with PVP, $K_{Bind}{}^{Comp}$ can be determined from the following relationship:

$$K_{Comp}K_{Bind}{}^{Comp} = K_{Bind}K_{Comp}{}^{P} \quad (8)$$

In the case of the aromatic bolaform electrolyte, DCBz6, more than one kind of dye/bolyte complex is evidently formed, so that the binding of the dye/bolyte complex with PVP was not investigated.

For R-1/DC6-3, R-2/DC3-3 and R-2/DC6-3 system, the plots of ϵ against $\{\epsilon_f + K_{Comp}C_{BL}\epsilon_{Comp} - (1 + K_{Comp}C_{BL})\epsilon\}/C_P$ were almost linear, as shown in Fig. 4. The $K_{Bind}{}^{Comp}$ values calculated at two bolyte concentrations are given in Table 4. They hardly varied with the bolaform electrolyte concentration.

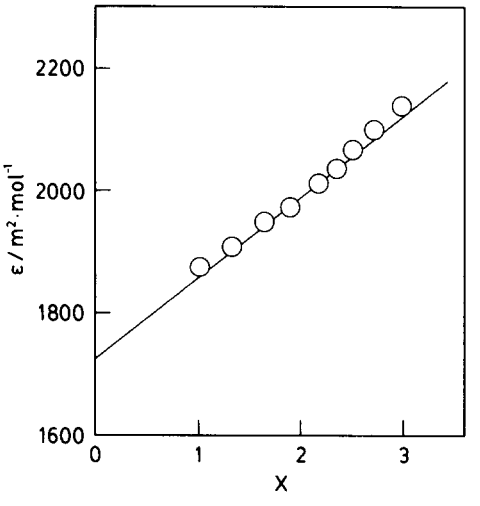


Fig. 4. Plot of ϵ against X for R-2 in the presence of DC6-3 at 298 K and 495 nm. X = $10^{-5} \cdot \{\epsilon_f + K_{Comp}C_{BL}\epsilon_{Comp} - (1 + K_{Comp}C_{BL})\epsilon\}/C_p$, $C_{BL} = 6 \times 10^{-4}$ mol dm ^{3}.

TABLE 4
Binding Constants, K_{Bind}^{Comp} (dm^3 mol^{-1}), at 495 nm

	288 K	*298 K*	*308 K*	*318 K*
R-1				
None (K_{Bind})	1330	880	600	410
DC6-3 (6×10^{-4} mol dm^{-3})	6090	3310	1800	
DC6-3 ($1{\cdot}2 \times 10^{-4}$ mol dm^{-3})	7490	4050	2120	
R-2				
None (K_{Bind})	232	174	144	106
DC3-3 (6×10^{-4} mol dm^{-3})	617	538	418	326
DC3-3 ($1{\cdot}2 \times 10^{-4}$ mol dm^{-3})	586	524	409	293
DC6-3 (6×10^{-4} mol dm^{-3})	381	322	276	230
DC6-3 (6×10^{-4} mol dm^{-3})	381	330	267	219

This suggests that eqn (7) is reasonable and applicable to the ternary system containing the dye, the bolyte and the polymer. Furthermore, if more than one kind of dye/bolyte complex is included in the system, the ratio of the complexes should change with the bolyte concentration. Such a situation could make the equilibria more complicated and the binding constants at two bolyte concentrations different. Therefore, the agreement between the binding constants at two bolyte concentrations indicates that a single complex exists in the system or that the complexes are indistinguishable, i.e. they have the same binding constant. In either event, the R-2/DC3-3 and R-2/DC6-3 system can be analyzed by using eqn (7).

The K_{Bind}^{Comp} values for the dye/bolyte complexes were much larger than the K_{Bind} values for the dyes themselves. This suggests that the aliphatic bolaform electrolytes enhance the binding constants, as was pointed out in a previous paper.[2] Here it is worthwhile to use the ratio K_{Bind}^{Comp}/K_{Bind} as the degree of the enhancement of the binding constants by the bolaform electrolytes. For the R-1/DC6-3, R-2/DC3-3 and R-2/DC6-3, the ratios are 3·0–5·6, 2·5–3·1 and 1·6–2·2, respectively. In the case of AS, which contains one benzene ring and one naphthalene ring, it was 1·0–1·7,[2] although a different bolyte, DC3-4, was used. The above result could show that the dye containing two naphthalene rings is influenced much more by the bolaform electrolytes than the dye having one benzene and one naphthalene ring. The degree of enhancement of the binding constants was reduced by the introduction of one more sulphonate group. The methylene chain length of the bolytes also affected the binding constants in the case of R-2. Thus the degree of enhancement is affected not only by the dye structure but also by the bolyte structure.

The thermodynamic parameters for the binding, viz. the enthalpy change, ΔH_{Bind}^{Comp}, and the entropy change, ΔS_{Bind}^{Comp}, were calculated from the

TABLE 5
Thermodynamic Parameters

	ΔH_{Bind}^{Comp} (kJ mol^{-1})	ΔS_{Bind}^{Comp} (J mol^{-1} K^{-1})
R-1		
None (ΔH_{Bind} and ΔS_{Bind})	−29·8 ± 0·3	−43·7 ± 0·9
DC6-3 (6×10^{-4} mol dm^{-3})	−43·4 ± 0·2	−78·1 ± 0·5
DC6-3 ($1·2 \times 10^{-4}$ mol dm^{-3})	−46·6 ± 1·6	−87 ± 5
R-2		
None (ΔH_{Bind} and ΔS_{Bind})	−19·1 ± 1·2	−21 ± 4
DC3-3 (6×10^{-4} mol dm^{-3})	−16·4 ± 1·8	−3 ± 6
DC3-3 ($1·2 \times 10^{-4}$ mol dm^{-3})	−18 ± 3	−8 ± 10
DC6-3 (6×10^{-4} mol dm^{-3})	−12·7 ± 0·5	−5·4 ± 1·6
DC6-3 ($1·2 \times 10^{-4}$ mol dm^{-3})	−14·2 ± 1·1	0 ± 4

temperature dependence of K_{Bind}^{Comp} (Table 5). The binding process of the R-1/bolyte complex with PVP was found to be more exothermic and less entropic than that of R-1 itself, whereas the thermodynamic parameters for the R-2/bolyte complexes behaved in an opposite manner. This might be due to the difference in the complex structure between R-1 and R-2: the R-1/bolyte complex has one positive charge, while the R-2/bolyte 1 : 1 complexes carry one positive and one negative charge. The different ionic structure is believed to make the thermodynamic parameters different.

From the above results, it is concluded that the degree of enhancement of the binding constants with PVP becomes much larger for dyes containing two naphthalene rings and the number of the sulphonate groups significantly influences the binding processes because of the different complex structure.

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