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Effects of Bolaform Electrolytes on the Interaction Between a Water-Soluble Polymer and Sulphonated Monoazo Dyes. Part 2: Aromatic Bolaform Electrolytes

Jiahe Qian, Kunihiro Hamada* & Masaru Mitsuishi

Faculty of Textile Science and Technology, Shinshu University,
3-15-1 Tokida, Ueda-shi, Nagano 386, Japan

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ABSTRACT

The effect of aromatic bolaform electrolytes which contain two quaternized amino groups and two phenyl rings on the interaction between sulphonated monoazo dyes and poly(vinylpyrrolidone) was investigated using visible absorption spectrum measurements. Since the aromatic bolaform electrolytes aggregated in a higher concentration range, the formation of complexes between the dyes and the bolaform electrolytes was investigated in the concentration range where no aggregate was formed. 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 poly(vinylpyrrolidone); the values were smaller than those of the dyes themselves. The effect of the aromatic bolaform electrolytes on the interaction between the dyes and poly(vinylpyrrolidone) is discussed, as compared with that of aliphatic bolaform electrolytes, by using thermodynamic parameters calculated from the temperature dependence of the first binding constants.

1 INTRODUCTION

We have studied various factors affecting the interaction between sulphonated monoazo dyes and poly(vinylpyrrolidone) (PVP), e.g. cosolutes, dye structures, temperature, etc.[1–5] Bolaform electrolytes (bolytes) were

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* To whom correspondence should be addressed.

found to enhance the first binding constants of the dyes with PVP.[5] However, the effect of the chemical structure of the bolytes on the interaction has not been elucidated.

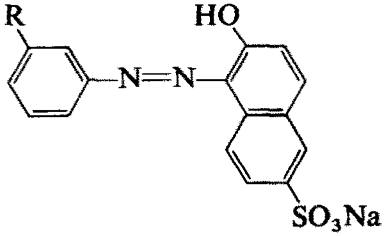
The effects of the terminal alkyl chain length and of the connecting alkyl chain length of bolaform electrolytes on surface activity, solubilization properties and micelle formation have been discussed.[6–8] Applications of bolaform amphiphiles containing the bispyridium moiety as counterions of anionic surfactants have also been reported.[9,10] Recently, the behaviour of micelles or vesicles formed by crown ether-based bolaform amphiphiles in aqueous solutions has been studied.[11] These researches confirmed that the behaviour of bolaform electrolytes in aqueous solutions is greatly dependent on their chemical structures.

In the present study, bolaform electrolytes containing two cationic groups (bisquaternary ammonium) and two phenyl rings were prepared and their effect on the interaction between PVP and sulphonated monoazo dyes in aqueous solutions was 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 a previous paper,[5] 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 with PVP in the presence of aliphatic bolaform electrolytes.[5]

2 EXPERIMENTAL

2.1 Materials

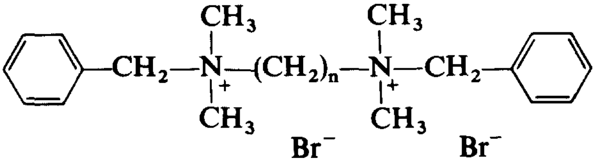
Three monoazo sulphonated dyes, viz. sodium 1-phenylazo-2-hydroxy-6-naphthalenesulphonate (AS), sodium 1-(3-methylphenylazo)-2-hydroxy-6-naphthalenesulphonate (m-TS), and 1-(3-trifluoromethylphenylazo)-2-hydroxy-6-naphthalenesulphonate (m-FTS) were used.



R = H: AS
R = CH_3: m-TS
R = CF_3: m-FTS

AS (Crocein Orange G) was purchased from Tokyo Kasei Kogyo Co. (Tokyo, Japan) and purified by repeated recrystallization from 80% aqueous ethanol. m-TS and m-FTS were prepared as described in previous papers.[1,12]

Two bolaform electrolytes, *N*,*N*′-bis(benzyldimethyl)-1,3-propanediammonium dibromide (DCBz3) and *N*,*N*′-bis(benzyldimethyl)-1,6-hexanediammonium dibromide (DCBz6) were used.



n = 3: DCBz3
n = 6: DCBz6

DCBz3 and DCBz6 were prepared as follows: a mixed solution of benzyl bromide and the corresponding diamine (*N*,*N*,*N*′,*N*′-tetramethyl-1,3-propanediamine or *N*,*N*,*N*′,*N*′-tetramethyl-1,6-diaminohexane) in nitromethane was stirred at room temperature for 3 days. The products were then filtered, purified by repeated precipitation from ethanol into ether for DCBz3, and from methanol into acetone for DCBz6, and dried. Purity was confirmed by elemental analysis. (Calculated for DCBz3 as water content 2·07%: C, 52·30; H, 6·92; N, 5·81; Br, 33·1%. Found: C, 52·47; H, 6·78; N, 5·79; Br, 33·9%. Calculated for DCBz6: C, 56·70; H, 7·40; N, 5·51; Br, 31·4%. Found: C, 55·98; H, 7·50; N, 5·58; Br, 32·5%.)

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

2.2 Visible absorption spectrum measurements

In the absence and presence of 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-240 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 also similarly measured, as were the spectra change of the aqueous bolyte solutions with increase in bolyte concentration.

3 RESULTS AND DISCUSSION

3.1 Behaviour of bolaform electrolytes in aqueous solutions

In contrast with aliphatic bolaform electrolytes containing two alkyl groups as terminal groups as described in our previous paper,[5] significant ultraviolet absorption was observed for DCBz3 and DCBz6 at 262 nm due to the presence of the phenyl rings. This makes it possible to investigate their behaviour in aqueous solutions using spectrophotometric methods. The concentration dependence of the extinction coefficients, ε, at maximum absorption wavelength (262 nm) for DCBz3 is shown in Fig. 1. The extinction coefficients for DCBz3 abruptly decreased at approximately $1{\cdot}2 \times 10^{-3}$ mol dm^{-3} and a similar decrease of the extinction coefficients was observed at approximately $1{\cdot}6 \times 10^{-3}$ mol dm^{-3} for DCBz6. These results might suggest that bolaform electrolytes containing phenyl rings aggregate easily in the higher concentration range. Bolaform electrolyte concentrations where no aggregate is formed were therefore employed in the following sections.

3.2 Interaction between the dyes and the bolaform electrolytes

The visible absorption spectra of aqueous solutions with a constant dye concentration and various bolyte concentrations changed gradually with

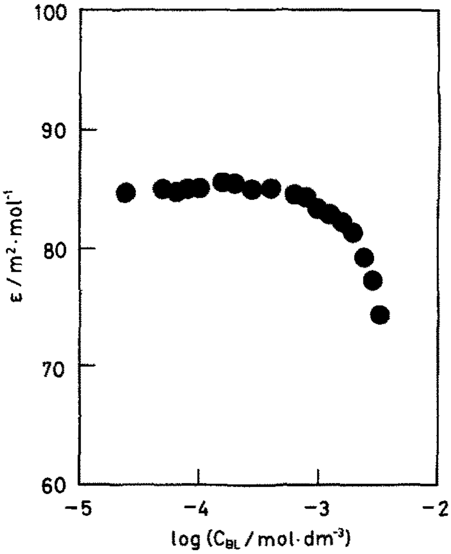


Fig. 1. Relationship between the extinction coefficients for DCBz3 on the bolyte concentration at 298 K and 262 nm.

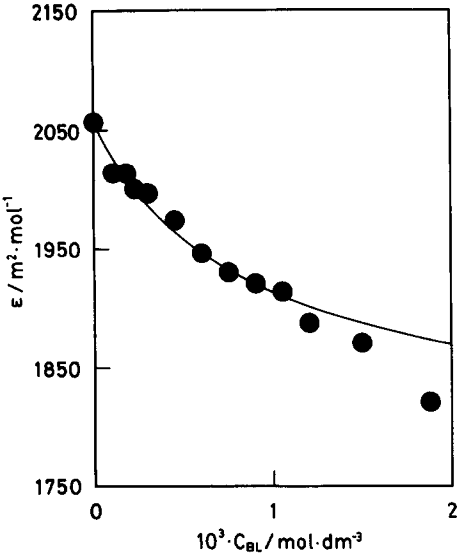


Fig. 2. Relationship between the extinction coefficients on the bolyte concentration for AS/DCBz3 system at 298 K and 480 nm.

increasing bolyte concentration. As shown in Fig. 2, for the AS/DCBz3 system, the extinction coefficients at the absorption maxima decrease with increasing bolaform electrolyte concentration, indicating that the dye binds with the bolaform electrolyte in the aqueous solutions. In the case of m-TS and m-FTS, precipitates of the dye/bolyte complexes were produced, so that visible absorption spectra could not be recorded. It seems that such precipitation is due to the chemical structure of the dyes, i.e. the substituents in the dyes. Thus, only results for AS are discussed below.

As the bolaform electrolyte concentration is much greater than the dye concentration, one of the positively charged groups in the bolytes and the negatively charged group in the dye are believed to form a 1:1 complex; the following single equilibrium exists in the dye/bolyte systems:

$$\mathrm{D} + \mathrm{BL} \rightleftarrows \mathrm{D}\cdot\mathrm{BL} \qquad (1)$$

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 electrolytes, 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 electrolytes, K_{Comp}, is represented by the following equation:

$$K_{\mathrm{Comp}} = \frac{C_{\mathrm{Comp}}}{(C_{\mathrm{BL}} - C_{\mathrm{Comp}})C_{\mathrm{f}}} \qquad (2)$$

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

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

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 dyes, respectively, then the observed extinction coefficients, ε, can be expressed as follows:

$$\varepsilon = \frac{C_f}{C_0}\varepsilon_f + \frac{C_{Comp}}{C_0}\varepsilon_{Comp} \tag{4}$$

By substituting eqn (3) and $C_f = C_0 - C_{Comp}$ into eqn (4), we obtain

$$\varepsilon = \varepsilon_f + \frac{\varepsilon_{Comp} - \varepsilon_f}{2C_0}\{A - (A^2 - 4C_0C_{BL})^{1/2}\} \tag{5}$$

On the basis of eqn (5), 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.[5] The solid line in Fig. 2 expresses the fitting curve calculated using K_{Comp} and ε_{Comp} obtained above, and shows good agreement with the observed values below $1{\cdot}2 \times 10^{-3}$ mol dm^{-3}. However, deviation of the observed values from the fitting curve was found above $1{\cdot}2 \times 10^{-3}$ mol dm^{-3}. Similar results were obtained at all temperatures used in this study. Such deviation is also observed for DCBz6, where the fitting curve deviated from the observed values above $1{\cdot}6 \times 10^{-3}$ mol dm^{-3}. This might be attributed to aggregation of the bolaform electrolytes in the higher concentration range, as noted above. These findings support the argument described in the preceding section.

The binding constants, K_{Comp}, and the thermodynamic parameters (the enthalpy change, ΔH_{Comp}, and the entropy change, ΔS_{Comp}) calculated from the temperature dependence of K_{Comp} for AS are given in Table 1. The positive values of the enthalpy change and the entropy change indicated that the binding process of the dye with the bolytes was endothermic and entropic; the binding process of the dye with the aromatic bolaform electrolytes was enthalpically unfavourable, but entropically favourable.

TABLE 1
Binding Constants, K_{Comp}, and Thermodynamic Parameters for AS

	K_{Comp} *(dm^3 mol^{-1})*				ΔH_{Comp}	ΔS_{Comp}
	288 K	*298 K*	*308 K*	*318 K*	*(kJ mol^{-1})*	*(J mol^{-1} K^{-1})*
DCBz3	860	1 150	1 550	1 690	18 ± 2	118 ± 8
DCBz6	3 580	3 850	4 160	4 410	5·36 ± 0·14	86·7 ± 0·5

Moreover, the K_{Comp} values for DCBz6 possessing a longer connecting alkyl chain were much greater than those for DCBz3. These results may be due to the hydrophobic interaction between the hydrophobic part of the dye and the connecting alkyl chain of the bolaform electrolytes.

3.3 Interaction between AS and PVP

The same changes in the visible absorption spectra for AS as reported in our previous paper[5] were observed with increasing polymer concentration. To analyze the spectral change with the polymer concentration based on monomer units, the extinction coefficients, ε, at the wavelength where the largest difference was observed are useful. These extinction coefficients decrease with increasing polymer concentration (C_{P}). To estimate the first binding constants, the same equation as used in our previous investigations was employed, i.e.

$$\varepsilon = \frac{\varepsilon_{\mathrm{f}} - \varepsilon}{C_{\mathrm{P}}} \frac{1}{K_{\mathrm{Bind}}} + \varepsilon_{\mathrm{b}} \tag{6}$$

where ε_{f} and ε_{b} are the extinction coefficients of the free and bound dyes, respectively. This equation includes the assumption that the bound dye concentration is much smaller than C_{P}, an assumption which is fulfilled in the AS/PVP system.

The plots of ε against $(\varepsilon_{\mathrm{f}} - \varepsilon)/C_{\mathrm{P}}$ gave good linearity at 480 and 530 nm, the former of which is shown in Fig. 3. The first binding

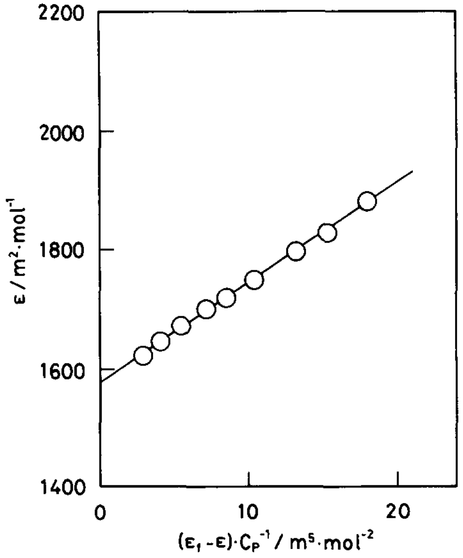


Fig. 3. Plots of ε against $(\varepsilon_{\mathrm{f}} - \varepsilon)/C_{\mathrm{P}}$ for AS at 298 K and 480 nm.

TABLE 2
Binding Constants, K_{Bind}, and Thermodynamic Parameters for AS

	K_{Bind} ($dm^3\ mol^{-1}$)				ΔH_{Bind}	ΔS_{Bind}
	288 K	*298 K*	*308 K*	*318 K*	($kJ\,mol^{-1}$)	($J\,mol^{-1}\,K^{-1}$)
480 nm	73·2	60·0	48·4	40·2	−15·3 ± 0·3	−17·5 ± 1·0
530 nm	66·0	55·5	47·1	37·8	−14·0 ± 0·9	−14·0 ± 3·0

constants, K_{Bind}, calculated from the slopes and the thermodynamic parameters (the enthalpy change, ΔH_{Bind}, and the entropy change, ΔS_{Bind}) determined from the temperature dependence of K_{Bind} are shown in Table 2; the values are in good agreement with those reported in previous papers.[3-5] On the other hand, the binding constants and the thermodynamic parameters at both the wavelengths also showed good agreement. This result confirms that only a single equilibrium exists in the dye and polymer system investigated.

3.4 Interaction between AS/bolaform electrolyte complexes and PVP

The spectral change with increasing polymer concentration was greater in the presence of the bolytes than in their absence. As shown in Fig. 4, the

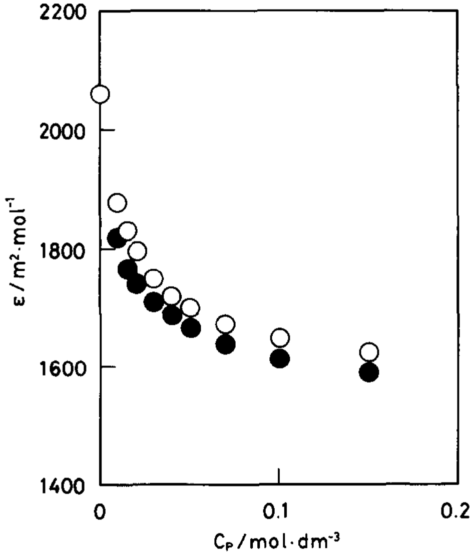


Fig. 4. Relationship between the extinction coefficients on the polymer concentration for AS in the absence (○) and presence (●) of DCBz3 (6×10^{-4} mol dm^{-3}) at 298 K and 480 nm.

extinction coefficients for the ternary systems were smaller than those for the binary systems in the polymer concentration region investigated, suggesting that the bolytes influence the interaction between the dye and PVP. Since the interaction between the dye and the bolaform electrolytes has been established, we assumed the following equilibria:

$$\begin{tikzcd}
\text{Dye} + \text{BL} \arrow[r, leftrightarrow, "K_{\mathrm{Comp}}"] & \text{Dye}\,.\,\text{BL} \\
+ & + \\
\text{PVP} \arrow[d, leftrightarrow, "K_{\mathrm{Bind}}"] & \text{PVP} \arrow[d, leftrightarrow, "K_{\mathrm{Bind}}^{\mathrm{Comp}}"] \\
\text{Dye}\cdot\text{PVP} + \text{BL} \arrow[r, leftrightarrow, "K_{\mathrm{Comp}}^{\mathrm{P}}"] & \text{Dye}\cdot\text{BL}\cdot\text{PVP}
\end{tikzcd} \tag{7}$$

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, the following equation can be derived, in the same manner as described in a previous paper.[5]

$$\varepsilon = \frac{\varepsilon_{\mathrm{f}} + K_{\mathrm{Comp}} C_{\mathrm{BL}} \varepsilon_{\mathrm{Comp}} - (1 + K_{\mathrm{Comp}} C_{\mathrm{BL}})\varepsilon}{K_{\mathrm{Bind}}(1 + K_{\mathrm{Comp}}^{\mathrm{P}} C_{\mathrm{BL}})} \cdot \frac{1}{C_{\mathrm{P}}} + \frac{\varepsilon_{\mathrm{b}} + K_{\mathrm{Comp}}^{\mathrm{P}} C_{\mathrm{BL}} \varepsilon_{\mathrm{bComp}}}{1 + K_{\mathrm{Comp}}^{\mathrm{P}} C_{\mathrm{BL}}} \tag{8}$$

where ε_{f}, ε_{b} and $\varepsilon_{\mathrm{Comp}}$ are as defined in eqns (4) and (6); $\varepsilon_{\mathrm{bComp}}$ represents the extinction coefficient of the dye/bolyte/PVP complex. The original bolaform electrolyte concentration is used as C_{BL}.

Using the values of ε_{f}, ε_{b}, $\varepsilon_{\mathrm{Comp}}$, K_{Comp} and K_{Bind} determined in the previous sections, the plots of the observed extinction coefficients, ε against $\{\varepsilon_{\mathrm{f}} + K_{\mathrm{Comp}} C_{\mathrm{BL}} \varepsilon_{\mathrm{Comp}} - (1 + K_{\mathrm{Comp}} C_{\mathrm{BL}})\varepsilon\}/C_{\mathrm{P}}$ would give a linear relationship, the slope and intercept of which can give $K_{\mathrm{Comp}}^{\mathrm{P}}$ and $\varepsilon_{\mathrm{bComp}}$. Furthermore, from the above equilibria, the following relationship can be obtained:

$$K_{\mathrm{Comp}} K_{\mathrm{Bind}}^{\mathrm{Comp}} = K_{\mathrm{Bind}} K_{\mathrm{Comp}}^{\mathrm{P}} \tag{9}$$

From eqn (9), the binding constant of the dye/bolyte complex with PVP, $K_{\mathrm{Bind}}^{\mathrm{Comp}}$ can be determined.

In all the cases investigated, the plots of ε against $\{\varepsilon_{\mathrm{f}} + K_{\mathrm{Comp}} C_{\mathrm{BL}} \cdot \varepsilon_{\mathrm{Comp}} - (1 + K_{\mathrm{Comp}} C_{\mathrm{BL}})\varepsilon\}/C_{\mathrm{P}}$ were almost linear, as shown in Fig. 5. The

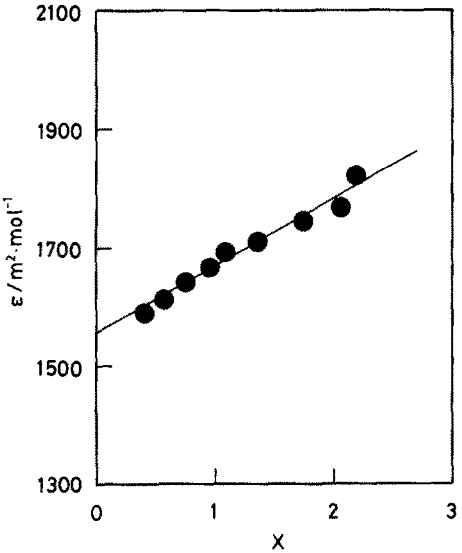


Fig. 5. Plots of ε against X for AS in the presence of DCBz3 at 298 K and 480 nm. $X = 10^{-4}\{\varepsilon_f + K_{\mathrm{Comp}}C_{\mathrm{BL}}\varepsilon_{\mathrm{Comp}} - (1 + K_{\mathrm{Comp}}C_{\mathrm{BL}})\varepsilon\}/C_{\mathrm{P}}$, $C_{\mathrm{BL}} = 6\times10^{-4}$ mol dm^{-3}.

$K_{\mathrm{Bind}}^{\mathrm{Comp}}$ calculated at two wavelengths are given in Table 3. The $K_{\mathrm{Bind}}^{\mathrm{Comp}}$ values for two bolaform electrolytes at 480 and 530 nm were smaller than the corresponding K_{Bind} values at all the temperatures. This result was contrary to the conclusion drawn in our previous paper[5] in which the aliphatic bolaform electrolytes containing alkyl groups as two terminal groups enhanced the first binding constants of the sulphonated

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

	288 K	*298 K*	*308 K*	*318 K*
480 nm				
None (K_{Bind})	73·2	60·0	48·4	40·2
DCBz3 (6×10^{-4} mol dm^{-3})	64·9	39·6	27·1	24·6
($1{\cdot}2\times10^{-3}$ mol dm^{-3})	78·3	48·1	36·3	22·1
DCBz6 (6×10^{-4} mol dm^{-3})	67·1	48·5	38·1	36·3
($1{\cdot}2\times10^{-3}$ mol dm^{-3})	61·7	46·2	44·6	35·1
530 nm				
None (K_{Bind})	66·0	55·5	47·1	37·8
DCBz3 (6×10^{-4} mol dm^{-3})	55·2	42·4	23·1	18·7
($1{\cdot}2\times10^{-3}$ mol dm^{-3})	53·6	36·7	32·3	19·7
DCBz6 (6×10^{-4} mol dm^{-3})	49·6	31·9	30·0	20·3
($1{\cdot}2\times10^{-3}$ mol dm^{-3})	51·5	37·1	36·7	28·8

TABLE 4
Thermodynamic Parameters

	$\Delta H_{\mathrm{Bind}}^{\mathrm{Comp}}$	$\Delta S_{\mathrm{Bind}}^{\mathrm{Comp}}$
	(*kJ mol*$^{-1}$)	(*J mol*$^{-1}$ *K*$^{-1}$)
480 nm		
None	−15·3 ± 0·3	−17·5 ± 1·0
DCBz3 (6 × 10^{-4} mol dm^{-3})	−25 ± 4	−53 ± 14
(1·2 × 10^{-3} mol dm^{-3})	−31 ± 2	−72 ± 8
DCBz6 (6 × 10^{-4} mol dm^{-3})	−16 ± 3	−21 ± 10
(1·2 × 10^{-3} mol dm^{-3})	−13 ± 2	−12 ± 8
530 nm		
None	−14·0 ± 0·9	−14 ± 3
DCBz3 (6 × 10^{-4} mol dm^{-3})	−29 ± 4	−68 ± 13
(1·2 × 10^{-3} mol dm^{-3})	−24 ± 4	−49 ± 13
DCBz6 (6 × 10^{-4} mol dm^{-3})	−21 ± 4	−40 ± 13
(1·2 × 10^{-3} mol dm^{-3})	−13 ± 3	−14 ± 10

monoazo dyes with PVP through the formation of the complexes. This fact suggests that the dye/aromatic bolyte complexes have a lower affinity for the polymer than the dye alone. Thus, the terminal groups of the bolaform electrolytes play an important role in the binding of the dye/bolyte complexes with PVP. Moreover, the $K_{\mathrm{Bind}}^{\mathrm{Comp}}$ values hardly varied with the bolaform electrolyte concentration, confirming that eqn (8) derived in a previous study[5] was reasonable, and applicable to the ternary system containing the dye, the bolaform electrolytes and the polymer. On the other hand, the small difference between the $K_{\mathrm{Bind}}^{\mathrm{Comp}}$ values at 480 and 530 nm also confirms that the four single equilibria as described in eqn (7) exist in the ternary system.

The thermodynamic parameters for the binding, viz. the enthalpy change, $\Delta H_{\mathrm{Bind}}^{\mathrm{Comp}}$, and the entropy change, $\Delta S_{\mathrm{Bind}}^{\mathrm{Comp}}$, were determined from the temperature dependence of $K_{\mathrm{Bind}}^{\mathrm{Comp}}$ (Table 4). As a result, the thermodynamic parameters for the two bolaform electrolytes were quite different. The binding process of the dye/DCBz3 complex with PVP was more exothermic and less entropic than that of the dye itself. This result might be attributed to the difference of hydration between the negatively charged dye and the positively charged dye/DCBz3 complex. However, in the case of DCBz6, except in the case of 6 × 10^{-3} mol dm^{-3} at 530 nm (which might be due to too small a change in the absorbance at 530 nm), the thermodynamic parameters for the dye/DCBz6 complex were similar to those for the dye itself. This result might be explained in that the varied lengths of the connecting alkyl chain between two positive charges may change the distribution of the charge density, and affect the hydration around the dye/bolyte complexes.

From the above results, it is concluded that the aromatic bolaform electrolytes containing two phenyl rings lower the first binding constants of the sulphonated monoazo dye with PVP through the formation of complexes, in contrast to the case of aliphatic bolaform electrolytes.

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