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Effects of Bolaform Electrolytes on the Interaction between a Water-Soluble Polymer and Sulphonated Monoazo Dyes. Part 1

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ABSTRACT

The interaction between sulphonated monoazo dyes and poly(vinylpyrrolidone) in the presence of bolaform electrolytes with two quaternized amino groups was investigated by means of visible absorption spectrum measurements. The first binding constants of the dyes with poly(vinylpyrrolidone), determined by neglecting the binding of the dyes with the bolaform electrolytes, were much larger than those in the absence of the bolaform electrolytes. However, interaction between the dyes and the bolaform electrolytes in aqueous solutions was found, so that the above assumption was not fulfilled. Therefore, the first binding constants of the dye/bolaform electrolyte complexes with poly(vinylpyrrolidone) were determined by using the equation based on the equilibria in the trinary systems containing the dyes, the bolaform electrolytes and poly(vinylpyrrolidone). The first binding constants of the complexes with poly(vinylpyrrolidone) were larger than those of the dyes, which suggests that the bolaform electrolytes enhance the affinity of the dyes for the polymer through the formation of dye/bolaform electrolyte complexes.

1 INTRODUCTION

Organic compounds possessing two cationic or anionic groups separated by relatively large distances have been named 'bolaform electrolytes (bolytes)' or 'bolaform amphiphiles (bola-amphiphiles)'.[1,2] Various physical properties of bolaform electrolytes or amphiphiles have been extensively studied. The surface activity, solubilization properties and micelle formation for some bolaform amphiphiles have been discussed in detail.[3–5] The application of bolaform amphiphiles to monolayer lipid membranes has also been reported.[6,7] Recently, a study on the micelles or vesicles formed from crown ether-based bolaform amphiphiles has been reported.[8] These studies show that the bolaform electrolytes or amphiphiles behave peculiarly compared to the corresponding compounds having a single positive or negative site.

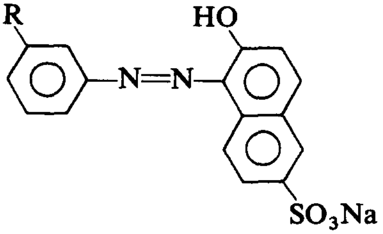
We have investigated the interaction between sulphonated monoazo dyes and poly(vinylpyrrolidone) (PVP) in aqueous solutions by means of visible absorption spectroscopy.[9–12] As a result, the effects of cosolutes (sodium chloride and sodium thiocyanate) as well as those of the substituents in the dyes were elucidated. In addition, the sorption behaviours of sulphonated monoazo dyes by nylon 6 film[13–15] and silk fibre[16] have been evaluated with respect to the dye structures. However, the effects of bolaform electrolytes or amphiphiles on the interaction and the sorption have, to date, not been fully clarified.

In the present study, bolaform electrolytes possessing two cationic groups (bisquaternary ammonium) were prepared and their effects on the interaction between PVP and sulphonated monoazo dyes in aqueous solutions were investigated using visible absorption spectroscopy. An equation based on the equilibria in trinary systems containing the dyes, the bolaform electrolytes and PVP is derived, and the first binding constants of the dye/bolaform electrolyte complexes are discussed, and compared with those obtained from equilibrium in binary systems containing the dyes and PVP.

2 EXPERIMENTAL

2.1 Materials

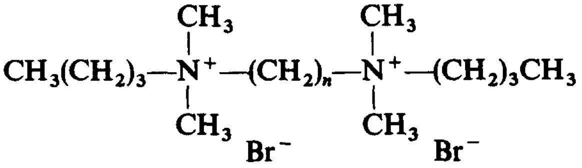
Three monoazo sulphonated dyes, sodium 1-phenylazo-2-hydroxy-6-naphthalenesulphonate (AS), sodium 1-(3-methylphenylazo)-2-hydroxy-6-naphthalenesulphonate (m-TS), and 1-(3-trifluoromethylphenylazo)-2-hydroxy-6-naphthalenesulphonate (m-FTS) were used.



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 solution; m-TS and m-FTS were prepared as described in previous papers.[9,17]

Two bolaform electrolytes, *N*,*N'*-bis(butyldimethyl)-1,3-propanediammonium dibromide(DC3-4) and *N*,*N'*-bis(butyldimethyl)-1,6-hexanediammonium dibromide (DC6-4) were used.



$$CH_3(CH_2)_3{-}\underset{CH_3}{\overset{CH_3}{N^+}}{-}(CH_2)_n{-}\underset{CH_3}{\overset{CH_3}{N^+}}{-}(CH_2)_3CH_3 \qquad Br^- \qquad Br^-$$

$n = 3$: DC3-4

$n = 6$: DC6-4

DC3-4 and DC6-4 were prepared as follows. A mixed solution of 1-bromobutane and the corresponding diamine (*N*,*N*,*N'*,*N'*-tetramethyl-1,3-propanediamine or *N*,*N*,*N'*,*N'*-tetramethyl-1,6-diaminohexane) in nitroethane or nitromethane was stirred at room temperature for four days. For DC3-4, the mixed solution was reacted at 323 K for a further two days. The products were then filtered, purified by repeated precipitation from ethanol into ether for DC3-4 and from methanol into acetone for DC6-4, and dried. Purity was confirmed by elemental analysis. (Calculated for DC3-4 at water content 1·8%: C, 43·76; H, 9·02; N, 6·80; Br, 38·8%. Found: C, 43·79; H, 9·27; N, 6·80; Br, 40·1%. Calculated for DC6-4 at water content 5·9%: C, 45·58; H, 9·59; N, 5·91; Br, 33·7%. Found: C, 45·15; H, 9·10; N, 5·96; Br, 35·0%.)

Poly(vinylpyrrolidone) (mol. wt 360 000) was purchased from Tokyo Kasei Co., and was 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 the 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 in conjunction 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 PVP without considering their binding with the bolaform electrolytes

The same spectral changes as reported in a previous paper[12] were observed for all the dyes in the absence and presence of the bolaform electrolytes. To analyse the spectral change with polymer concentration based on monomer units, the extinction coefficients, ε, at the wavelength where the largest difference was observed are useful. These extinction coefficients decreased with increasing polymer concentration (C_p) for all the dyes, as shown in Fig. 1. To estimate the first binding constants, the same equation as that used in previous studies was employed[9-12] for the polymer and dye systems. If the binding of the dyes with the bolytes is neglected, this equation is also applicable to the trinary systems containing the dyes, the bolaform electrolytes and PVP. This equation enables the first binding constants, K_{Bind}, to be determined from the change in ε:

$$\varepsilon = \frac{\varepsilon_f - \varepsilon}{C_p} \cdot \frac{1}{K_{\mathrm{Bind}}} + \varepsilon_b \tag{1}$$

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. The above assumption is fulfilled in all the systems investigated.

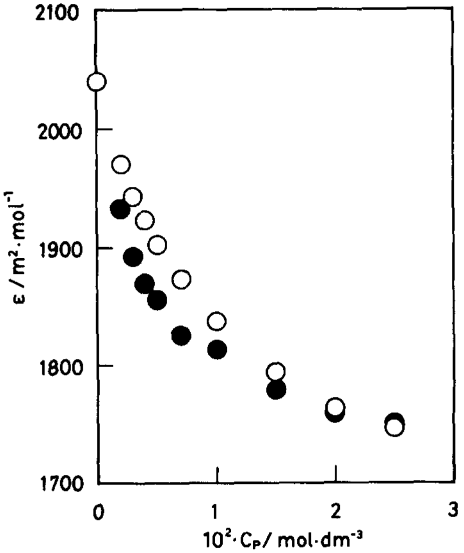


Fig. 1. Relationship between extinction coefficients and polymer concentration for m-TS in the absence (○) and presence (●) of DC3-4 (6×10^{-4} mol dm^{-3}) at 298 K and 487 nm.

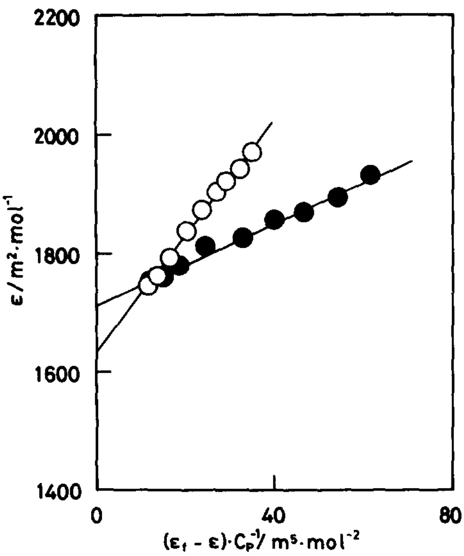


Fig. 2. Plots of ε against $(\varepsilon_f - \varepsilon)/C_p$ for m-TS in the absence (○) and presence (●) of DC3-4 (6×10^{-4} mol dm^{-3}) at 298 K and 487 nm.

The plots of ε against $(\varepsilon_f - \varepsilon)/C_p$ gave good linearity, except for m-FTS, as shown in Fig. 2. The binding constants, K_{Bind}, are calculated from the gradients (Table 1). The values in the absence of the bolaform electrolytes are in good agreement with those reported in a previous paper,[12] except for m-FTS. The measurements for m-FTS appear to show large errors, as pointed out in our previous study.[12]

The K_{Bind} values in the presence of the bolaform electrolytes were much larger than those for the binary systems. This result suggests that DC3-4 and DC6-4 significantly enhance the affinity of the dyes for PVP, if they behave as NaCl and NaSCN without binding with the dyes. However, account should be taken of the electrostatic interaction between the dyes and the bolaform electrolytes, because the former has a negatively charged group and the latter has two positively charged groups. Taking the above interaction into consideration, we now discuss the binding of the dyes with PVP.

3.2 Interaction between dyes and bolaform electrolytes

The visible absorption spectra of the aqueous dye solutions containing the bolaform electrolytes changed with the concentration of the bolaform electrolyte, as in the case of the dye/PVP systems. As shown in Fig. 3, the extinction coefficients for AS at the absorption maxima decreased with increasing bolaform electrolyte concentration, indicating that the dyes

TABLE 1

Binding Constants, K_{Bind} ($\mathrm{dm^3\ mol^{-1}}$), in the Absence and Presence of the Bolaform Electrolytes

	288 K	*298 K*	*308 K*	*318 K*
AS				
None	73·1 ± 1·4	59 ± 2	52 ± 2	39 ± 3
DC3-4[a]	123 ± 7	105 ± 6	97 ± 5	86 ± 6
DC3-4[b]	141 ± 13	135 ± 12	126 ± 15	128 ± 17
DC6-4[a]	173 ± 14	181 ± 17	171 ± 19	190 ± 20
DC6-4[b]	150 ± 13	149 ± 15	146 ± 13	150 ± 13
m-TS				
None	120 ± 3	102 ± 2	86 ± 4	62 ± 5
DC3-4[a]	280 ± 20	292 ± 13	276 ± 18	280 ± 20
DC3-4[b]	300 ± 30	290 ± 40	260 ± 30	260 ± 30
DC6-4[a]	261 ± 18	240 ± 20	232 ± 12	204 ± 15
DC6-4[b]	330 ± 20	310 ± 30	290 ± 30	310 ± 30
m-FTS				
None	68 ± 3	54 ± 4	60 ± 4	47 ± 2
DC3-4[a]	270 ± 40	280 ± 40	360 ± 50	380 ± 40
DC3-4[b]	530 ± 130	580 ± 100	580 ± 70	740 ± 90
DC6-4[a]	370 ± 30	410 ± 80	470 ± 80	560 ± 110
DC6-4[b]	360 ± 60	400 ± 60	410 ± 50	380 ± 40

[a] $6{\cdot}00 \times 10^{-4}$ mol dm^{-3}.
[b] $1{\cdot}20 \times 10^{-3}$ mol dm^{-3}.

bind with the bolaform electrolytes in the aqueous solutions. A similar result was obtained for m-TS and m-FTS. Since the dye concentration is much smaller than the bolyte concentrations, the negatively charged group in the dye and one of the positively charged groups in the bolytes is believed to form a 1:1 complex; the following single equilibrium exists in the dye/bolyte systems:

$$\mathrm{D} + \mathrm{BL} \rightleftarrows \mathrm{D}\cdot\mathrm{BL} \tag{2}$$

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 bolyte, K_{Comp}, is represented by eqn (3):

$$K_{\mathrm{Comp}} = \frac{C_{\mathrm{Comp}}}{(C_{\mathrm{BL}} - C_{\mathrm{Comp}}) \cdot C_{\mathrm{f}}} \tag{3}$$

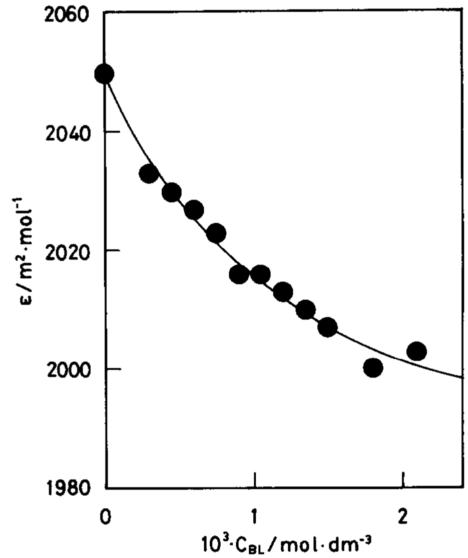


Fig. 3. Relationship between extinction coefficients and the bolyte (DC3-4) concentration for AS at 298 K and 480 nm.

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

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

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, ε, is

$$\varepsilon = \frac{C_f}{C_0} \cdot \varepsilon_f + \frac{C_{Comp}}{C_0} \cdot \varepsilon_{Comp} \tag{5}$$

Substituting eqn (4) and $C_f = C_0 - C_{Comp}$ into eqn (5), we obtain

$$\varepsilon = \varepsilon_f + \frac{\varepsilon_{Comp} - \varepsilon_f}{2C_0} \cdot \{A - (A^2 - 4C_0C_{BL})^{1/2}\} \tag{6}$$

On the basis of eqn (6), the binding constant, K_{Comp}, and the extinction coefficient of the bound dye, ε_{Comp}, were calculated by using the non-linear least-squares method. The solid line in Fig. 3 expresses the fitting curve calculated using K_{Comp} and ε_{Comp} obtained above and shows good agreement with the observed values.

The binding constants, K_{Comp}, for all dyes are given in Table 2. For the m-TS/DC6-4 and m-FTS/DC6-4 systems, K_{Comp} increased with increase in temperature, whereas for the other systems, the temperature dependence of K_{Comp} values does not exhibit such a specific tendency. This might be attributed to a small change in the extinction coefficients, so that the

TABLE 2
Binding Constants, K_{Comp} ($\text{dm}^3\ \text{mol}^{-1}$), for AS, m-TS and m-FTS

	288 K	*298 K*	*308 K*	*318 K*
AS				
DC3-4	1 520	700	840	1 420
DC6-4	1 130	930	1 180	1 550
m-TS				
DC3-4	2 790	5 090	3 080	4 210
DC6-4	1 140	2 290	3 200	4 620
m-FTS				
DC3-4	1 450	2 330	2 730	2 650
DC6-4	1 170	1 160	1 810	3 350

K_{Comp} values, especially for DC3-4, involve large errors. However, approximate estimation leads to the athermic process for DC3-4 and the endothermic process for DC6-4. Furthermore, the K_{Comp} values increased in the order AS $\leq$ m-FTS $<$ m-TS, indicating the influence of the functional groups on the interaction between the dyes and bolytes.

3.3 Interaction between the dyes and PVP with consideration of their binding with the bolaform electrolytes

Because the interaction between the dyes and the bolaform electrolytes was confirmed, we can assume the following equilibria (eqn (7)):

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

In eqn (7) Dye · PVP and Dye · BL · PVP represent the dye/PVP and the dye/bolyte/PVP complex, respectively. $K_{\text{Comp}}^{\text{P}}$ and $K_{\text{Bind}}^{\text{Comp}}$ are the binding constant of the dye/PVP complex with the bolaform electrolytes and that of the dye/bolyte complex with PVP, respectively. On the basis of the above four equilibria, the following equations can then be derived:

$$C_{\text{b}} = K_{\text{Bind}} C_{\text{p}} C_{\text{f}} \tag{8}$$

$$C_{\text{Comp}} = K_{\text{Comp}} C_{\text{BL}} C_{\text{f}} \tag{9}$$

$$\begin{aligned} C_{\mathrm{b}}^{\mathrm{Comp}} &= K_{\mathrm{Comp}}^{\mathrm{p}} C_{\mathrm{b}} C_{\mathrm{CL}} \\ &= K_{\mathrm{Bind}} K_{\mathrm{Comp}}^{\mathrm{p}} C_{\mathrm{BL}} C_{\mathrm{p}} C_{\mathrm{f}} \end{aligned} \tag{10}$$

where C_{f}, C_{b}, C_{Comp} and $C_{\mathrm{b}}^{\mathrm{Comp}}$ are the concentrations of the free dye, the dye/PVP complex, the dye/bolyte complex and the dye/bolyte/PVP complex, respectively. Although these equations contain the assumption that $C_{\mathrm{p}} \gg C_0$ and $C_{\mathrm{BL}} \gg C_0$, the experimental conditions used in the present study satisfy this assumption. Substituting eqns (8), (9) and (10) into $C_{\mathrm{f}} + C_{\mathrm{b}} + C_{\mathrm{Comp}} + C_{\mathrm{b}}^{\mathrm{Comp}} = C_0$, we obtain

$$C_0 = C_{\mathrm{f}}\{(1 + K_{\mathrm{Comp}} C_{\mathrm{BL}}) + K_{\mathrm{Bind}} C_{\mathrm{p}}(1 + K_{\mathrm{Comp}}^{\mathrm{p}} C_{\mathrm{BL}})\} \tag{11}$$

On the other hand, if ε_{f}, ε_{b}, $\varepsilon_{\mathrm{Comp}}$ and $\varepsilon_{\mathrm{b}}^{\mathrm{Comp}}$ are the extinction coefficients of the free dye, the dye/PVP complex, the dye/bolyte and the dye/bolyte/PVP, respectively, then the observed extinction coefficient, ε, is

$$\varepsilon = \frac{C_{\mathrm{f}}}{C_0} \cdot \varepsilon_{\mathrm{f}} + \frac{C_{\mathrm{Comp}}}{C_0} \cdot \varepsilon_{\mathrm{Comp}} + \frac{C_{\mathrm{b}}}{C_0} \cdot \varepsilon_{\mathrm{b}} + \frac{C_{\mathrm{b}}^{\mathrm{Comp}}}{C_0} \cdot \varepsilon_{\mathrm{b}}^{\mathrm{Comp}} \tag{12}$$

Substituting eqns (8), (9), (10) and (11) into eqn (12), we obtain

$$\varepsilon = \frac{\varepsilon_{\mathrm{f}} + K_{\mathrm{Comp}} C_{\mathrm{BL}} \varepsilon_{\mathrm{Comp}} - (1 + K_{\mathrm{Comp}} C_{\mathrm{BL}}) \cdot \varepsilon}{K_{\mathrm{Bind}}(1 + K_{\mathrm{Comp}}^{\mathrm{p}} C_{\mathrm{BL}})} \cdot \frac{1}{C_{\mathrm{p}}} + \frac{\varepsilon_{\mathrm{b}} + K_{\mathrm{Comp}}^{\mathrm{p}} C_{\mathrm{BL}} \varepsilon_{\mathrm{b}}^{\mathrm{Comp}}}{1 + K_{\mathrm{Comp}}^{\mathrm{p}} C_{\mathrm{BL}}} \tag{13}$$

Using the values determined in the previous sections as ε_{f}, ε_{b}, $\varepsilon_{\mathrm{Comp}}$, K_{Bind} and K_{Comp}, the plots of ε against $\{\varepsilon_{\mathrm{f}} + K_{\mathrm{Comp}} C_{\mathrm{BL}} \varepsilon_{\mathrm{Comp}} - (1 + K_{\mathrm{Comp}} C_{\mathrm{BL}}) \cdot \varepsilon\}/C_{\mathrm{p}}$ give $K_{\mathrm{Comp}}^{\mathrm{p}}$ and $\varepsilon_{\mathrm{b}}^{\mathrm{Comp}}$. Furthermore, from the above equilibria, the following relationship can be obtained.

$$K_{\mathrm{Comp}} K_{\mathrm{Bind}}^{\mathrm{Comp}} = K_{\mathrm{Bind}} K_{\mathrm{Comp}}^{\mathrm{p}} \tag{14}$$

From eqn (14), the binding constants 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 $\{\varepsilon_{\mathrm{f}} + K_{\mathrm{Comp}} C_{\mathrm{BL}} \varepsilon_{\mathrm{Comp}} - (1 + K_{\mathrm{Comp}} C_{\mathrm{BL}}) \cdot \varepsilon\}/C_{\mathrm{p}}$ were almost linear, as shown in Fig. 4. The $K_{\mathrm{Bind}}^{\mathrm{Comp}}$ values were calculated from the plots in the above manner (Table 3). The $K_{\mathrm{Bind}}^{\mathrm{Comp}}$ values for all the dyes were larger than the corresponding K_{Bind} values at all temperatures. This result suggests that the dye/bolyte complexes possess greater affinity for the polymer than the dyes themselves. If the procedure mentioned above is reasonable, the $K_{\mathrm{Bind}}^{\mathrm{Comp}}$ values should be independent of the bolaform electrolyte concentration, C_{BL}. For AS/DC3-4, m-TS/DC3-4 and m-TS/DC6-4 system, the binding constants of the dye/bolyte complex were not dependent upon C_{BL}, while for the other systems, the $K_{\mathrm{Bind}}^{\mathrm{Comp}}$ values varied with a change in the bolyte con-

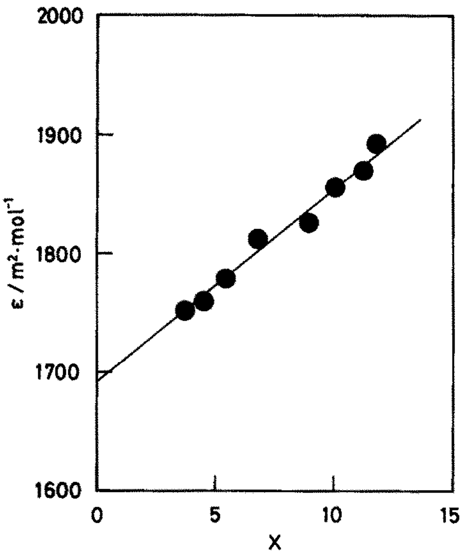


Fig. 4. Plots of ε against X for m-TS in the presence of DC3-4 at 298 K and 487 nm. $X = 10^{-4}\{\varepsilon_f + K_{\mathrm{Comp}}C_{\mathrm{BL}}\varepsilon_{\mathrm{Comp}} - (1 + K_{\mathrm{Comp}}C_{\mathrm{BL}})\cdot\varepsilon\}/C_p$, $C_{\mathrm{BL}} = 6\times10^{-4}$ mol dm^{-3}.

TABLE 3

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

	288 K	*298 K*	*308 K*	*318 K*
AS				
None (K_{Bind})	73·1	59	52	39
DC3-4[a]	111	100	85	39
DC3-4[b]	107	99	86	57
DC6-4[a]	225	222	154	151
DC6-4[b]	115	97	62	55
m-TS				
None (K_{Bind})	120	102	86	62
DC3-4[a]	242	166	134	94
DC3-4[b]	238	217	156	104
DC6-4[a]	330	208	130	108
DC6-4[b]	282	217	162	127
m-FTS				
None (K_{Bind})	68	54	60	47
DC3-4[a]	182	111	97	129
DC3-4[b]	254	139	113	140
DC6-4[a]	322	212	136	36
DC6-4[b]	162	186	73	83

[a] 6·00 × 10^{-4} mol dm^{-3}.

[b] 1·20 × 10^{-3} mol dm^{-3}.

TABLE 4
Thermodynamic Parameters

	$\Delta H_{\mathrm{Bind}}^{\mathrm{Comp}}$ (*kJ mol*$^{-1}$)	$\Delta S_{\mathrm{Bind}}^{\mathrm{Comp}}$ (*J mol*$^{-1}$ *K*$^{-1}$)
AS		
None	$-15{\cdot}3 \pm 1{\cdot}8$ (ΔH_{Bind})	-17 ± 6 (ΔS_{Bind})
DC3-4	-20 ± 7	-30 ± 20
m-TS		
None	-16 ± 2 (ΔH_{Bind})	-16 ± 8 (ΔS_{Bind})
DC3-4	-22 ± 2	-31 ± 8
DC6-4	$-24{\cdot}7 \pm 1{\cdot}6$	-38 ± 5

centration. This result might be attributed to the uncertain values of K_{Bind}, K_{Comp}, ε_{b} and $\varepsilon_{\mathrm{Comp}}$. As described in a previous section, K_{Comp} has large errors, resulting in an uncertain value for $K_{\mathrm{Bind}}^{\mathrm{Comp}}$. Furthermore, as these values are determined by the measurements in the binary systems, they may change in the trinary systems. Therefore the binding constants are discussed only for the systems in which the $K_{\mathrm{Bind}}^{\mathrm{Comp}}$ values at both concentrations are similar.

The ratio $K_{\mathrm{Bind}}^{\mathrm{Comp}}/K_{\mathrm{Bind}}$ is useful in explaining the degree of the enhancement of the binding constants by the bolaform electrolytes. For the AS/DC3-4, m-TS/DC3-4 and m-TS/DC6-4 systems, the ratios are 1·0–1·7, 1·5–2·1 and 1·5–2·8, respectively, suggesting that the binding of m-TS is influenced more by the bolaform electrolytes than the binding of AS. In the case of m-TS, the methylene chain length of the bolytes hardly affects its binding with PVP.

The thermodynamic parameters for the binding, viz. the enthalpy change, $\Delta H_{\mathrm{Bind}}^{\mathrm{Comp}}$, and the entropy change, $\Delta S_{\mathrm{Bind}}^{\mathrm{Comp}}$, are calculated from the temperature dependence of $K_{\mathrm{Bind}}^{\mathrm{Comp}}$. In this calculation, the average values of $K_{\mathrm{Bind}}^{\mathrm{Comp}}$ obtained at different C_{BL} values were used. The thermodynamic parameters thus determined are given in Table 4. As a result, the binding process of the dye/bolyte complexes with PVP was more enthalpic and less entropic than that of the dyes themselves, although the thermodynamic parameters for the AS/DC3-4 complex had very large errors. This result may be attributed to the difference in hydration between the two species, i.e. the dyes themselves and the dye/bolyte complexes.

From the above results, it is concluded that the bolaform electrolytes containing two cationic groups enhance the first binding constants of the sulphonated azo dyes with PVP through the formation of complexes.

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