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Interaction between Water-Soluble Polymers and Azo Dyes Containing Fluorine Atoms. 2. Sulphonated Monoazo Dyes Containing Pentafluoroaniline as a Diazo Component

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ABSTRACT

The interaction between sulphonated monoazo dyes derived from pentafluoroaniline as a diazo component and poly(vinylpyrrolidone) was investigated by means of visible absorption spectrum measurements. To elucidate the effects of the fluorine atoms, the corresponding dyes using aniline as diazo component were also investigated. In the difference absorption spectra for sodium pentafluorophenylazo-2-hydroxy-3,6-naphthalenedisulphonate, no distinct isosbestic point was observed at the ratio of the polymer concentration based on the monomer mol unit to the dye of more than 300 and multiple binding equilibria were apparent. On the other hand, the difference absorption spectra for the solutions with ratio less than 300 showed distinct isosbestic points, resulting in a single equilibrium. Using the first binding constants, the enthalpy change, and the entropy change, the effects of the fluorine atoms of the dye molecules and also of those of cosolutes (NaCl and NaSCN) are discussed.

1 INTRODUCTION

In a previous paper,[1] the interaction between poly(vinylpyrrolidone) (PVP) and sulphonated monoazo dyes containing a trifluoromethyl group at the 3-

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position to the azo linkage was investigated by means of visible absorption spectroscopy. Furthermore, the effects of the trifluoromethyl group attached at the 4-position to the azo group have been studied.[2] The results of these studies elucidated the effects of the fluorine atoms as well as those of the sulphonate groups in the dye molecules.

The aggregation behaviour of dyes containing a trifluoromethyl group has been investigated by means of the visible absorption spectrum and ^{19}F-NMR measurements, the results suggesting that the fluorine atoms have a significant influence on the aggregation behaviour of the dyes in aqueous solutions.[2-5] The aggregation behaviour of the sulphonated monoazo dyes derived from pentafluoroaniline as diazo component have also been studied[6] and it has been found that the effects of the fluorine atoms when attached directly to the benzene ring differ from those of the trifluoromethyl groups.

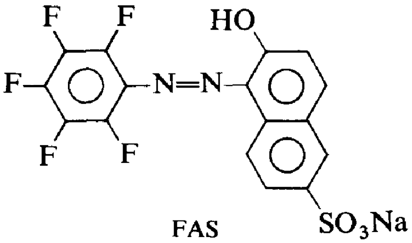
In this present study, the binding of the dyes from pentafluoroaniline as a diazo component with PVP is investigated by visible absorption spectroscopy, and comparisons made with dyes containing a trifluoromethyl group. As in previous studies,[1] the effects of the fluorine atoms as well as of the cosolute species on the interaction are discussed by using the first binding constants and thermodynamic parameters.

2 EXPERIMENTAL

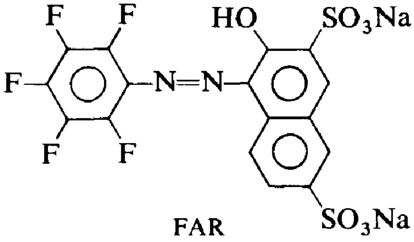
Four sulphonated monoazo dyes were used, viz. sodium salts of 1-pentafluorophenylazo-2-hydroxy-6-naphthalenesulphonic acid (FAS), 1-pentafluorophenylazo-2-hydroxy-3,6-naphthalenedisulphonic acid (FAR), 1-phenylazo-2-hydroxy-6-naphthalenesulphonic acid (AS), and 1-phenylazo-2-hydroxy-3,6-naphthalenedisulphonic acid (AR). The syntheses of FAS and FAR have been previously described.[6] AS (Crocein Orange G) and AR (Ponceau G) were purchased from Tokyo Kasei Co., (Tokyo, Japan) and purified by repeated recrystallization from aqueous ethanol.

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

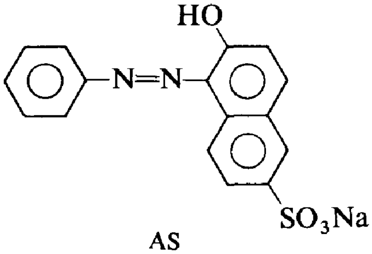
The difference visible absorption spectra of aqueous solutions having various polymer concentrations and a constant dye concentration (FAS: $5{\cdot}13 \times 10^{-5}$, FAR: $4{\cdot}86 \times 10^{-5}$, AS: $3{\cdot}15 \times 10^{-5}$, AR: $3{\cdot}52 \times 10^{-5}$ mol dm^{-3}) with reference to aqueous solutions containing only the dyes were measured using a Hitachi (Tokyo, Japan) 556 double-wavelength double-beam spectrophotometer at 288, 293, 298, and 303 K. The sample solutions in the presence of cosolutes NaSCN and NaCl (0·05 mol dm^{-3}) were similarly investigated.



FAS



FAR



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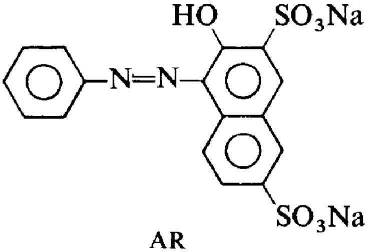

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3 RESULTS AND DISCUSSION

The difference spectra of the aqueous solutions containing FAR and PVP are shown in Fig. 1. At a polymer to dye concentration ratio (P/D) < 300, distinct isosbestic points were observed, while at $P/D > 300$ such isosbestic points were not found, where the polymer concentration is expressed based on monomer units. This suggests that more than one equilibrium exists in the FAR–PVP system. On the other hand, the other dye solutions gave distinct isosbestic points in the P/D region investigated (as shown in Fig. 2), indicating the formation of a single equilibrium. Dye FAR thus behaves anomalously in aqueous PVP solutions and therefore, the following discussion does not include this dye.

Employing the equation used to calculate the binding constants for various polymer and dye systems,[1,2,7-10] we determined the first binding constants, K_{Bind}, from the difference spectra. Denoting ε as the observed extinction coefficient and C_p as the total polymer concentration, the following equation holds:

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

where ε_f and ε_b are the extinction coefficients of the free and bound dye, respectively. This equation includes the assumption that C_p is much more than the bound dye concentration. In all the systems investigated, the above assumption is fulfilled.

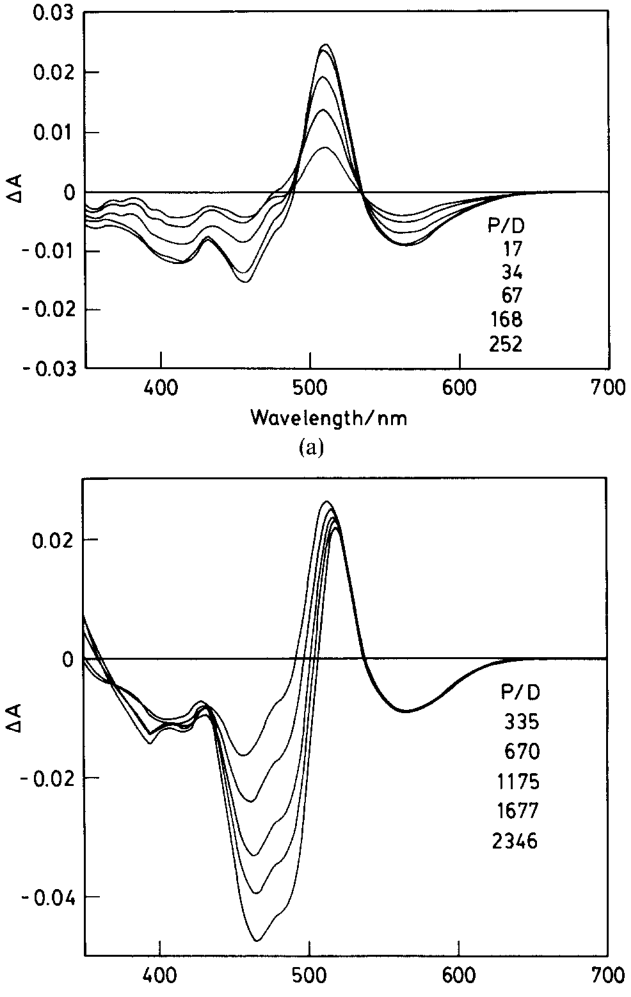

Fig. 1. Difference spectra of FAR ($4{\cdot}86 \times 10^{-5}$ mol dm^{-3}) in aqueous PVP solutions at 298 K. (a) $P/D < 300$; (b) $P/D > 300$. ΔA is the difference between the absorbance of aqueous dye solutions in the absence and presence of the polymer.

The plots of ε against $(\varepsilon_f - \varepsilon)/C_p$ gave good linearity, as shown in Fig. 3, and the first binding constants, K_{Bind}, and the extinction coefficients of the bound dye, ε_b, were calculated from the slope and intercept of the plots, which are given in Tables 1 and 2, respectively. For all the systems, the ε_b values did not change with temperature. The addition of cosolutes caused a small variation in ε_b, but no general tendency was observed for different cosolutes. This might be due to the variation in the microenvironment around the bound dyes.

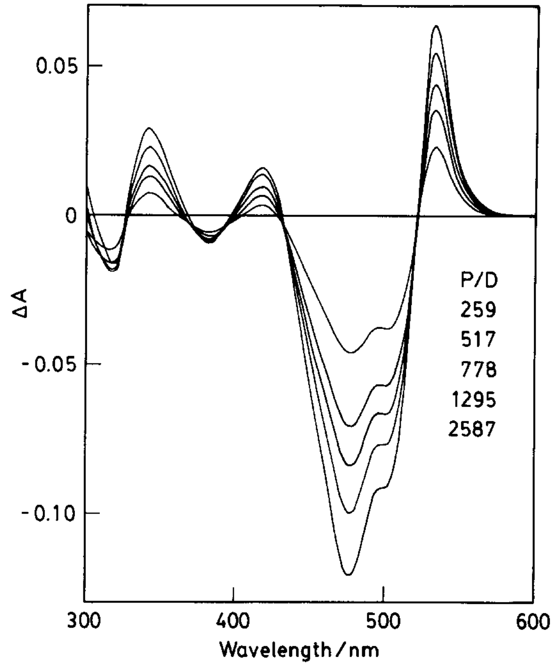

Fig. 2. Difference spectra of AS ($3{\cdot}15 \times 10^{-5}$ mol dm^{-3}) in aqueous PVP solutions at 298 K. ΔA is the difference between the absorbance of aqueous dye solutions in the absence and presence of the polymer.

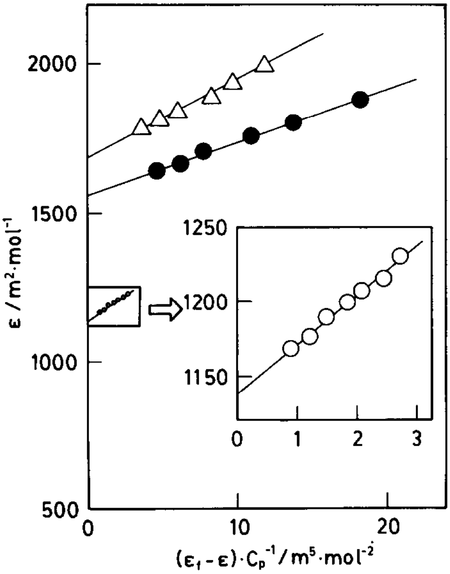

Fig. 3. Plots of ε against $(\varepsilon_f - \varepsilon)/C_p$ at 298 K. ○, FAS (462 nm); ●, AS (477 nm); △, AR (485 nm).

TABLE 1
The First Binding Constants, K_{Bind}

	K_{Bind} ($dm^3\ mol^{-1}$)			
	288 K	*293 K*	*298 K*	*303 K*
FAS				
None	36·6 ± 1·5	33 ± 2	30·2 ± 1·4	27·8 ± 1·7
NaSCN	41 ± 6	32 ± 5	29·7 ± 1·1	19·8 ± 1·1
NaCl	30 ± 3	38 ± 4	44 ± 12	51 ± 8
AS				
None	66·4 ± 1·9	60 ± 3	57·0 ± 1·3	52·2 ± 1·4
NaSCN	62 ± 2	56·6 ± 1·9	49 ± 2	44·6 ± 1·6
NaCl	66·6 ± 1·4	62 ± 3	56·2 ± 1·4	53·3 ± 0·8
AR				
None	44 ± 3	41 ± 2	37·6 ± 1·7	35·4 ± 1·2
NaSCN	30·3 ± 0·9	28·0 ± 0·6	25·9 ± 1·5	23·6 ± 0·9
NaCl	51·9 ± 1·7	49·4 ± 1·6	44·3 ± 0·4	39·3 ± 1·4

The K_{Bind} values for AS were greater than those for FAS in both the absence and presence of the cosolutes. This is consistent with the result that the introduction of a trifluoromethyl group into the dye molecules decreases the K_{Bind} values.[1,2] It is thus concluded that the fluorine atoms of the dyes weaken the binding force between polymer and dye molecules.

Here it is worthwhile to point out the anomalous temperature dependence of K_{Bind} in the case of FAS. For the other dyes, the K_{Bind} values decreased with increasing temperature in the absence and presence of NaSCN or NaCl, whereas only for the FAS–PVP system containing NaCl, K_{Bind} increased with an increase in temperature. To clarify this behaviour, the enthalpy change, ΔH_{Bind}, and the entropy change, ΔS_{Bind}, were calculated from the temperature dependence of K_{Bind} and are given in Table 3. As K_{Bind} is not the intrinsic binding constant but the first binding constant, the ΔS_{Bind} values should be treated as relative ones:[11] it is unreasonable to discuss whether the ΔS_{Bind} values are positive or negative. Both the ΔH_{Bind} and ΔS_{Bind} values for AS and AR hardly changed with the cosolutes, while those for FAS were greatly affected by the cosolutes. This result is explained by hydrophobic interactions as described in our previous paper.[1] Takagishi *et al.* attributed the change of the thermodynamic parameters to the conformational change of PVP caused by the structural change of water in the presence of cosolutes.[12] NaSCN, a water structure-breaker salt,[13] extends the polymer chain[14] and decreases the contribution of hydrophobic interactions, resulting in more negative ΔH_{Bind} and ΔS_{Bind}. This electrolyte thus makes the binding reaction more exothermic and less entropic. On the

TABLE 2
The Extinction Coefficients, ε_b

	ε_b ($m^2\,mol^{-1}$)			
	288 K	*293 K*	*298 K*	*303 K*
FAS (at 462 nm, $\varepsilon_f = 1\,275\ \mathrm{m^2\,mol^{-1}}$)				
None	1 137 ± 2	1 140 ± 3	1 137 ± 3	1 133 ± 4
NaSCN	1 163 ± 7	1 158 ± 9	1 161 ± 2	1 138 ± 5
NaCl	1 141 ± 5	1 149 ± 6	1 163 ± 12	1 161 ± 6
AS (at 477 nm, $\varepsilon_f = 2\,025\ \mathrm{m^2\,mol^{-1}}$)				
None	1 550 ± 5	1 554 ± 9	1 557 ± 5	1 555 ± 6
NaSCN	1 523 ± 7	1 534 ± 7	1 533 ± 11	1 536 ± 8
NaCl	1 586 ± 3	1 593 ± 8	1 582 ± 5	1 569 ± 3
AR (at 485 nm, $\varepsilon_f = 2\,100\ \mathrm{m^2\,mol^{-1}}$)				
None	1 672 ± 12	1 680 ± 11	1 681 ± 10	1 675 ± 7
NaSCN	1 692 ± 7	1 706 ± 4	1 716 ± 12	1 716 ± 9
NaCl	1 735 ± 5	1 744 ± 5	1 745 ± 2	1 743 ± 6

other hand, NaCl, which is a water structure-maker,[13] leads to the opposite result.[14] In the case of the FAS–PVP systems, NaSCN made the binding reaction more exothermic and less entropic, whereas NaCl changed the exothermic into an endothermic reaction and allows the reaction to be more entropic. This result coincides with that explained using hydrophobic interactions, suggesting that the hydrophobic binding is dominant in the FAS–PVP systems.

TABLE 3
The Enthalpy Change ΔH_{Bind} and the Entropy Change ΔS_{Bind}

	ΔH_{Bind} ($kJ\,mol^{-1}$)	ΔS_{Bind} ($J\,mol^{-1}\,K^{-1}$)
FAS		
None	−13·2 ± 0·3	−15·8 ± 0·9
NaSCN	−33 ± 7	−83 ± 22
NaCl	25 ± 2	116 ± 7
AS		
None	−11·2 ± 0·9	−4 ± 3
NaSCN	−16·4 ± 1·1	−23 ± 4
NaCl	−11·1 ± 1·8	−14 ± 6
AR		
None	−10·7 ± 0·5	−5·6 ± 1·5
NaSCN	−12·0 ± 0·5	−13·3 ± 1·6
NaCl	−13·7 ± 1·8	−14 ± 6

4 CONCLUSIONS

In the FAR–PVP system, more than one equilibrium exists, while in the other systems there was a single equilibrium. Furthermore, the FAS–PVP system showed anomalous thermodynamic behaviour, suggesting that hydrophobic interactions play an important role. It is thus concluded that fluorine atoms attached directly to the benzene ring of the dyes greatly affect their binding with PVP.

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