Dyes and Pigments 22 (1993) 151–162

Interaction Between Water-Soluble Polymers and Azo Dyes Containing Fluorine Atoms. Part 3. Positional Effects of Trifluoromethyl Groups on the Interaction

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(Received 1 February 1993; accepted 8 March 1993)

ABSTRACT

The interaction between sulphonated monoazo dyes containing trifluoromethyl groups at various positions to the azo linkage and poly(vinylpyrrolidone) was investigated by means of visible absorption spectrum measurements. The positional effects of the trifluoromethyl groups on the binding of the dyes with poly(vinylpyrrolidone) are discussed using the first binding constants and thermodynamic parameters, and compared with the results for the corresponding dyes containing methyl groups. The results show that the position at which the trifluoromethyl groups are attached to the benzene ring greatly affected the binding behaviour, while such effects could not be observed in the case of the methyl groups. Furthermore, dyes containing one or two trifluoromethyl groups at the meta *position to the azo group gave nonlinear van't Hoff plots, suggesting that the binding behaviour of these two dyes with poly(vinylpyrrolidone) is unusual.*

1 INTRODUCTION

In previous papers,[1-3] the interaction between poly(vinylpyrrolidone) (PVP) and sulphonated monoazo dyes containing a trifluoromethyl group at the *meta* or *para* position to the azo linkage in aqueous solutions was investigated by means of visible absorption spectroscopy and the binding of the azo dyes derived from pentafluoroaniline as a diazo component with

Dyes and Pigments 0143-7208/93/$06·00 © Elsevier Science Publishers Ltd, England. Printed in Great Britain

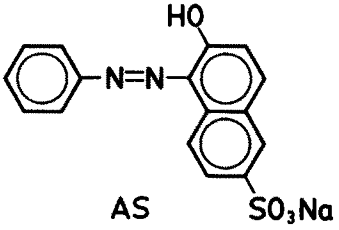
PVP was discussed. The results showed that the introduction of fluorine atoms into dye molecules reduced their binding constants.

The sorption behaviour of sulphonated monoazo dyes containing a trifluoromethyl group by nylon 6 film has also been examined.[4–6] In these studies, the sorption isotherms were interpreted by considering the dual sorption mechanism, which is composed of partition and Langmuir type sorption, and the thermodynamic parameters calculated from the temperature dependence of the intrinsic binding constants for the Langmuir type sorption were discussed in detail. The conclusion was reached that not only the types of substituents, but also their position, greatly affect the sorption behaviour. Recently, the sorption of sulphonated monoazo dyes containing a trifluoromethyl group by silk fibre has also been investigated.[7]

In the present study, the positional effects of a trifluoromethyl group on the interaction between PVP and sulphonated monoazo dyes in aqueous solutions are discussed using the first binding constants determined by means of visible absorption spectroscopy. Additionally, the binding of an azo dye having two trifluoromethyl groups at the *meta* position to the azo linkage with PVP is also investigated and compared with the results for the dyes containing one trifluoromethyl group.

2 EXPERIMENTAL

Nine sulphonated monoazo dyes were used, viz. sodium 1-phenylazo-2-hydroxy-6-naphthalenesulphonate (AS), sodium 1-(2-methylphenylazo)-2-hydroxy-6-naphthalenesulphonate (*o*-TS), sodium 1-(3-methylphenylazo)-2-hydroxy-6-naphthalenesulphonate (*m*-TS), sodium 1-(4-methylphenylazo)-2-hydroxy-6-naphthalenesulphonate (*p*-TS), sodium 1-(3,5-dimethylphenylazo)-2-hydroxy-6-naphthalenesulphonate (BMS), sodium 1-(2-trifluoromethylphenylazo)-2-hydroxy-6-naphthalenesulphonate (*o*-FTS), sodium 1-(3-trifluoromethylphenylazo)-2-hydroxy-6-naphthalenesulphonate (*m*-FTS), sodium 1-(4-trifluoromethylphenylazo)-2-hydroxy-6-naphthalenesulphonate (*p*-FTS) and sodium 1-(3,5-bistrifluoromethylphenylazo)-2-hydroxy-6-naphthalenesulphonate (BFS). AS (Crocein Orange G) was purchased from Tokyo Kasei Co. (Tokyo, Japan) and purified by repeated recrystallization from aqueous ethanol. *o*-TS, *m*-TS, *p*-TS, *o*-FTS, *m*-FTS and *p*-FTS were synthesized as reported in previous papers.[1,2,6,8] BMS and BFS were synthesized by coupling diazotized 3,5-dimethylaniline and 3,5-bistrifluoromethylaniline, respectively, with Schaeffer's acid (2-naphthol-6-sulphonic acid) in alkaline conditions. The dyes thus obtained were purified by repeated salting-out with sodium chloride and recrystallization from 20% aqueous ethanol (BMS) or methanol (BFS). Purity was confirmed by elemental analysis (Calculated for BMS: C, 57·14; H, 4·00; N, 7·40%. Found: C, 58·11; H, 4·11; N, 7·35%. Calculated for BFS as water content = 7·2%: C, 41·25; H, 2·53; N, 5·35; S, 6·1; F, 21·8; Na, 4·4%. Found: C, 41·50; H, 2·25; N, 5·31; S, 6·4; F, 20·0; Na, 4·0%).



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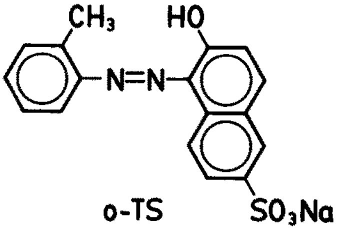
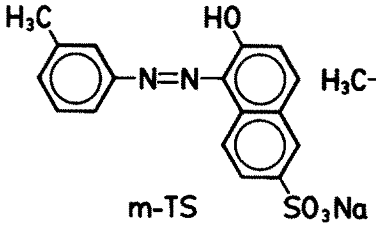


o-TS



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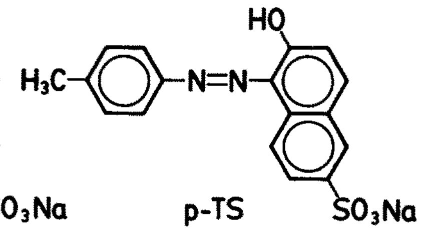

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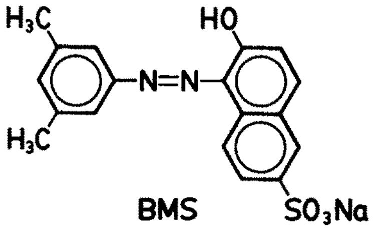

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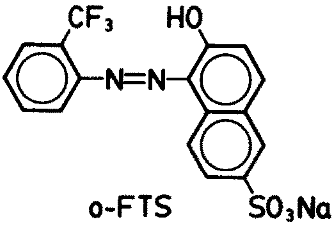
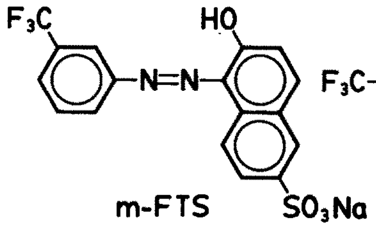


o-FTS



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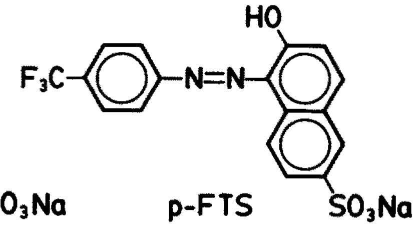
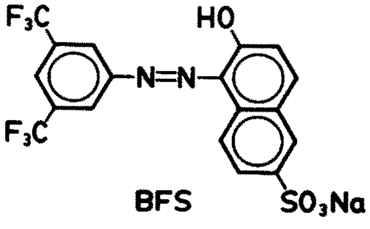


p-FTS



BFS

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

The visible absorption spectra of the aqueous solutions with various polymer concentrations and a constant due 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.

3 RESULTS AND DISCUSSION

The visible absorption spectra of *o*-FTS aqueous solutions in the absence and presence of PVP are shown in Fig. 1. Isosbestic points were defined in the polymer concentration region examined, where the polymer concentration is expressed based on monomer units. Such spectral changes were also observed for all the other dyes. The existence of the isosbestic points makes it possible to assume a single equilibrium in the dye-PVP systems. In previous papers,[1-3] the difference spectra of aqueous dye solutions containing PVP

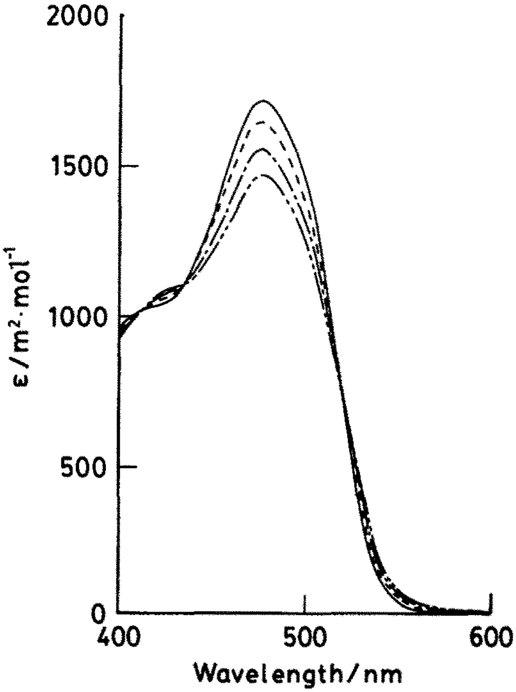


Fig. 1. Visible absorption spectra of *o*-FTS aqueous solutions in the absence and presence of PVP at 298 K. PVP concentrations: (———) 0; (- - - - -) 0·002; (— - —) 0·007; (— · · —) 0·02 mol dm^{-3}.

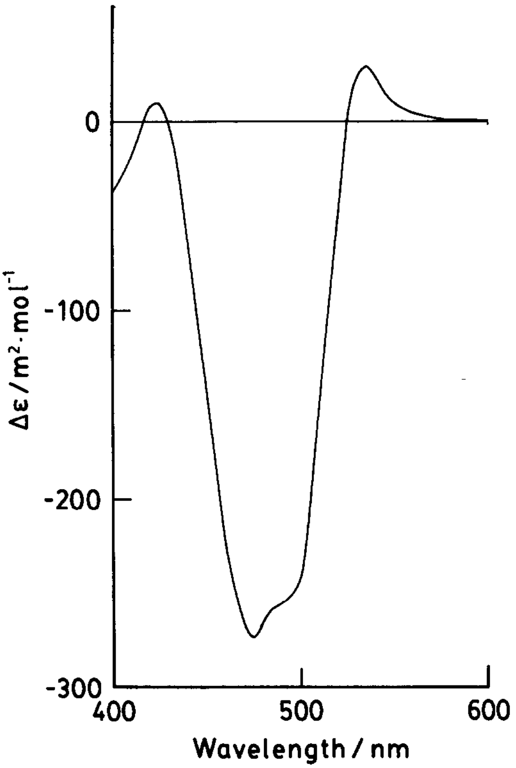


Fig. 2. Difference absorption spectrum of *o*-FTS aqueous solution between the absence and presence of PVP at 298 K. PVP concentration, 0·02 mol dm^{-3}.

were recorded. Since the aqueous dye solutions with a constant concentration are used as reference to measure the difference spectra, the dye concentration is liable to change for prolonged measurement at higher temperature owing to evaporation of water. Therefore, in the present study, the visible absorption spectra of the aqueous dye solutions in the absence and presence of PVP were individually recorded and the difference spectra were computed from the difference between the two spectra (Fig. 2).

To analyze the spectral change with the polymer concentration, 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. 3. Employing the equation used to calculate the binding constants for PVP and dye systems in previous papers,[1-3] the first binding constants, K_{Bind}, from the change of ε were determined:

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

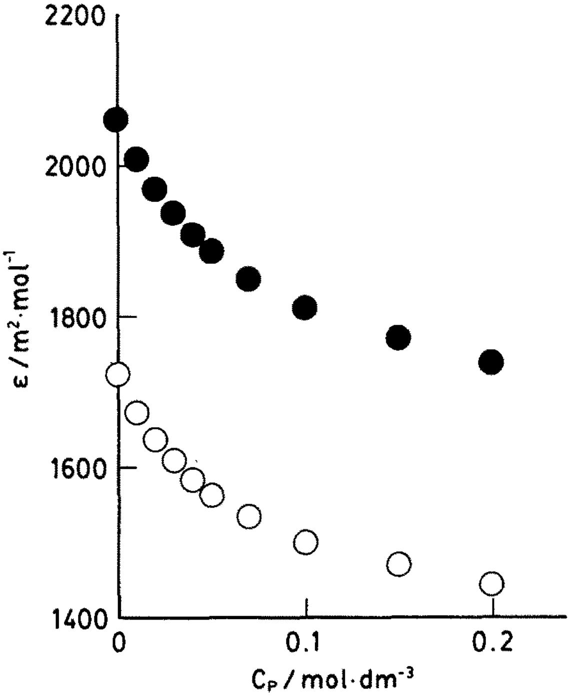


Fig. 3. Dependence of the extinction coefficients on the polymer concentration at 298 K. (●) *o*-TS (481 nm); (○) *o*-FTS (476 nm).

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

The plots of ε against $(\varepsilon_f - \varepsilon)/C_P$ gave good linearity with correlation coefficient above 0·99, as shown in Fig. 4, for all the dyes except *m*-FTS and BFS. The linear plots for *m*-FTS and BFS had large errors, so that more than one measurement was carried out and the average values of the binding constants were estimated (Table 1). The first binding constants, K_{Bind}, for AS, *o*-TS, *m*-TS, *p*-TS, BMS, *o*-FTS and *p*-FTS are given in Table 2. The K_{Bind} values for AS, *m*-TS, *p*-TS, *m*-FTS and *p*-FTS were different from those reported in previous papers.[1-3] The reasons for the discrepancy are thought to be as follows. First, in this present study, the polymer was dissolved with the aqueous dye solution of a constant concentration to prepare the stock solution, and the aqueous solutions with various polymer concentrations and a constant dye concentration were prepared by diluting the stock solution with the aqueous dye solution. On the other hand, in the authors' studies,[1-3] the aqueous dye and polymer solution were prepared by

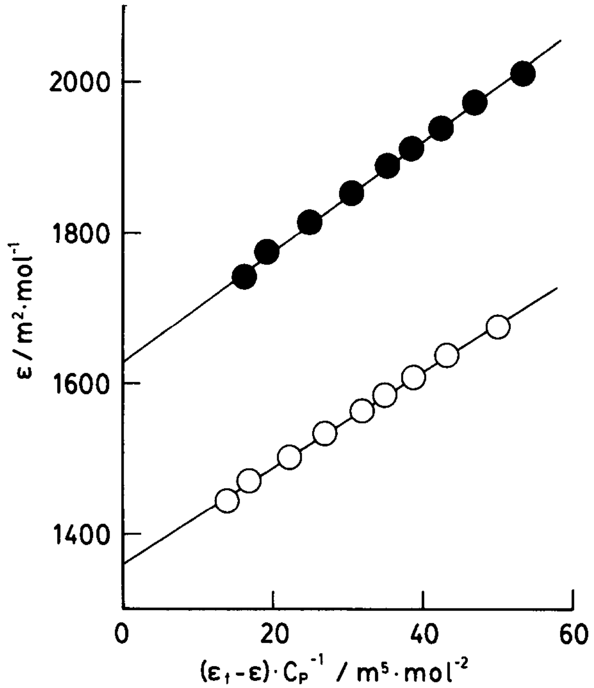


Fig. 4. Plots of ε against $(\varepsilon_f - \varepsilon)/C_P$ at 298 K. (●) *o*-TS (481 nm); (○) *o*-FTS (476 nm).

TABLE 1
The First Binding Constants, K_{Bind} (dm^3 mol^{-1}), for *m*-FTS and BFS

	Run 1	*Run 2*	*Run 3*	*Average*
m-*FTS*				
288 K	82 ± 5	80 ± 5	—	81 ± 5
293 K	68 ± 3	67 ± 5	—	68 ± 4
298 K	68 ± 3	63 ± 6	—	66 ± 5
303 K	58 ± 2	53 ± 4	—	56 ± 3
308 K	54 ± 4	57 ± 11	—	56 ± 8
313 K	58 ± 4	50 ± 3	—	54 ± 4
318 K	60 ± 4	52 ± 6	—	56 ± 5
BFS				
288 K	31 ± 4	27 ± 3	27 ± 6	28 ± 4
293 K	—	24·2 ± 1·0	25 ± 4	25 ± 3
298 K	19 ± 3	18 ± 2	24 ± 2	20 ± 2
303 K	—	17 ± 2	17·3 ± 1·4	17·2 ± 1·7
308 K	17·5 ± 4	19·0 ± 0·3	16·7 ± 0·9	17·7 ± 0·8
313 K	—	19·4 ± 1·5	17·7 ± 0·9	18·6 ± 1·2
318 K	20 ± 2	19·8 ± 1·6	14·5 ± 0·2	18·1 ± 1·3

TABLE 2
The First Binding Constants, K_{Bind} ($dm^3 mol^{-1}$), for AS, *o*-TS, *m*-TS, *p*-TS, BMS, *o*-FTS and *p*-FTS

	288 K	*298 K*	*308 K*	*318 K*
AS	73·8 ± 1·0	63 ± 2	53·6 ± 1·1	46·5 ± 0·7
o-TS	172 ± 4	136 ± 2	101 ± 3	82 ± 6
m-TS	130 ± 4	104 ± 2	81 ± 2	64 ± 4
p-TS	122 ± 2	96·2 ± 1·6	79·3 ± 1·6	63·1 ± 0·5
BMS	268 ± 3	201 ± 4	145 ± 3	119·8 ± 1·8
o-FTS	212 ± 4	157 ± 2	127 ± 2	98 ± 5
p-FTS	37·1 ± 1·6	33·6 ± 1·7	28·7 ± 1·0	27·2 ± 9·8

combining a constant volume of the aqueous dye solution and various volumes of the polymer solution, and water was added to fix the total volume. Thus, the present procedure keeps the dye concentration more constant and has less errors. The other reason is that the absorbance of PVP was considered. The isosbestic points of the difference spectra reported in previous papers[1-3] did not lie on $\Delta A = 0$. This is due to the absorbance of the polymer. Consideration of this absorbance leads to more accurate results and for the above two reasons, it is concluded that the first binding constants obtained in the present study have higher accuracy.

The K_{Bind} values for *o*-TS, *m*-TS, *p*-TS and BMS were larger than those for

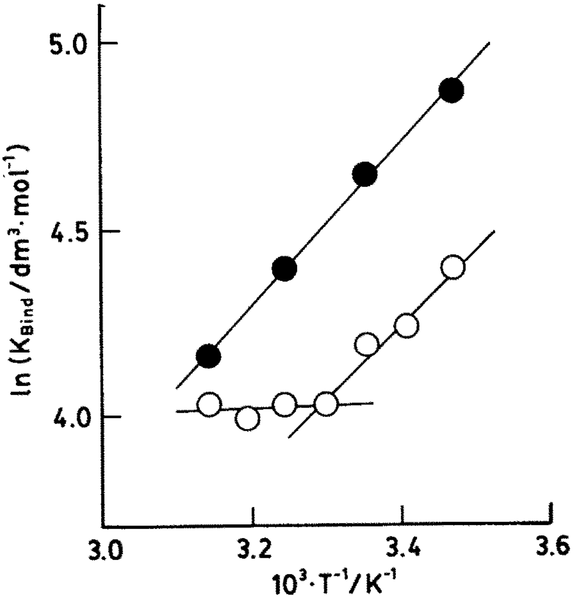


Fig. 5. Van't Hoff plots of K_{Bind}. (●) *m*-TS; (○) *m*-FTS.

AS at all the temperatures, suggesting that the introduction of methyl groups into the dye increases the binding constants, irrespective of the position and number of the methyl groups. On the other hand, the effects of trifluoromethyl groups on the K_{Bind} values were dependent on their position and number. The first binding constants for the dye containing a trifluoromethyl group at the *ortho* position to the azo linkage, *o*-FTS, were much greater than those for AS. The K_{Bind} values for *m*-FTS were a little larger than those for AS, whereas the dye having two trifluoromethyl groups at the *meta* position, BFS, gave much smaller values than AS. In the case of *p*-FTS, much smaller K_{Bind} values were also obtained. It is very difficult to explain such complicated effects of the trifluoromethyl groups, and so the manner how the trifluoromethyl groups affect the binding behaviour is not clear.

In further studies, the thermodynamic parameters for the binding, viz. the enthalpy change, ΔK_{Bind}, and the entropy change, ΔS_{Bind}, were determined from van't Hoff plots. The van't Hoff plots (the plots of ln K_{Bind} against $1/T$, where T is the absolute temperature) are shown in Figs 5 and 6. Here it is

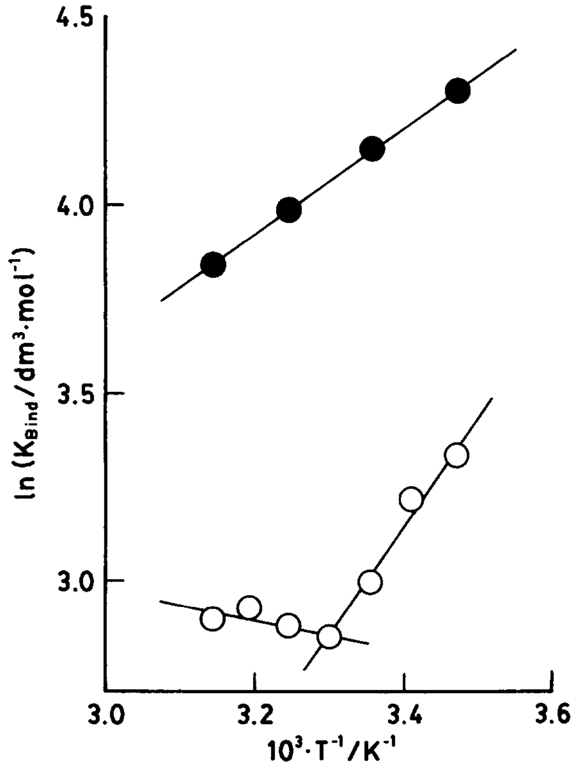


Fig. 6. Van't Hoff plots of K_{Bind}. (●) AS; (○) BFS.

worthwhile to point out the nonlinear van't Hoff plots for *m*-FTS and BFS: the plots for all the other dyes, except the dyes containing one or two trifluoromethyl groups at the *meta* position to the azo linkage lay on a straight line, while those for *m*-FTS and BFS were concave upward, or divided into the linear parts with a crossover point around 303 K. In a previous paper,[1] only the first binding constants for *m*-FTS below 303 K were estimated, so that the peculiar temperature dependence of K_{Bind} could not be observed. The peculiar temperature dependence on the binding of azo dyes with polymers has been previously reported, e.g. van't Hoff plots for butyl orange-bovine serum albumin,[9] pentyl orange-crosslinked poly(vinylpyrrolidone)[10] and butyl orange-2-hydroxyethylmethylate-*N*-vinyl-2-pyrrolidone copolymers[11] gave a bell-shaped curve. However, the curve is concave downward, having the opposite concave direction to those given in Figs 5 and 6. Furthermore, such a bell-shaped curve is not observed for poly(vinylpyrrolidone) itself, but for the modified poly(vinylpyrrolidone)s. Thus, the anomalous thermodynamic behaviour observed in the present study is the first case found for the binding of dyes with PVP itself.

The unusual temperature dependence, i.e. decrease of the enthalpy change from positive to negative with increasing temperature has been explained[9-11] in terms of the balance of energetic and hydrophobic interaction; the hydrophobicity of the dyes and polymers contributes to the enthalpy change. On the basis of this explanation, the thermodynamic behaviour for the binding of *m*-FTS and BFS with PVP might be concerned with hydrophobic interaction, i.e. hydration around the dye molecules.

The thermodynamic parameters obtained are given in Table 3. The values for *m*-FTS and BFS were calculated by assuming that their van't Hoff plots can be divided into two linear parts, with a crossover point around 303 K. To make sure that the hydrophobic interaction is concerned with the binding of the dyes with PVP, the compensation relationship[12,13] between ΔH_{Bind} and ΔS_{Bind} (Fig. 7) is useful. The plots of ΔH_{Bind} against ΔS_{Bind} lay on a straight line for all the dyes except *m*-FTS and BFS, giving 410 ± 30 K as compensation temperature. This fact might suggest that the binding processes for *m*-FTS and BFS are different from those for the other dyes, but the assumption to determine the thermodynamic parameters for *m*-FTS and BFS makes the suggestion ambiguous.

In addition, *m*-FTS and BFS formed polyaggregates and their aqueous solutions at higher concentration became gelatinous.[8,14] Such polyaggregation could not be observed for the other dyes. This result might also be related to the unusual binding behaviour of *m*-FTS and BFS with PVP.

From the above results, it is concluded that the position and number of the trifluoromethyl groups greatly influences the binding behaviour of the azo dyes with PVP.

TABLE 3

The Thermodynamic Parameters

	ΔH_{Bind} ($kJ\,mol^{-1}$)	ΔS_{Bind} ($J\,mol^{-1}\,K^{-1}$)
AS	−11·80±0·14	−5·2±0·5
o-TS	−19·2±0·8	−24±3
m-TS	−18·1±0·6	−22·2±1·9
p-TS	−16·5±0·5	−17·5±1·6
BMS	−20·9±1·2	−26±4
o-FTS	−19·3±0·7	−22±2
m-FTS		
LT region	−17±3	−21±10
HT region	−0·6±1·5	31±5
p-FTS	−8·3±1·0	1±3
BFS		
LT region	−24±2	−57±7
HT region	−3·3±1·8	35±6

LT, Low temperature; HT, high temperature.

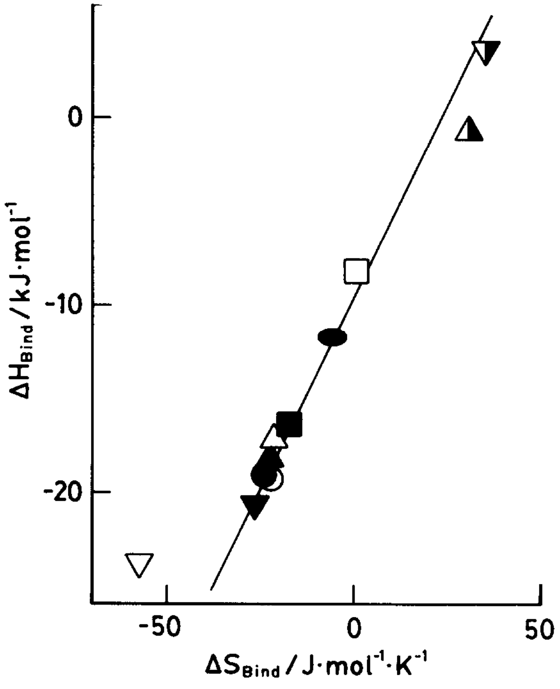


Fig. 7. Compensation relationship between ΔH_{Bind} and ΔS_{Bind}. (●) AS; (●) *o*-TS; (▲) *m*-TS; (■) *p*-TS; (▼) BMS; (○) *o*-FTS; (△) *m*FTS (low temperature region); (▲) *m*-FTS (high temperature region; (□) *p*-FTS; (▽) BFS (low temperature region); (▼) BFS (high temperature region).

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