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Interaction Between Water-soluble Polymers and Azo Dyes Containing Fluorine Atoms. Part 4. Comparison with Azo Dyes having Different Chain Length of Alkyl Groups

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ABSTRACT

The interaction between sulphonated monoazo dyes having different chain length of alkyl groups and poly(vinylpyrrolidone) was investigated by means of visible absorption spectrum measurements, and compared with the results for sulphonated monoazo dyes containing fluorine atoms. The first binding constants increased with an increase in the alkyl chain length induced into the dyes. The first binding constants for dyes carrying branched chains were affected only by the carbon number in their main chains. The thermodynamic parameters for the binding processes changed with the alkyl chain length in an opposite manner to those reported for Methyl Orange derivatives. This is explained in terms of the accessibility of the alkyl groups in the dyes to the polymer chains. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: Azo dye, poly(vinylpyrrolidone), interaction, binding, fluorine, visible absorption spectroscopy.

INTRODUCTION

In previous papers [1–4], the interaction between poly(vinylpyrrolidone) (PVP) and derivatives of sodium 1-phenylazo-2-hydroxy-6-naphthalenesulphonate was investigated by means of visible absorption spectroscopy. As a

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result, the introduction of trifluoromethyl groups into the dye was found to influence the binding behavior with PVP. Particularly, the position and number of the trifluoromethyl groups greatly changed the first binding constants of the azo dyes with PVP [4].

On the other hand, the binding behavior of dye/bolaform electrolyte complexes with PVP have been studied by means of visible absorption spectroscopy [5–8]. The dye/bolaform electrolyte complexes had alkyl groups with different chain length, which affected their binding behavior.

Additionally, sodium 4-(4-dialkylaminopheylazo)-1-benzenesulphonate (methyl orange homologues) and PVP have been studied [9–11] and the results explained from the standpoint of hydrophobic interaction; longer alkyl chains make a relatively larger contribution to the hydrophobic interaction between the dyes and PVP.

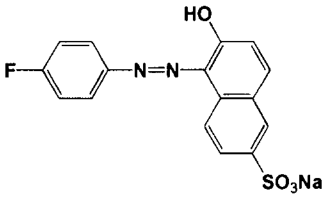
In this context, ethyl, n-propyl, iso-propyl, n-butyl, sec-butyl, and tert-butyl groups were introduced into sodium 1-phenylazo-2-hydroxy-6-naphthalenesulphonate, whose binding with PVP was investigated by means of visible absorption spectroscopy. The effects of the substituents are discussed using the first binding constants and the thermodynamic parameters for the binding processes, and compared with those of fluorine atoms.

EXPERIMENTAL

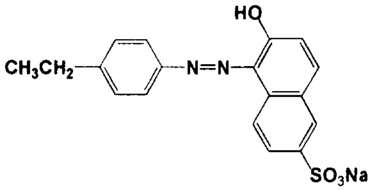
Seven sulphonated monoazo dyes were used, viz. sodium 1-(4-fluorophenylazo)-2-hydroxy-6-naphthalenesulphonate (*p*-FAS), sodium 1-(4-ethylphenylazo)-2-hydroxy-6-naphthalenesulphonate (*p*-EAS), sodium 1-(4-*n*-propylphenylazo)-2-hydroxy-6-naphthalenesulphonate (*p*-*n*-PAS), sodium 1-(4-*iso*-propylphenylazo)-2-hydroxy-6-naphthalenesulphonate (*p*-*iso*-PAS), sodium 1-(4-*n*-butylphenylazo)-2-hydroxy-6-naphthalenesulphonate (*p*-*n*-BAS), sodium 1-(4-*sec*-butylphenylazo)-2-hydroxy-6-naphthalenesulphonate (*p*-*sec*-BAS), and sodium 1-(4-*tert*-butylphenylazo)-2-hydroxy-6-naphthalenesulphonate (*p*-*tert*-BAS). All the dyes were synthesized by coupling the corresponding diazotized aniline derivatives with Schaeffers acid (2-naphthol-6-sulphonic acid) in alkaline conditions. The dyes thus obtained were purified by repeated salting-out with sodium acetate and recrystallization from 80 % aqueous methanol (*p*-FAS) or washing with ethanol (*p*-EAS, *p*-*n*-PAS, *p*-*iso*-PAS, *p*-*n*-BAS, *p*-*sec*-BAS, and *p*-*tert*-BAS). Their purity was confirmed by elemental analysis (Table 1).

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

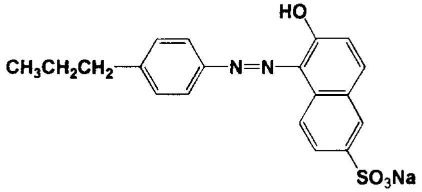
The visible absorption spectra of the aqueous solutions with various polymer concentrations and a constant dye concentration (3.00×10^{-5} mol dm^{-3})



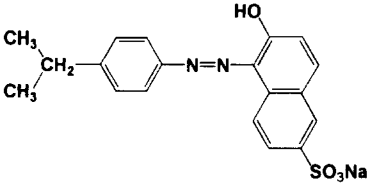
p-FAS



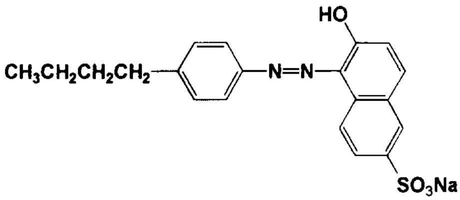
p-EAS



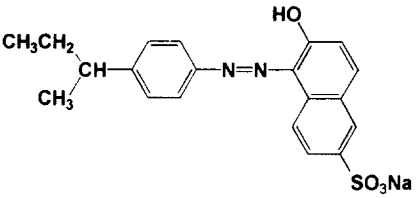
p-n-PAS



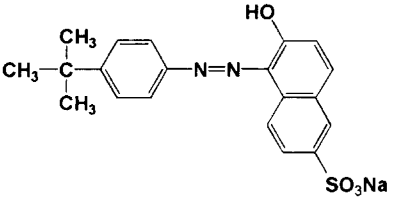
p-iso-PAS



p-n-BAS



p-sec-BAS



p-tert-BAS

were recorded using a Shimadzu UV-3100 spectrophotometer together with a Shimadzu SPR-5 temperature controller.

RESULTS AND DISCUSSION

For all the dyes investigated, similar spectral changes to those previously reported [4] were observed with increasing polymer concentration. To analyze the spectral change with polymer concentration, the extinction coefficients, ε, at an appropriate wavelength were used. For *p*-EAS, the extinction

TABLE 1
Elemental Analysis of the Dyes

	Water content (%)		*C (%)*	*H (%)*	*N (%)*	*S (%)*	*F (%)*	*Na (%)*
p-FAS	Calculated	0	52.18	2.74	7.61	8.7	5.2	6.2
	Found		51.66	2.76	7.69	8.0	4.7	6.1
p-EAS	Calculated	0	57.14	4.00	7.40	8.5		6.1
	Found		57.44	4.02	7.59	8.4		5.8
p-*n*-PAS	Calculated	0	58.16	4.37	7.14			
	Found		58.39	4.55	7.13			
p-*iso*-PAS	Calculated	4.0	55.83	4.64	6.85			
	Found		58.90	4.89	6.84			
p-*n*-BAS	Calculated	0	59.10	4.71	6.89			
	Found		58.90	4.89	6.84			
p-*sec*-BAS	Calculated	3.3	57.15	4.92	6.66			
	Found		56.72	5.19	6.72			
p-*tert*-BAS	Calculated	4.7	56.33	5.01	6.57			
	Found		56.64	5.49	6.53			

coefficients at 486 nm decreased with increasing polymer concentration based on the monomer unit (C_P), while those at 545 nm showed the opposite behavior, as shown in Fig. 1. For all the other dyes, similar changes were observed.

Two kinds of equations were employed to calculate the first binding constants, K_{Bind}, from the change of ε. One was the equation derived on the

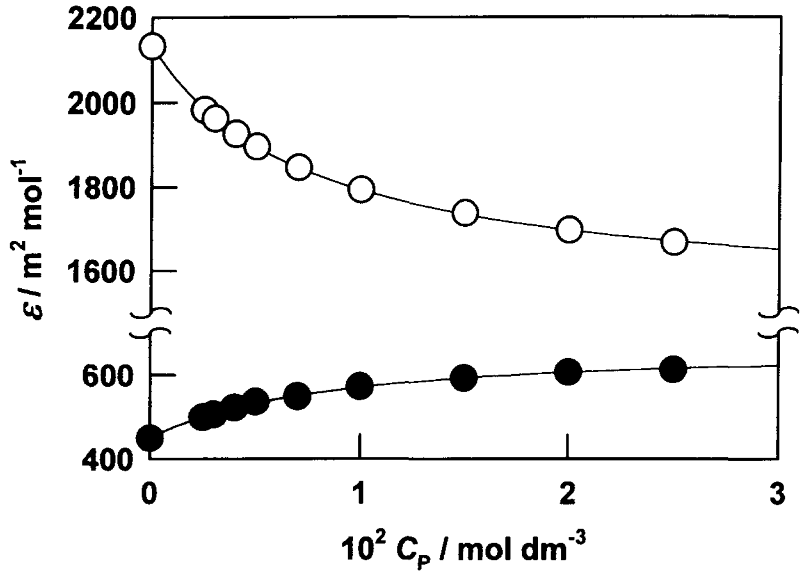


Fig. 1. Relationship between extinction coefficients and polymer concentration for *p*-EAS at 298 K. (*) 486 nm; (•) 545 nm.

assumption that C_P is much greater than the bound dye concentration, which was used to calculate the first binding constants of dyes with PVP in the previous studies [1–4];

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

in which ε_f and ε_b are the extinction coefficients of the free and bound dye, respectively.

Linear plots of ε against $(\varepsilon - \varepsilon_f)/C_P$ gave the first binding constants, K_{Bind} (Fig. 2). The other equation was similar to that derived for the determination of the equilibrium constants between dyes and bolytes, and K_{Bind} and ε_b were calculated using the nonlinear least-squares method [5–8]:

$$\varepsilon = \varepsilon_f + \frac{\varepsilon_b - \varepsilon_f}{2C_0} \cdot \left\{ A - \left(A^2 - 4C_0C_P \right)^{1/2} \right\} \tag{2}$$

where C_0 is the total dye concentration and $A = C_0 + C_P + 1/K_{Bind}$. The solid lines in Fig. 3 express the fitting curve calculated using K_{Bind} and ε_b obtained above and show good agreement with the observed values.

The K_{Bind} values for *p*-EAS determined using the above two equations at 486 and 545 nm are given in Table 2. They were not dependent on the

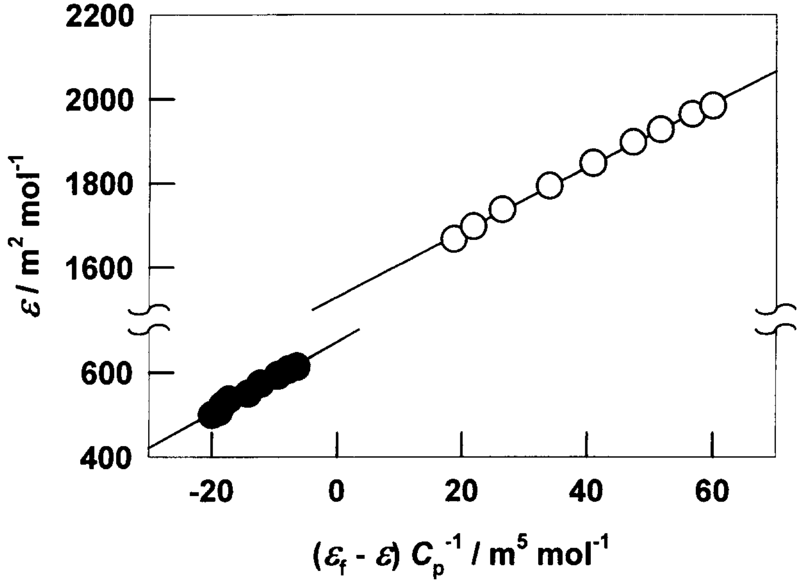


Fig. 2. Plots of ε against $(\varepsilon_f - \varepsilon)/C_P$ at 298 K. (○) 486 nm; (●) 545 nm.

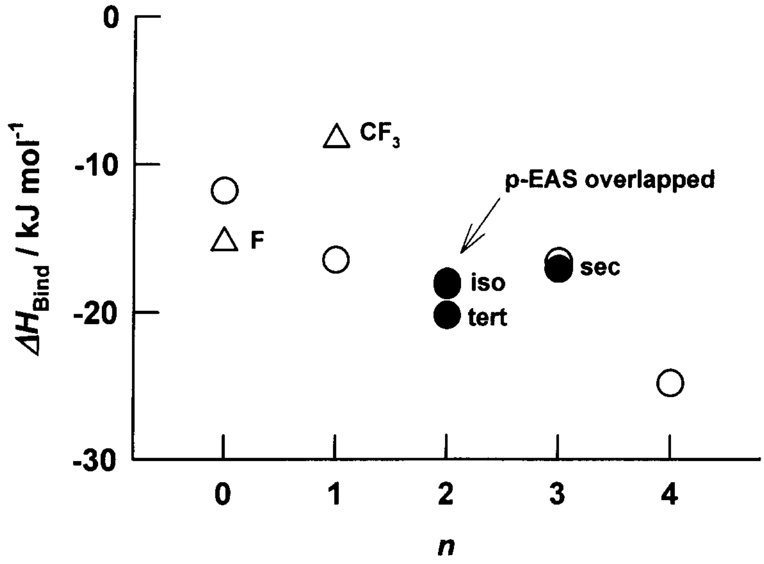


Fig. 3. Dependence of the enthalpy change for the binding of the dyes with PVP on the number of carbon atoms in the main chains of the alkyl groups of the dyes, *n*.

TABLE 2

The First Binding Constants, K_{Bind} (dm^3 mol^{-1}), for *p*-EAS at 298 K

	486 nm	*545 nm*
Equation (1)	130.7 ± 1.7	120 ± 6
Equation (2)	128	124

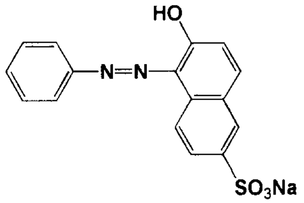
determination procedures and wavelengths, suggesting that a single equilibrium exists and the assumption included in eqn (1) ($C_P \gg C_b$) is fulfilled. Similar results were obtained for all the other dyes. Therefore, the K_{Bind} values were calculated from the change of the extinction coefficients (ε), at the wavelength where the largest difference was observed with the polymer concentration using eqn (1).

The first binding constants, (K_{Bind}), thus obtained are given in Table 3. As was pointed out in a previous paper [4], the way in which the trifluoromethyl groups affect the binding behavior depends on their position and number in the dyes. However, one can demonstrate that the introduction of a fluorine atom and a trifluoromethyl group into the dye at the *para* position to the azo linkage markedly reduced the K_{Bind} values. On the other hand, the K_{Bind} values for the dyes containing alkyl groups were much larger than that for sodium 1-(4-phenylazo)-2-hydroxy-6-naphthalenesulphonate (AS) and they increased with increasing alkyl chain length. Such enhancement was also observed in the case of methyl orange homologues [9]. This suggests that

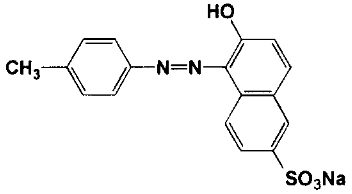
TABLE 3
The First Binding Constants, K_{Bind} ($\mathrm{dm^3\ mol^{-1}}$)

	288 K	*298* K	*308* K	*318* K
AS[a]	73.8 ± 1.0	63 ± 2	53.6 ± 1.1	46.5 ± 0.7
p-FAS	57.1 ± 1.2	47.6 ± 1.2	39.3 ± 0.9	31.1 ± 0.8
p-TS[a]	122 ± 2	96.2 ± 1.6	79.3 ± 1.6	63.1 ± 0.5
p-FTS[a]	37.1 ± 1.6	33.6 ± 1.7	28.7 ± 1.0	27.2 ± 0.8
p-EAS	166 ± 3	130.7 ± 1.7	101.6 ± 1.4	82 ± 2
p-*n*-PAS	244 ± 6	190 ± 3	153 ± 6	127 ± 4
p-*iso*-PAS	190 ± 3	160 ± 3	121 ± 3	94 ± 4
p-*n*-BAS	460 ± 30	326 ± 17	238 ± 9	173 ± 9
p-*sec*-BAS	256 ± 8	200 ± 5	162 ± 7	130 ± 6
p-*tert*-BAS	221 ± 7	167 ± 3	131 ± 6	99 ± 6

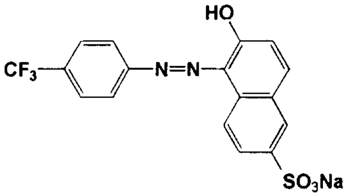
[a] Ref. 4.



AS



p-TS



p-FTS

longer alkyl chains make the affinity higher. Furthermore, the chain branching reduced the first binding constants; the K_{Bind} values decreased in the order of *p*-*n*-PAS > *p*-*iso*-PAS or *p*-*n*-BAS > *p*-*sec*-BAS > *p*-*tert*-BAS. The carbon number in the main chains of the alkyl groups is designated as n: $n = 0$ for AS and *p*-FAS; $n = 1$ for *p*-TS and *p*-FTS; $n = 2$ for *p*-EAS, *p*-*iso*-PAS, and *p*-*tert*-BAS; $n = 3$ for *p*-*n*-PAS and *p*-*sec*-BAS; $n = 4$ for *p*-*n*-BAS. The first binding constants increased with an increase in n, suggesting that the main chain length affects the binding behavior.

For further discussion, the thermodynamic parameters for the binding, viz. the enthalpy change, ΔH_{Bind}, and the entropy change, ΔS_{Bind}, were determined from the temperature dependence of K_{Bind} (Table 4). The ΔH_{Bind} values for all the dyes were negative, showing that the binding processes are exothermic. The longer alkyl group makes the process more exothermic.

TABLE 4
Thermodynamic Parameters

	$\Delta H_{Bind}/kJ\ mol^{-1}$	$\Delta S_{Bind}/J\ mol^{-1}K^{-1}$
AS[a]	−11.80 ± 0.14	−5.2 ± 0.5
p-FAS	−15.3 ± 1.0	1 ± 3
p-TS[a]	−16.5 ± 0.5	−17.5 ± 1.6
p-FTS[a]	−8.3 ± 1.0	−19 ± 3
p-EAS	−18.0 ± 0.3	−20.1 ± 1.0
p-*n*-PAS	−16.6 ± 0.4	−12.0 ± 1.4
p-*iso*-PAS	−18.2 ± 1.5	−19 ± 5
p-*n*-BAS	−24.8 ± 0.3	−34.9 ± 0.9
p-*sec*-BAS	−17.1 ± 0.2	−13.3 ± 0.8
p-*tert*-BAS	−20.2 ± 0.6	−25.2 ± 1.9

[a] Ref. 4.

Furthermore, the ΔS_{Bind} values decreased with increasing alkyl chain length. The plot of ΔH_{Bind} against the carbon number in the main chains of the alkyl groups, (n), designated in the previous section is shown in Fig. 3. This figure suggests that the absolute values of ΔH_{Bind} increase with an increase in n. Thus the main chain length play an important role in the binding.

The dependence of the thermodynamic parameters on the alkyl chain length obtained in the present study is opposite to that for methyl orange homologues [9]: the longer alkyl chains in methyl orange homologues allows ΔH_{Bind} and ΔS_{Bind} to become less negative and more positive, respectively. Such dependence of the thermodynamic parameters on the alkyl chain length observed for methyl orange homologues is due to the increased attribution of hydrophobic interaction between the longer alkyl chains and PVP. The discrepancy between two dye series in the thermodynamic parameters might arrive from the difference in the manner of the interaction between the dyes and PVP, as shown in Fig. 4. The pyrrolidine rings of PVP can be protonated in aqueous solutions, as shown in Scheme 1 [9].

Therefore, the anionic sulphonate groups of the dyes may bind with positively charged pyrrolidine rings. It is also possible for the amino and hydroxyl groups of the dyes to interact with the pyrrolidine groups through hydrogen bonding. If hydrogen bonding occurs, the alkyl chains in methyl orange derivatives are accessible by the polymer chains [Fig. 4(a)]. This fact induces hydrophobic interaction. On the other hand, the alkyl chains in the dyes used in the present study are not accessible by the PVP chains, despite the hydrogen bonding between the hydroxyl group and the pyrrolidine ring [Fig. 4(b)]. Consequently, the hydrophobic interaction cannot play an important role.

From the above results, it is concluded that not only the chain length of the alkyl groups but also their relative position to the functional groups

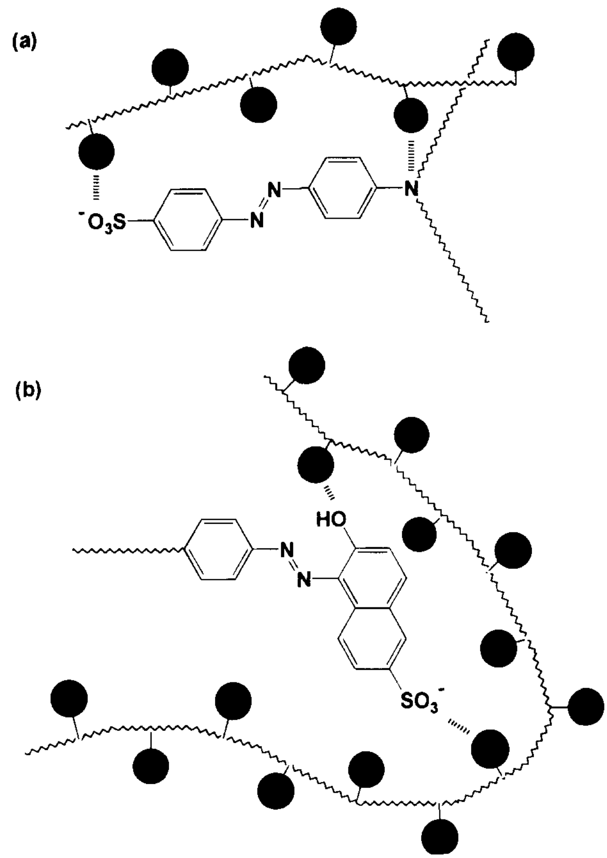
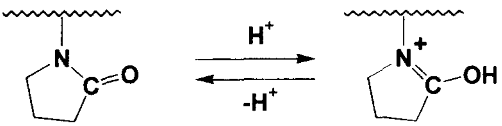


Fig. 4. Schematic illustration of the interaction between dyes and PVP.



Scheme 1.

forming hydrogen bonds is one of the most important factors affecting the thermodynamic parameters for the binding of the dyes with PVP.

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