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Sorption Behaviour of Fluorinated Azo Sulphonated Dyes by Silk Fibre

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ABSTRACT

The sorption behaviour of sodium 1-phenylazo-2-hydroxy-6-naphthalenesulphonate and its derivatives containing a trifluoromethyl or methyl group by silk fibre under acidic conditions was investigated. For all the dyes, the equilibrium sorption was established after the silk fibre was immersed in the aqueous dye solutions for 24 h. The sorption isotherms obtained were explained on the basis of the single Langmuir type sorption mechanism or the dual sorption mechanism formulated by the sum of Langmuir and partition type sorption. The number of binding sites for Langmuir type sorption was consistent with the content of amino groups in the silk fibre, indicating the stoichiometric binding of the anionic dyes with the positively charged amino groups. The thermodynamic parameters calculated from the temperature dependence of the intrinsic binding constants for Langmuir type sorption were greatly affected by the introduction of a trifluoromethyl or methyl group into the dye molecule. On the basis of these results, the effects of the substituents are discussed.

1 INTRODUCTION

Sorption and diffusion are a matter of interest in various research fields such as polymer chemistry, surface science, biochemistry, and dyeing chemistry; the sorption and diffusion of dyes in various fibres and films have been investigated extensively.

Silk is one of the most important fibres, and many studies on the sorption behaviour of dyes by silk fibres have been reported. Not only the analysis of the sorption isotherms,[1,2] but also the elucidation of mixture dyeing with acid dyes[3,4] has been reported. The effects of silk and dye structure have been also investigated.[5-7] Recently, a study on the thermodynamic affinity determined by using the Gilbert–Rideal model has been reported.[8]

We have also investigated various behaviours of fluorinated azo sulphonated dyes in aqueous solution, e.g. aggregation,[9-12] binding with a water-soluble polymer,[12,13] and sorption by nylon 6 film.[14,15] As a result, the interesting effects of fluorine atoms were apparent. In particular, for sorption by nylon 6 film, the influence of the orientation, as well as the type of substituent (trifluoromethyl or methyl group) was elucidated.

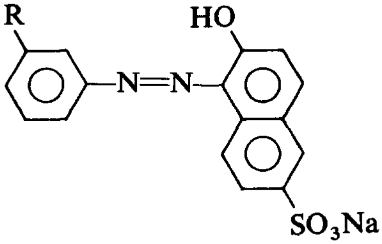
In this context, the sorption behaviour of an azo sulphonated dye containing a trifluoromethyl group by silk fibre was investigated together with the sorption of the corresponding dyes having no substituent or a methyl group. The sorption isotherms were interpreted by using a single Langmuir or a dual type sorption mechanism. Considering the parameters obtained for the sorption, the effects of the functional groups, especially the trifluoromethyl group, are discussed.

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 (Structure 1).

AS (Crocein Orange G) was purchased from Tokyo Kasei Kogyo Co. (Tokyo, Japan) and purified by repeated recrystallization from 80% aqueous ethanol solution. The other dyes, m-TS and m-FTS were prepared as described in previous papers.[9,13] The purity was confirmed by elemental analysis.



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

Structure 1

A 55D raw silk of Bombyx mori made in Gunma, Japan was used for the sorption. The raw silk was degummed by treating twice in a 0·5% Marseilles soap solution, with liquor ratio of 1:50, for 40 min at 95–99°C, in 0·05% sodium carbonate solution for 10 min at 45–50°C, and in water for 60 min at 90–93°C. The degummed silk fibre was rinsed with hot and cold water, dried at room temperature, and left in a desiccator with silica gel for further drying. The degumming loss of the silk fibre was 24·1%. The water content of 6·8% was calculated from the difference between the weight of the silk fibres left in a desiccator and dried *in vacuo* at 120°C.

2.2 Dye sorption by the silk fibre

The time dependence of dye sorption was determined by 50 mg of the degummed silk fibre in the dye solution (50 ml) conditioned at pH 3 by a suitable amount of hydrochloric acid. After a given time, the sample was removed from the dye bath, rinsed in cold water, blotted with filter paper to remove the remaining dye solution from the fibre surface, and dried in a desiccator with silica gel. The dye sorbed by the silk fibre was extracted with 25 ml of 40% aqueous pyridine solution and its concentration was determined spectrophotometrically using a Shimadzu UV-240 spectrophotometer. The extinction coefficients at the visible absorption maxima in 40% aqueous pyridine solution were 1697 ± 4 (490 nm), 1697 ± 4 (492 nm) and 1702 ± 4 (480 nm) for AS, m-TS and m-FTS, respectively.

The absorption isotherms for the three dyes were determined in the same manner as described above.

3 RESULTS AND DISCUSSION

3.1 Time dependence of dye sorption

The time dependence of the amount of dye sorbed by the silk fibre for AS and m-FTS are shown in Fig. 1, where *r* is the amount (mol) of dye sorbed by 1 g of the dried silk fibre. A similar result was obtained for m-TS. Thus, for all the dyes, equilibrium sorption was established after immersion of the fibre in the aqueous dye solution for a period of 24 h.

On the other hand, in the case of the nylon 6 film, the amount of dye sorbed increased regularly and equilibrium sorption was not attained even after the film was soaked in the aqueous dye solution for 7 days.[14] This result is thought to be due to the change in the film structure and degradation during the dyeing process. Considering this fact, it is concluded that the structure of the silk fibre is more stable throughout the dyeing process.

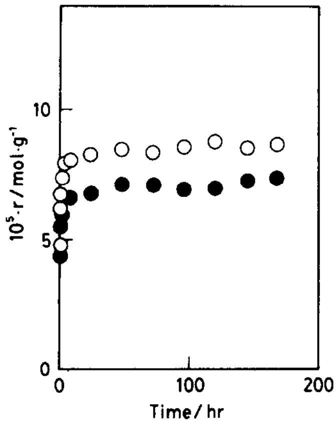


Fig. 1. Time dependence of the amount of dye sorbed by the silk fibre. Initial dye concentration: 1×10^{-4} mol dm^{-3} (●, AS (323 K); ○, m-FTS (333 K)).

3.2 Sorption isotherms

Equilibrium sorption was established after sorption for 24 h and the equilibrium sorption isotherms for all the dyes were determined from the sorption data at 24 h. The sorption isotherms thus determined are given in Fig. 2, where C_{free} expresses the concentration of free dyes in the bath.

For AS, the amount of dye sorbed increased with increasing free dye concentration and became constant in the high dye concentration region, while for m-TS and m-FTS, it continued to increase even in the high concentration region. This suggests that the sorption for m-TS and m-FTS cannot be explained only by the Langmuir type sorption mechanism. Furthermore, the amount of dye sorbed at a given free dye concentration followed the order AS < m-TS < m-FTS, indicating the influence of the functional groups on the dye sorption.

The sorption isotherms for AS were analysed by means of a single Langmuir type sorption mechanism:

$$r = \frac{nK_L C_{\text{free}}}{1 + K_L C_{\text{free}}} \tag{1}$$

where n is the number of binding sites for Langmuir type sorption (mol g^{-1}) and K_L is the intrinsic binding constant for Langmuir type sorption (dm^3 mol^{-1}). To analyse the sorption isotherms for m-TS and m-FTS, the following dual sorption equation was used:

$$r = \frac{nK_L C_{\text{free}}}{1 + K_L C_{\text{free}}} + K_P C_{\text{free}} \tag{2}$$

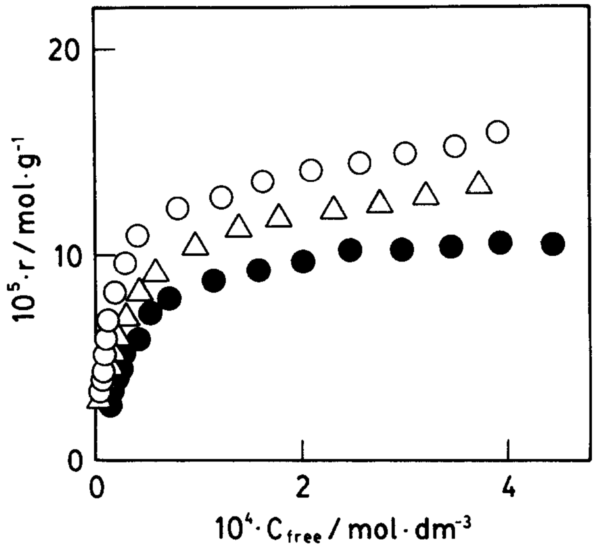


Fig. 2. Sorption isotherms of the dyes for the silk fibre at 333 K (●, AS; ○, m-FTS; △, m-TS).

where K_P is the partition coefficient ($dm^3\ g^{-1}$). The second term in the right-hand side of eqn (2) shows the contribution of the partition type sorption. The K_P value was calculated from the slope of a straight line in the high concentration region of the sorption isotherms. K_L and n were determined by using the modified eqn (2):

$$\frac{1}{r - K_P C_{\text{free}}} = \frac{1}{nK_L} \cdot \frac{1}{C_{\text{free}}} + \frac{1}{n} \qquad (3)$$

Assuming $K_P = 0$, eqn (3) is also the modified equation of eqn (1) and utilized to determine the parameters for the Langmuir type sorption of AS by the silk fibre. The plots of $1/(r - K_P C_{\text{free}})$ against $1/C_{\text{free}}$ are shown in Fig. 3. All the plots gave good linearity, whose slope and intercept provided the K_L and n values. The sorption isotherm curve calculated by using the parameters thus obtained fitted in with the experimental data very well (Fig. 4), suggesting that the sorption mechanism used for the dye–silk fibre system in the present study is valid.

The K_P, K_L and n values calculated above are given in Table 1. The K_P values exhibited a tendency to increase slightly with an increase in temperature, indicating that the partition mode is endothermic, as observed for the sorption of dibasic dyes by a nylon 6 film.[16] The number of binding sites for Langmuir type sorption, n, hardly depended on the dye species and temperature, which ranged from 1 to $1{\cdot}5 \times 10^{-4}$ mol g^{-1}. These values were comparable with the amino group content in the silk fibroin of Bombyx mori

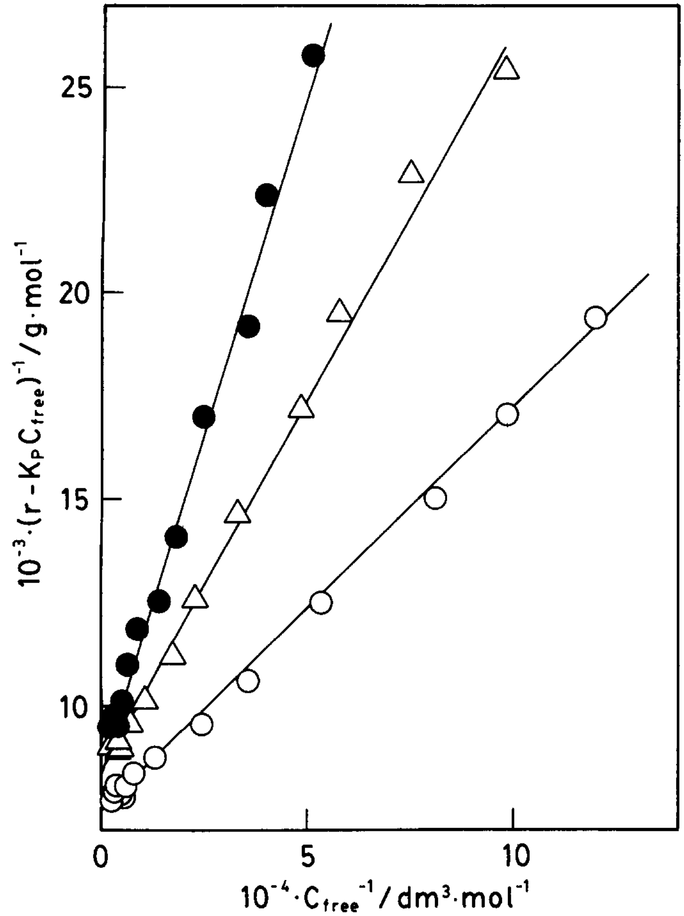


Fig. 3. Reciprocal plots of the sorption isotherms at 333 K (plots of $1/(r - K_PC_{free})$ against $1/C_{free}$) (●, AS; ○, m-FTS; △, m-TS).

determined experimentally; 0·96, 1·35, 1·16, 1·66 and $1{\cdot}31 \times 10^{-4}$ mol g^{-1} have been reported as the values of the amino group content.[17–21] This result demonstrates that the positively charged amino groups act as the binding sites for the dye anions.

The intrinsic binding constants for Langmuir type sorption, K_L, decreased with increasing temperature for all the dyes, and the Langmuir mode was exothermic. The exothermic behaviour was also observed for the dye–nylon 6 system, but the K_L values for the Langmuir type sorption for the nylon 6 film were increased about two orders of magnitude over those for the silk fibre.[14] This is believed to be due to the difference in the microenvironment around the amino groups between the silk fibre and nylon 6 film.

At all the temperatures measured, the K_L values for the silk fibre increased

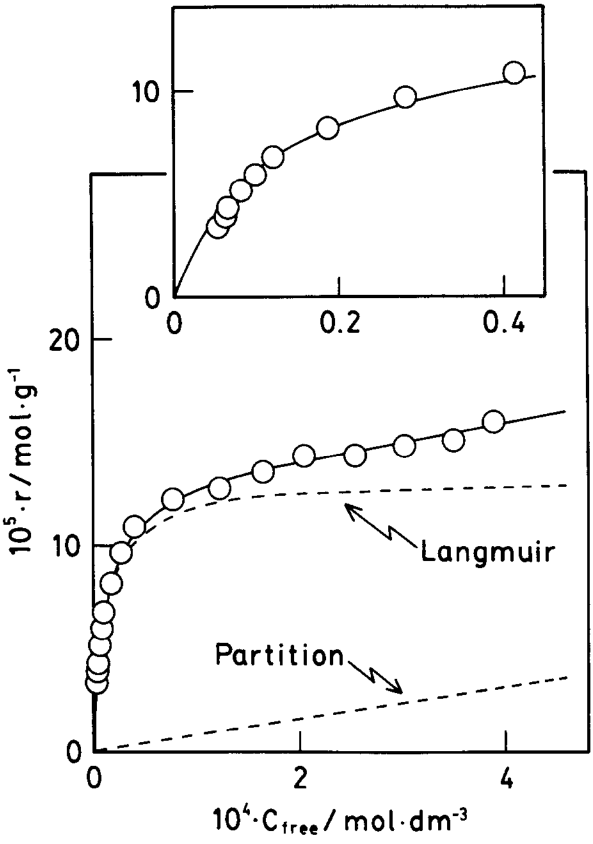


Fig. 4. Sorption isotherm calculated using the sorption parameters based on the dual sorption mechanism for the sorption of m-FTS at 333 K.

in the order of AS < m-TS < m-FTS, whereas the order of those for the nylon 6 film varied from temperature to temperature.[14] However, in both cases, the order of AS < m-TS was maintained at all temperatures; the K_L values for m-FTS made it complicated to interpret the effects of the subsituents in the dye molecules. Here it is worthwhile to utilize the affinity, $-\Delta\mu^0$ ($= RT \ln K_L$, where R is the gas constant and T is the absolute temperature), for explaining the effects of the functional groups. The gain in the affinity produced by the introduction of the substituents has been considered in relationship to the influence of the functional groups.[1,22] The difference in the affinity between AS and m-TS was 2·17, 2·18, 2·23 and 2·46 kJ mol^{-1} at 323, 333, 343 and 353 K, respectively, which was in good agreement with the value of 2·05 kJ mol^{-1} obtained from the gain in the affinity for CI Acid Orange 7 and CI Acid Orange 8 at 333 K.[1] From this, it might be concluded that the contribution of the methyl group to the sorption affinity of acid dyes by the silk fibre is 2–3 kJ mol^{-1}.

TABLE 1
The K_P, K_L and n Values

	323 K	*333 K*	*343 K*	*353 K*
$10^2 K_P$ ($dm^3 g^{-1}$)				
m-TS	6·2	4·3	8·7	10·7
m-FTS	6·6	7·6	9·3	10·0
$10^{-4} K_L$ ($dm^3 mol^{-1}$)				
AS	2·4	2·0	1·6	1·3
m-TS	5·4	4·4	3·5	3·0
m-FTS	8·9	7·8	7·0	6·5
$10^4 n$ ($mol g^{-1}$)				
AS	1·18	1·34	1·39	1·50
m-TS	1·07	1·20	1·17	1·27
m-FTS	1·30	1·33	1·27	1·45

The thermodynamic parameters, the enthalpy change, ΔH_L, and the entropy change, ΔS_L, for the Langmuir type sorption were calculated from the temperature dependence of K_L. The values obtained are given in Table 2 together with those for the nylon 6 film.[14] In the case of both silk fibre and nylon 6 film, the introduction of the methyl group made the binding process less exothermic and more entropic, indicating that hydrophobic interaction plays an important role. On the other hand, the introduction of the trifluoromethyl group made the enthalpy and entropy change less negative and more positive, respectively, for the silk fibre, while the opposite behaviour was observed for the nylon 6 film. The result is thought to be concerned with the peculiarity of the fluorine atoms and the complicated structure of the silk fibre. Furthermore, anomalous thermodynamic behaviour for the interaction between m-FTS and poly(vinylpyrrolidone) in aqueous solutions has been observed:[23] the van't Hoff plot for this system

TABLE 2
The Enthalpy Change, ΔH_L, and the Entropy Change, ΔS_L

	Silk fibre		*Nylon 6 film*[a]	
	ΔH_L ($kJ mol^{-1}$)	ΔS_L ($J mol^{-1} K^{-1}$)	ΔH_L ($kJ mol^{-1}$)	ΔS_L ($J mol^{-1} K^{-1}$)
AS	−19·8±1·7	23±5	−34±5	22±14
m-TS	−18·9±0·8	32±2	−21±5	60±14
m-FTS	−10·0±0·7	64±2	−45±2	−9±5

[a] Ref. 14.

had a crossover point and two kinds of thermodynamic parameters were obtained. Thus the effects of fluorine atoms are peculiar, so that it is difficult to discuss the effects on the binding generally.

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