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Adsorption Thermodynamics and Diffusion of Disperse Anthraquinone Dyes in Acetate Fibre

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SUMMARY

Diffusion coefficients, thermodynamic parameters and adsorption equilibrium isotherms of some anthraquinone dyes for acetate fibre are reported. The chemical constitution seems to be more important than the size factor in determining dye diffusion into the interior of the fibres. The activation energies of diffusion decreased strongly when o*-dichlorobenzene was present, due to the plasticising effect of carrier. Nernst partition isotherms were obtained, up to saturation. Substantivity decreased when water-solubilising groups are present in the molecule.*

The aqueous solubilities and heats of solution have been measured; the higher ΔH_w *values were found for the derivatives which can form intermolecular hydrogen bonding in the crystalline state.*

1. INTRODUCTION

It has been observed that substantivity of disperse dyes for acetate fibre depends on the absence of hydrophilic groups from the dye, as such groups cause the dye molecules to be attracted to the aqueous phase, thus reducing the amount of dye taken up by the substrate. On the other hand, a coplanar structure and the presence of hydrogen-bonding groups are very important factors and probably account for the major part of the standard affinity.[1,2]

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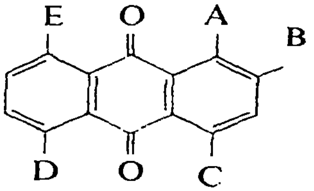
Moreover, the dyeing rate is greatly dependent on the chemical constitution of the dye; in fact, the dye solubility is dependent upon its polarity, while diffusion into the interior of the fibre mainly depends on steric hindrance and the bonds with substrate functional groups.[3,4] In addition, the tinctorial properties are largely due to the chemical composition of the dye and to the substituent groups present in its molecule; small differences in structure produce large variations in behaviour. These factors have been previously put forward to explain the dyeing properties of representative mono-azo non-ionic dyes.[5,6]

In connection with these studies and following our previous researches on disperse dye–hydrophobic fibre systems,[5-8] we now report the results relative to substantivity $(-\Delta\mu^\circ)$, standard heat $(\Delta\bar{H}^\circ)$ and standard entropy $(\Delta\bar{S}^\circ)$ of dyeing of several anthraquinone derivatives, the constitution of which is given below (**I**–**V**). These compounds are suitable for dyeing hydrophobic substrates in shades ranging from orange to blue.



I: A = NH_2; C = NH_2; B = D = E = H.
II: A = NH_2; B = CH_3; C = D = E = H.
III: A = NH_2; C = $NHCH_3$; B = D = E = H.
IV: A = $NHCH_3$; C = $NHCH_2CH_2OH$; B = D = E = H.
V: A = C = D = E = NH_2; B = H.

Further, investigations were carried out to determine the diffusion coefficients and equilibrium adsorption isotherms, with the aim of providing an additional contribution to the knowledge of the dyeing mechanism. Taking into account the correlations between the solubility of disperse dyes and their dyeing behaviour, we have also measured the aqueous solubilities of compounds **I**–**V** over the temperature range 60–90 °C, in order to calculate the heats of solution in water, which may be of great interest in the interpretation of the kinetics and thermodynamics of disperse dyeing.[9]

2. EXPERIMENTAL

The fibre employed in this study was a commercial sample of acetate (supplied by Montefibre) in the form of a continuous filament yarn. It consisted of 85·5 dtex with a radius of $3{\cdot}9 \times 10^{-2}$ cm. Before dyeing, a conventional scouring pretreatment was given to remove spin finish.

The dyes selected were five representative anthraquinoid derivatives: Disperse Violet 1 (C.I. 61 100) [I], Disperse Orange 11 (C.I. 60 700) [II], Disperse Violet 4 (C.I. 61 105) [III], Disperse Blue 3 (C.I. 61 505) [IV] and Disperse Blue 1 (C.I. 64 500) [V]. No problems of instability of the dye arose in any experiment with the acetate substrate.

The compounds were chromatographed, using a silica gel column with a mixture of benzene and acetone (3:1 v/v) as eluent, to remove extraneous products; purification was regarded as adequate when only one spot was developed on silica gel, using a mixture of benzene and acetone (4:1 v/v) as eluent. The dye was finally recrystallised to constant melting point. The melting points of the purified dyes agreed with literature values. Satisfactory combustion analytical data for C and H (±0·2%) were obtained.

The procedures used to determine the diffusion coefficients have been previously described.[7,10,11] The activation energy of diffusion (E) can be calculated from the slope of the linear relationship obtained by plotting $\ln D$ vs $1/T$, using eqn. (1), since the diffusion is an activated process of the Arrhenius type:[12]

$$D = D_0 \mathrm{e}^{-E/RT} \tag{1}$$

in which D is the diffusion coefficient at temperature T and D_0 is the pre-exponential factor.

Equilibrium adsorption measurements were carried out in tubes, fitted with reflux condensers and placed in a thermostatted bath (±0·01 °C), in the range 70–90 °C, keeping a liquor-to-goods ratio of 25/1 at neutral pH. In these experiments, the fibre sample (1 g) was immersed in the well-stirred dye liquor containing aqueous dispersions of the purified dye, and allowed to equilibrate. Preliminary experiments indicated that two days are necessary for the equilibrium to be attained. At the end of the dyeing, the dyed substrate was removed from the dyebath, rinsed with cold water, soaped, then dried. The dye content was estimated colorimetrically, after dissolution in acetone, with the aid of a Hitachi Perkin–Elmer EPS-3T spectrophotometer.

The thermodynamic affinity, i.e. the standard free-energy change $-\Delta\mu^\circ$ for the adsorption process, was calculated from measurements at equilibrium, using eqn. (2):

$$-\Delta\mu^\circ = RT \ln K = RT \ln \frac{(C_\mathrm{f})_\infty}{(C_\mathrm{s})_\infty} \tag{2}$$

where K (partition coefficient) $= (C_f)_\infty / (C_s)_\infty$; and $(C_f)_\infty$ and $(C_s)_\infty$ are the equilibrium dye concentrations in the fibre and solution phases, expressed in mol kg^{-1} of dry fibre and mol litre^{-1}, respectively.

Affinity values were also measured at various temperatures, in order to determine the standard heat of dyeing ($\Delta\bar{H}^\circ$) and entropy change ($\Delta\bar{S}^\circ$), according to eqn. (3):

$$-\Delta\mu^\circ = \Delta\bar{H}^\circ - T\Delta\bar{S}^\circ \tag{3}$$

The standard errors in $\Delta\bar{H}^\circ$ and $\Delta\bar{S}^\circ$ values are 0·6 kcal mol^{-1} and 2 e.u., respectively.

The solubilities of dyes were measured in duplicate at seven temperatures, following the procedure described by Bird *et al.*;[13] 72 hours were necessary for the solutions to become saturated. The reproducibility of such measurements was ±6%. The plots of the logarithm of the water solubility (S) vs the reciprocal of the temperature gave straight lines according to the van't Hoff equation (4):

$$\Delta H_w = \frac{R \mathrm{d} \ln S_T}{\mathrm{d} 1/T} \tag{4}$$

from which the heat of solution in water (ΔH_w) can be evaluated.

All calculations were carried out using a Texas PC-100C calculator.

3. RESULTS AND DISCUSSION

As with many polymers, only the amorphous regions of the acetate fibre are accessible and available to accommodate the dye molecules. This fact may affect both the equilibrium adsorption and the diffusion of the dye.

The diffusion coefficients (D) of disperse dyes **I**–**V** on acetate polymer at different temperatures are reported in Table 1, together with the activation energies of diffusion. Generally in a dyeing system the diffusion coefficient decreases with increasing molecular weight of the dye, because large holes must be formed with a smaller probability. Various correlations have been previously obtained between a parameter related to the molar volume (V_m) of dye and its diffusion coefficient;[14] Merian[15] and Giles[16] observed the following relation (5):

$$\log D = \log A - BV_m - Cd \tag{5}$$

in which A, B and C are constants and d is the minimum molecular diameter of the diffusing molecule.

TABLE 1

Diffusion Coefficients and Activation Energies in the Absence and Presence of *o*-Dichlorobenzene (3 mol kg^{-1} of fibre)

Dye	*Without carrier*				*With carrier*			
	$D \times 10^8$ ($cm^2 s^{-1}$)			E ($kcal\,mol^{-1}$)	$D \times 10^8$ ($cm^2 s^{-1}$)			E ($kcal\,mol^{-1}$)
	70°C	*80°C*	*90°C*		*70°C*	*80°C*	*90°C*	
I	0·62	1·52	2·35	15·6	1·86	2·27	2·98	5·49
II	0·55	0·93	1·29	9·96	1·62	2·07	2·55	5·30
III	0·034	0·17	0·85	37·4	0·62	0·84	1·02	5·82
IV	1·23	1·80	2·99	15·4	3·07	3·50	4·14	3·48
V	0·01	0·05	0·28	38·8	0·36	0·43	0·54	4·72

However, in this study no linear relationship was found, even though a small range of molecular weights was investigated. The results are consistent with those obtained by other authors,[17] who have also failed to observe such a correlation for some anthraquinone dyes.

It is therefore necessary to consider the possibility that the chemical constitution of the dye could also be a critical factor in relation to its diffusion into the interior of the polymer network. It was well recognised that dyes are attracted to fibres by physicochemical forces[18,19] which affect dye adsorption and dye binding to the substrate. Since the anthraquinone derivatives **I**–**V** here investigated contain —NH_2 or —NHR (R = CH_3, CH_2CH_2OH), hydrogen bonding could possibly take place between dye molecules and the acetyl groups of the fibre. On the other hand, several experiments, especially adsorption refractive index tests and chromatography,[20] have revealed physical bonds formed by proton donation of particular groups in the dye to the substrate and *vice versa*.

Moreover the chemical factor seems to be more important than the size factor, as suggested by Glenz *et al.*[14] for dyes having good substantivity due to the presence of groups which can form hydrogen bonds with the substrate.

The values of E indicate that the energies required to form a hole necessary for dye penetration into the acetate fibre are high, especially for the dyes **III** and **V**.

A considerable diminution of the activation energies of diffusion was observed, using *o*-dichlorobenzene as carrier (Table 1). In fact, these

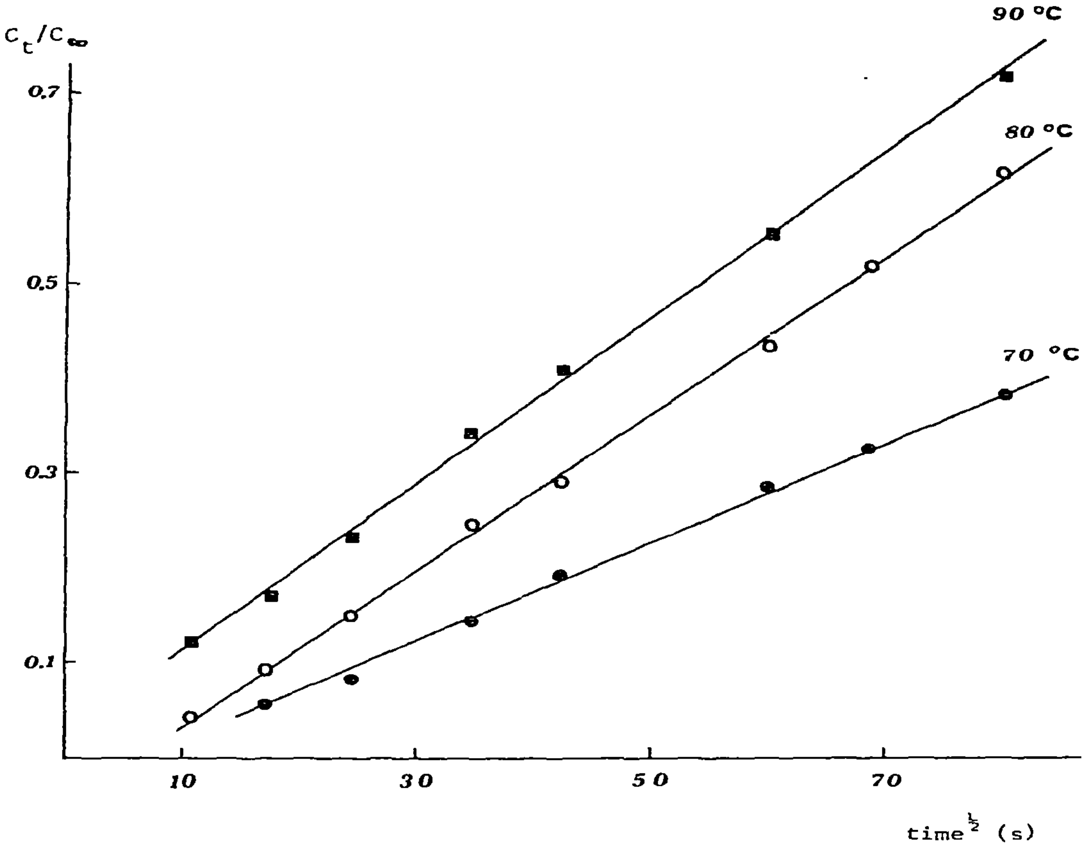


Fig. 1. Plots of C_t/C_∞ vs time$^{1/2}$ for Disperse Blue 3 (IV).

values are 3·48–5·82 kcal mol^{-1} when the carrier is used. This plasticises the fibre structure, reducing the glass-transition (T_g) temperature of the polymer and enabling more rapid entry of the dye molecules into the interior of the substrate.[7,11,21]

The dyeing rate constants (k) for dyes here investigated are listed in Table 2, while Fig. 1 shows the effect of temperature on dyeing rate of Disperse Blue 3 (**IV**) on acetate fibre.

The highest values of the activation energy of dyeing (E_A), as well as the pre-exponential factor ($\log A$) are those of Disperse Blue 1 (**V**), while the other derivatives have lower but similar values (Table 2). In addition, inspection of the dye uptake curves shows that dye **V** exhibits the lowest dyeing rate and reaches the lowest dye uptake at equilibrium. This is also

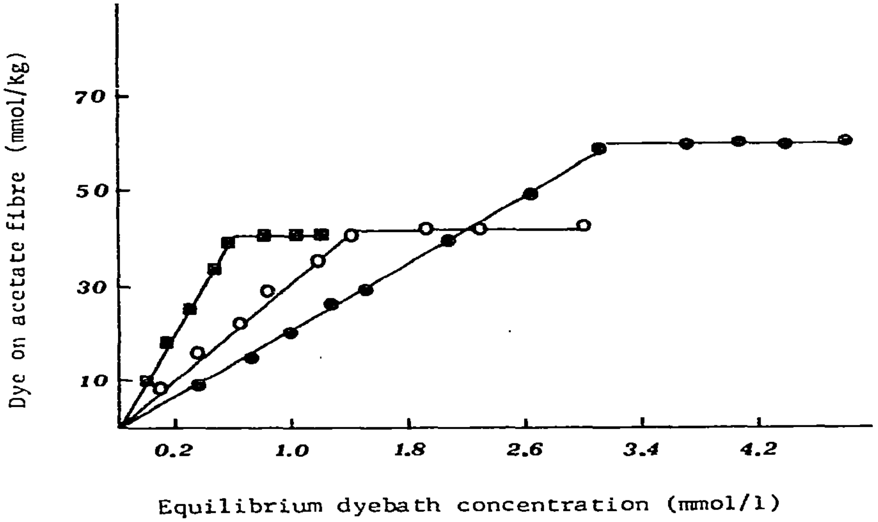


Fig. 2. Adsorption isotherms for dyes I (●), IV (○) and V (■) on acetate fibre at 90 °C.

confirmed by the saturation values listed in Table 3. In all cases the E_A values increase in the same order of pre-exponential factors and a good relationship between E_A and ΔS^* was found.

The distribution coefficient between the dyebath and the fibre follows a linear Nernst isotherm up to saturation of the dyebath solution for dyes I–V on acetate (Fig. 2). After equilibrium, addition of further dye to the dyebath does not produce an increase in dye uptake by the fibre. Furthermore, the partition coefficient decreases with increase in dyeing temperature, because heating increases the aqueous solubility.

Thermodynamic parameters for dyes I–V are reported in Table 4. It

TABLE 2
Dyeing Rate Constants and Activation Parameters of Anthraquinone Dyes I–V

Dye	k (*mmol kg*$^{-1}$ *s*$^{-1/2}$)			*log A*	E_A (*kcal mol*$^{-1}$)	$\Delta S^{\circ}_{80^{\circ}C}$ (*cal mol*$^{-1}$ *K*$^{-1}$)
	70°C	*80°C*	*90°C*			
I	0·22	0·32	0·46	4·9	8·60	−38·6
II	0·20	0·26	0·35	3·4	6·38	−45·4
III	0·17	0·23	0·32	3·8	7·15	−43·4
IV	0·21	0·29	0·39	3·9	7·18	−42·9
V	0·07	0·13	0·22	7·4	13·3	−27·1

TABLE 3

Saturation Values (mmol kg^{-1}) in the Presence and Absence of Carrier[a]

Dye	*70°C*		*80°C*		*90°C*	
	No carrier	*Carrier*	*No carrier*	*Carrier*	*No carrier*	*Carrier*
I	36·83	51·98	46·38	62·39	63·59	73·12
II	35·39	46·68	46·02	54·37	53·06	57·75
III	51·34	97·70	77·71	102·87	92·04	113·97
IV	34·70	40·67	40·28	46·57	43·32	46·83
V	27·91	35·97	37·00	46·78	42·96	52·56

[a] The carrier used was *o*-dichlorobenzene (3 mol kg^{-1} of the substrate).

TABLE 4

Thermodynamic Parameters of Dyes I–V

Dye	$-\Delta\mu^\circ$ (*kcal mol*$^{-1}$)			$\Delta\bar{H}^\circ$ (*kcal mol*$^{-1}$)	$\Delta\bar{S}^\circ$ (*cal mol*$^{-1}$ *K*$^{-1}$)
	70°C	*80°C*	*90°C*		
I	4·71	4·37	4·03	−18·0	−37·1
II	4·08	3·76	3·53	−14·9	−30·2
III	4·47	4·15	3·84	−16·8	−34·4
IV	3·44	3·20	2·93	−13·4	−27·7
V	5·62	5·23	4·82	−21·3	−43·6

TABLE 5

Solubilities at Various Temperatures and Heats of Solution in Water of Disperse Dyes I–V

Dye	*S* (*mg litre*$^{-1}$)							ΔH_w (*kcal mol*$^{-1}$)
	60°C	*65°C*	*70°C*	*75°C*	*80°C*	*85°C*	*90°C*	
I	1·6	2·2	3·0	3·7	4·4	5·5	6·8	11·2
II	1·8	2·7	4·1	4·9	6·0	9·0	11·8	14·3
III	1·5	2·0	2·5	3·3	4·3	4·9	6·3	11·3
IV	2·2	3·7	5·4	8·2	12·5	18·5	28·0	19·9
V	—	1·0	1·1	1·6	1·9	2·4	3·1	11·4

can be seen that the presence of hydrophilic groups considerably decreases the affinity for the acetate substrate. On the other hand when amino groups are incorporated in the molecule the affinity increases due to lower solubility in the aqueous phase.

The standard heat of dyeing ($\Delta\bar{H}^\circ$) observed for Disperse Blue 3 is lower than that of compounds containing amino groups, because of the hydrophilic character of the hydroxyethyl group.

The standard entropies of dyeing ($\Delta\bar{S}^\circ$), which are consequent on a change in structure balance on forming a dye–fibre bond after breaking a fibre–water and a dye–water bond, are almost double the $\Delta\bar{H}^\circ$ values. The large decrease in $\Delta\bar{S}^\circ$ is ascribed to the more ordered packing of the dye molecules, when sorbed by the acetate polymer.

The solubilities in the range 60–90 °C are given in Table 5, together with the heats of solution in water (ΔH_w).

The heat of solution depends upon the difference between the heat evolved due to the separation of dye molecules and that needed for the formation of dye–water bonds. The ΔH_w values, which have been found to be in the range 10–20 kcal mol^{-1}, may be taken as a measure of the attractive intermolecular forces between dye molecules.[22] The largest heats of solution were observed for the derivatives containing hydrophilic groups in their structures and which can therefore form strong intermolecular hydrogen bonds in the crystalline state.

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