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Correlation between Dyeing Rate and Thermodynamic Affinity of Disperse Reactive Dyes

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ABSTRACT

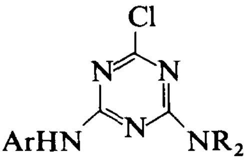
As part of a study on nylon dyeing with disperse reactive dyes, the thermodynamic affinities of some monochlorotriazine dyes have been determined.

A linear correlation was found between diffusion and partition coefficients and therefore between dyeing rates and thermodynamic affinities.

The results showed that the affinity of a dye and the nature of the heterocyclic ring are the determining factors of the whole process: affinity, because the quantity of the dye fixed in the alkaline dyebath is related to the quantity adsorbed in the acid dyebath by the fibre, and the type of heterocyclic ring because it determines the stability of the dye to hydrolysis.

INTRODUCTION

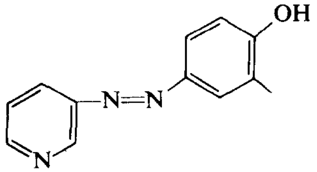
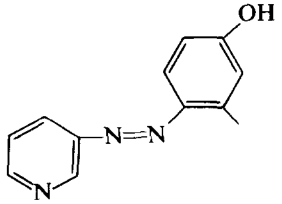
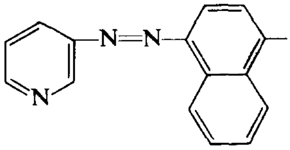
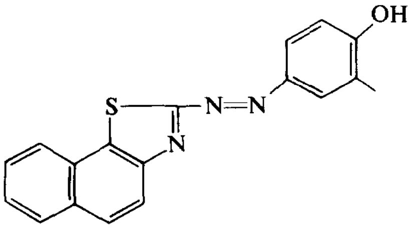
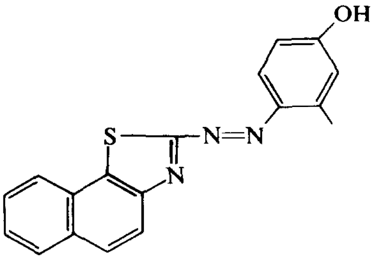
In nylon dyeing, the greatest difficulty consists in obtaining uniform dyeing and at the same time wet- and light-fastnesses. Because disperse dyes give good coverage on nylon but suffer somewhat from having lower fastnesses than desired, some reactive disperse dyes have been synthesized containing the monochlorotriazine group as reacting group and having the following general formula **I**.



I

They are listed in Table 1.

TABLE 1
Disperse Reactive Dyes I

Dye number	*Ar*	*R*
1		—CH_2CH_3
2		—CH_2CH_2OH
3		—CH_2CH_3
4		—CH_2CH_2OH
5		—CH_2CH_3
6		—CH_2CH_2OH
7		—CH_2CH_3
8		—CH_2CH_2OH
9		—CH_2CH_3
10		—CH_2CH_2OH

These dyes, which are stable in water and in weak acidic conditions,[1] contain a group carrying a labile chlorine atom capable of reacting with nylon in alkaline conditions by means of the nucleophilic substitution reaction.[2] Our past research[3-5] on the reaction rate between nylon and reactive dyes has pointed out the influence of the structure of the dye, more precisely the influence of the heterocyclic ring, on the rate of the nucleophilic substitution reaction between fibre and dye, and consequently also on the rate of hydrolysis of the dye in alkaline conditions. During this research it emerged that, besides the nature of the heterocyclic ring regulating the rate of the nucleophilic reaction between dye and fibre and between dye and hydroxyl ions, the study of the first dyeing stage, i.e. adsorption in acid conditions, is fundamental.

In fact the fixation of the dye in alkaline conditions is dependent on the adsorbed surface concentration and the diffusion coefficient of the dye. The former is evaluated by the affinity or the substantivity ratio. However, affinity cannot be measured directly when using the reactive dyes in the alkaline conditions adopted in dyeing, because of the simultaneous reactions of fixation and hydrolysis.

Sumner & Taylor[6] have overcome this problem indirectly by measuring the affinities of two inactive forms of the dye over a range of alkaline conditions; in the present study, on the other hand, the thermodynamic affinities of the synthesized dyes have been determined in acid conditions so that the dyes may be inactive and the thermodynamic equilibrium assured.

EXPERIMENTAL

Intermediates

N-(4-Chloro-6-diethylamino-*s*-triazin-2-yl)-2-aminophenol was prepared according to Harayama *et al.*[7]

N-(4-Chloro-6-diethylamino-*s*-triazin-2-yl)-3-aminophenol, *N*-(4-chloro-6-diethanolamino-*s*-triazin-2-yl)-2-aminophenol and *N*-(4-chloro-6-diethanolamino-*s*-triazin-2-yl)-3-aminophenol were prepared and purified as previously described.[4]

Dyes

Monochlorotriazinyl dyes (**1–4** and **7–10**) were obtained by substitution of the first chlorine atom of 2,4,6-trichlorotriazine at 0–5°C and pH 5–6 with *o*- or *m*-aminophenol. The second chlorine atom was substituted at 60–65°C with diethylamine or diethanolamine. The diazonium salts of 3-aminopyridine[8] and α-naphthothiazole[9] were prepared separately and added to the solutions of the various monochlorotriazine derivatives with stirring at 10°C and pH 8. Dyes **5** and **6** were prepared by substitution at 0–5°C of the first chlorine atom with the dye obtained by coupling α-naphthylamine with the diazonium salt of 3-aminopyridine, and further substitution of the second chlorine atom of trichlorotriazine with diethylamine or diethanolamine.[3]

Diffusion and rate coefficients

The diffusion coefficients of the dyes on nylon fibre were determined by application of the Hill equation,[10] using infinite-bath conditions at 95 ± 0·1°C, and the kinetic coefficients k were calculated by means of the equation:[11]

$$kt = \frac{1}{M_\infty - M_t} - \frac{1}{M_\infty}$$

where M_∞ is the amount of dye adsorbed after infinite time and M_t the amount of dye taken up in time t, as described previously.[5]

Determination of affinities

The affinities were determined in thermostated round-bottomed flasks equipped with condenser and stirrer, by dyeing nylon hanks (1 g) from a bath (50 ml) containing 1·5% of the dye o.w.f. and 1 g litre^{-1} Dispersol EL (a non-ionic polyoxyethylate product by FTR of Albano S. Alessandro) at 95 ± 0·1°C and pH 4 (obtained by an acetic acid and sodium acetate buffer) for 5 h, the time necessary to reach equilibrium.

The quantity of dye adsorbed by the fibre was determined spectrophotometrically after extraction with *n*-propanol.

By means of the equation:

$$-\Delta\mu^\ominus = RT \ln \frac{D_\mathrm{f}}{D_\mathrm{s}} = RT \ln K$$

where K is the partition ratio, the affinity for each single dye was calculated.

The dyeing tests were carried out on delustrant free nylon-6 yarns (titre 78/18 × 2, torsion 100 S, radius $1{\cdot}1 \times 10^{-3}$ cm).

All dyeings were carried out in duplicate with less than 5% deviation between the two values of $-\Delta\mu^\ominus$.

The dyed fibres were tested for fastness according to standard procedures.[12]

RESULTS AND DISCUSSION

The research[3-5] carried out on the reaction between nylon and reactive dyes has pointed out the influence of the structure of the dye on the rate of the two competitive reactions: dye fixation and hydrolysis. The reaction rates of the pyridine dyes (**1–6**) are higher than those of the α-naphthothiazole dyes (**7–10**); in fact, since the pyridine ring is electron-deficient, it creates an electron suction that increases both the fixing and the hydrolysis rate.[5] During studies on the dyeing rate of the triazinyl dyes and on the pyrimidinic reactive dyes,[13] it was shown that dyes with a higher fixation exhaust the dyebath better; i.e. the greater the dye adsorption, the greater the fixation. For this reason the partition coefficients and the related thermodynamic affinities were determined and the respective values are given in Table 2.

Table 3 shows the diffusion and dyeing rate coefficients in an acid dyebath at 95°C.

From an examination of Tables 2 and 3, it can be seen that the pyridyl dyes with higher diffusion and dyeing rate coefficients than the naphthothiazolyl dyes, show lower affinity values. Moreover, between analogous dyes, i.e. between dyes that differ only in the dispersing group, the ethanolaminic dyes have the greater affinities.

The plot of $\ln D$ versus $\ln K$ is linear (Fig. 1). The correlation found between diffusion and partition coefficients may be explained theoretically by considering a very simple model, in which the fibre is made up of intercommunicating channels or pores which are filled with the dye liquor.[14] If we indicate the fraction of the fibre occupied by the pores and accessible to

TABLE 2
Partition Ratios and Thermodynamic Affinities in an Acid Dyebath at 95°C

Dye	*K* (*litre kg*$^{-1}$)	$-\Delta\mu^{\circ}$ (*kJ mol*$^{-1}$)
1	134·81	15·02 ± 0·04
2	229·26	16·64 ± 0·06
3	174·02	15·80 ± 0·05
4	206·95	16·33 ± 0·05
5	240·03	16·78 ± 0·06
6	513·29	19·11 ± 0·07
7	693·18	20·03 ± 0·08
8	749·43	20·27 ± 0·06
9	325·69	17·71 ± 0·05
10	1 019·71	21·21 ± 0·07

TABLE 3
Kinetic and Diffusion Coefficients in an Acid Dyebath at 95°C

Dye	$k \times 10^2$ ($kg\ mol^{-1}\ s^{-1}$)	$D \times 10^{11}$ ($cm^2\ s^{-1}$)
1	10·20 ± 0·05	20·16 ± 0·11
2	7·47 ± 0·04	15·47 ± 0·08
3	8·89 ± 0·01	17·75 ± 0·09
4	7·91 ± 0·04	16·28 ± 0·08
5	7·08 ± 0·02	15·12 ± 0·07
6	4·70 ± 0·07	10·35 ± 0·06
7	4·05 ± 0·09	8·91 ± 0·11
8	3·56 ± 0·08	8·57 ± 0·09
9	6·33 ± 0·05	12·24 ± 0·08
10	2·93 ± 0·05	7·35 ± 0·05

the dye by α, the tortuosity factor of the fibre by τ, and the dye concentration free to move in the pores by C_i, then assuming an ideal process, the flux according to Fick's law can be written:

$$J = -D_i \frac{\alpha}{\tau} \frac{\delta C_i}{\delta x} \qquad (1)$$

where D_i represents the diffusion coefficient in the pore. In this model it is assumed that the dye is instantaneously adsorbed in the walls, and therefore an equilibrium between adsorbed and diffused dye is established. If C_a is the

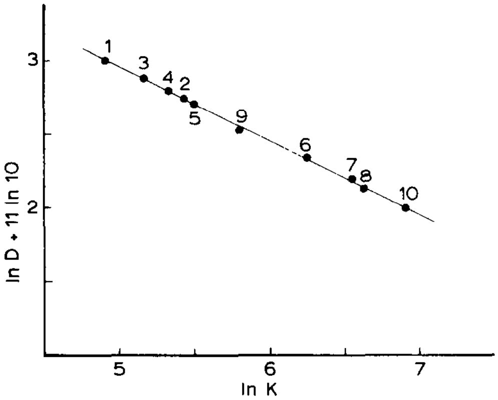


Fig. 1. Correlation between diffusion and partition coefficients ($r = 0{\cdot}999$).

concentration of adsorbed dye, then the equilibrium can be written in terms of the partition coefficient K:

$$K=\frac{C_a}{C_i}$$

and eqn (1) can be written according to Peters:[14]

$$D=\frac{\alpha}{\tau}D_i\frac{dC_i}{dC_a}=\frac{\alpha D_i}{\tau K} \tag{2}$$

In eqn (2), D is the diffusion coefficient calculated by Hill's equation, i.e. the apparent diffusion coefficient.

In applying these equations, it is assumed that the internal isotherm is equal to that of the bath, since the dye is considered free to move in the fibre. By rewriting eqn (2) in logarithmic form, we obtain eqn (3), which implies a linear correlation between diffusion and partition coefficients:

$$\ln D=\ln D_i+\ln\frac{\alpha}{\tau}-\ln K \tag{3}$$

In previous work[5] we found a linear correlation between rate and diffusion coefficient values (Fig. 2) which confirms that the diffusion is the determining step[15] in the overall dyeing process. Since the dyeing rate coefficients are correlated with the diffusion coefficients and the latter with the partition ratios, it follows that there is also a linear correlation between dyeing rate and thermodynamic affinity (Fig. 3).

In order to evaluate the diffusion coefficient in the pore D_i, and therefore the true diffusion rate, it is necessary to know the porosity factor α and the tortuosity factor τ. Using the values reported by Weisz & Zollinger[16] for

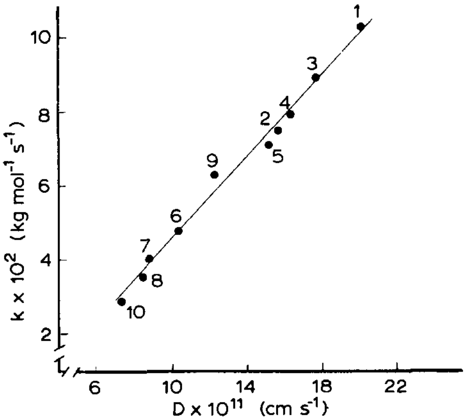


Fig. 2. Linear correlation between rate and diffusion coefficients ($r=0{\cdot}996$).

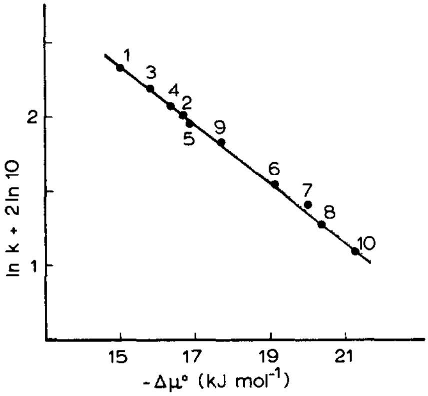


Fig. 3. Linear correlation between rate coefficients and thermodynamic affinities ($r = 0{\cdot}997$).

nylon (i.e. $\alpha = 0{\cdot}04$ and $\tau \simeq \sqrt{3}$), the true diffusion coefficient D_i of about $10^{-6}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$ was calculated. A comparison with the apparent diffusion rate indicates that the true diffusion rate is much higher than the apparent one, and that the true diffusion rate of dyes of this type is similar to that of disperse dyes. Therefore in the adsorption process, the prevailing parameter is not the diffusion in the pore, which has practically no influence, but the partition coefficient, which is due to the affinity of the dye for the fibre.

The higher affinity of the diethanolamine-derived dyes with respect to the diethylamino analogues could be attributed partly to a better dispersion caused by the hydroxyethylamino groups, and partly to the increased ability of such dyes to form hydrogen bonds with the polyamide chain of nylon.

The relation between dyeing rate and standard affinity is in effect intuitive, in that the diffusion rate of the dye depends on the size and shape of the molecule, but mainly on its affinity to the fibre, and increases on decreasing the affinity. Consequently, the dyes with lower affinity are characterized by a better penetration in the fibre and a faster dyeing rate.

Table 4 reports the washing fastness values of the ten synthesized dyes and the percentage of dye hydrolysed, obtained from the concentration of the fixed dye in alkaline conditions and the concentration of adsorbed dye in acid conditions.[5] There is a relationship between percentage of dye hydrolysed and fastness values. In fact the naphthothiazolyl dyes, which are stable to hydrolysis, always showed excellent fastnesses, whilst the pyridyl dyes, which undergo a partial hydrolysis due to the electron-attracting nature of the pyridine ring, showed good fastnesses to strong washing.

Among the pyridyl dyes, **3** and **4** showed the worst properties with respect to hydrolysis and fastness. The explanation lies in their structure; both dyes contain a hydroxyl group in the *meta* position with respect to the imine bridge which, by a negative inductive effect, increases the positive charge

TABLE 4
Washing Fastness and Percentage of Dye Hydrolysed

Dye	*Washing fastness*			*Dye hydrolysed (%)*
	Mild	*Medium*	*Strong*	
1	5	5	4	7·61
2	5	5	4–5	5·48
3	5	4	4	13·32
4	5	4–5	4	10·83
5	5	5	4	8·17
6	5	5	4–5	6·69
7	5	5	5	2·08
8	5	5	5	0·00
9	5	5	5	3·99
10	5	5	5	0·00

density on the carbon atom, thus facilitating the nucleophilic substitution reaction both with the fibre and with water. The hydrolysed dye remains adsorbed on the fibre and is eliminated with strong washing.

CONCLUSIONS

From an examination of the various parameters determined, it can be concluded that two factors determine the good quality of the process (i.e. uniform dyeing with good fastness). These factors are the affinity of the dye to the fibre and the reaction rate between fibre and dye. The dye affinity to the fibre is fundamental because the quantity of dye fixed in an alkaline dyebath is related to the quantity adsorbed in an acid dyebath by the fibre. In fact, the dye still not adsorbed when the bath becomes alkaline most likely undergoes hydrolysis before being bonded to the fibre.

The nature of the heterocyclic chromophore, on the other hand, regulates the rate of the nucleophilic reaction and therefore of the two competitive reactions of fixation and hydrolysis. For this reason it is not convenient to introduce electron-deficient heterocycles, such as pyridine, into the dye molecule, because an increase in fixation rate provokes an analogous increase in the hydrolysis rate.

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