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Effects of the Phenol on the Dyeing of Polyester Fibre with Some Disperse Azo-Dyes

Antonino Arcoria, Maria L. Longo and Giovanni Parisi

Istituto Dipartimentale di Chimica e Cimica Industriale,
Università di Catania, Viale A. Doria, 6-95125 Catania, Italy

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SUMMARY

The effects of the phenol, as carrier, on the dyeing rates, apparent diffusion coefficients, solubilities, thermodynamic affinities and T_D values of some disperse azo-dyes on polyester fibre are reported.

The dyeing rates of less soluble dyes are higher than those of more soluble hydrophilic dyes, while the affinity and T_D values show a reversed behaviour.

The carrier efficiency on the dyeing parameters studied appears to be correlated with the structure of dyes.

1. INTRODUCTION

The presence of carriers in the dyeing of polyester fibre by disperse azo-dyes favours the dye diffusion into the fibre owing to plasticizing effects.[1]

The chemical structure of the carrier negligibly influences the glass transition temperature of the fibre (T_g), because equimolecular concentrations of different carriers cause similar decrements of the T_g values.[2-4] Nevertheless, it has been pointed out that the effect of carrier on the rate of diffusion of the dye is influenced by the structure of the dye.[3,5-7] On the other hand, the effect of the carrier on the dyeing transition temperature (T_D) seems to be independent of the chemical structure of the dye.[8]

Therefore, further information is much needed to clarify the effects of carriers in the dyeing process.

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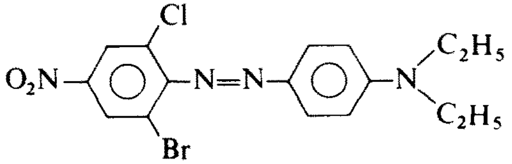
We previously reported on the effect of carriers on the diffusion of some disperse dyes in polyester and acrylic fibres[9,10] and now report the effects of the phenol on the solubilities, dyeing kinetics, apparent diffusion coefficients, thermodynamic affinities and T_D values of some disperse azo-dyes (**I**–**IV**) on polyester fibre.

I



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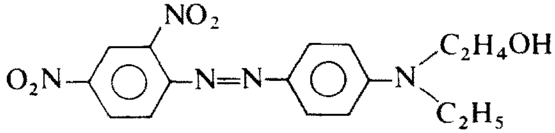

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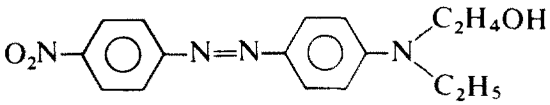

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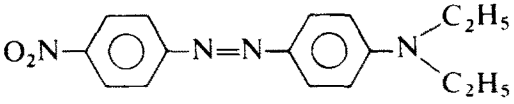

2. EXPERIMENTAL

The azo-disperse dyes **I**–**IV** (supplied by ACNA, Milan, Italy) were purified by silica-gel chromatography using a mixture of $H_2O/EtOH/NH_3$ (1/1/0·03) as eluent. The carrier used was phenol, laboratory reagent grade. In all experiments a commercial sample of polyester fibre was used in the form of discontinuous filament yarn (30 tex, $T_g = 77\,°C$).

The dyeing kinetic studies were carried out both in the absence and in the presence of carrier at various concentrations. Linear plots of the dye uptake against $\sqrt{t}$ are observed (Fig. 1). The rate constants were calculated by the rate law (1), using the least squares method.

$$C_D = k\sqrt{t} \qquad (1)$$

The measurements of the affinities $(-\Delta\mu)$ of the dyes were performed as previously described.[11] The solubilities of dyes in the dyebath were

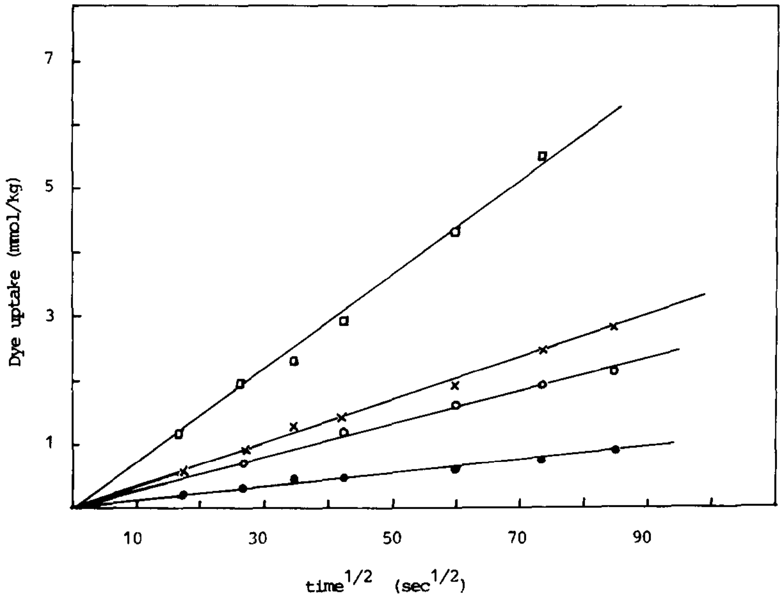

Fig. 1. Dye uptake versus $t^{1/2}$ plots for dye **III** at 85 °C and different phenol concentrations (mol litre^{-1}): ●, 0·0; ○, 0·09; ×, 0·12; □, 0·20.

measured in duplicate at different temperatures, following the procedure described by Bird *et al.*[12] The reproducibility of such measurements was ±6%.

The dyeing transition temperatures (T_D) were obtained by dyeing methods, according to Ingamells *et al.*[13] The polyester fibre was dyed with the dyes **I–IV** in a pyrex flask placed in a thermostatted bath at different temperatures in the range 60–100 °C, keeping a liquor-to-goods ratio of 50:1. In these experiments the azo-disperse dyes were dissolved in a few millilitres of acetone and entered into the dyebath. After 30 min, the dyed material was removed from the dyebath, rinsed with cold water and then dried. The dye uptake was estimated colorimetrically, after extraction from the fibre with hot *N*,*N*-dimethylformamide, using a Hitachi Perkin–Elmer EPS-3T spectrophotometer.

3. RESULTS AND DISCUSSION

The dyeing transition temperatures (T_D) measured by the dyes **I–IV** and in the absence and in the presence of phenol as carrier are reported in

TABLE 1
Glass Transition Temperature (°C)[a] Obtained by Dyeing Method (T_D) in Presence of Different Carrier Concentrations

Dye	*Phenol (mol litre^{-1})*			
	0·0	*0·1*	*0·15*	*0·2*
I	98	93	89	85
II	89	88	86	81
III	87	84	83	80
IV	90	87	84	80

[a] Average values from at least three runs. The reproducibility is ±2°C.

Table 1. The values were higher than the T_g values of fibre measured in water.[8]

The presence of phenol generally decreases the T_D values. The T_D values for dyes **II**, **III** and **IV** are comparable, whereas with dye **I** more remarkable effects were observed.

The solubility of the dyes (Table 2) increases in the presence of phenol, but it does not increase noticeably on increasing the carrier concentration within the limits studied. The affinities of dyeing ($-\Delta\mu$) at 85 °C are also reported in Table 2.

The effects of the carrier concentration on the $-\Delta\mu$ values are greater with those dyes bearing *ortho*-substituents. In fact, the affinity values at

TABLE 2
Dye Solubilities at Various Temperatures and Thermodynamic Affinities at Different Phenol Concentrations (mol litre^{-1})

Dye	*Solubility (mol litre^{-1})*							*$-\Delta\mu$ (kcal mol^{-1})*		
	60°C		*70°C*		*80°C*			*85°C*		
	[Phenol] = 0·1	*0·2*	*0·1*	*0·2*	*0·0*	*0·1*	*0·2*	*0·0*	*0·1*	*0·2*
I	0·04	0·05	0·06	0·07	7×10^{-4}	0·09	0·10	4·18	6·27	6·33
II	0·37	0·38	0·60	0·62	0·036[a]	0·69	0·70	3·66	4·56	4·63
III	0·35	0·26	0·57	0·43	0·024[a]	0·70	0·64	4·30	4·50	5·00
IV	0·06	0·07	0·11	0·10	7×10^{-4}[a]	0·11	0·11	4·39	4·53	5·16

[a] Reference 12.

TABLE 3
Dyeing Rate Constants (mmol kg^{-1} s^{-1}) and Apparent Diffusion Coefficients (cm^2 s^{-1}) for Dyes I–IV at 85 °C in the Presence of Phenol at Different Concentrations

Dye	*Phenol* (*mol litre*$^{-1}$)	k (*mmol kg*$^{-1}$ *s*$^{-1}$)	$D \times 10^9$ (*cm*^{2} *s*$^{-1}$)
I	0·0	0·013	3·40
I	0·09	0·014	1·60
I	0·12	0·016	1·00
I	0·20	0·019	0·20
II	0·0	0·006	8·40
II	0·09	0·014	0·10
II	0·12	0·016	0·10
II	0·20	0·023	0·004
III	0·0	0·010	0·10
III	0·09	0·024	0·40
III	0·12	0·034	0·40
III	0·20	0·075	0·30
IV	0·0	0·022	0·10
IV	0·09	0·044	0·30
IV	0·12	0·056	0·30
IV	0·20	0·096	0·20

0·1 mol/litre of phenol are greater by about 2 kcal mol^{-1} for the dye **I** and 0·9 kcal mol^{-1} for the dye **II**, whereas there is a negligible increment for the corresponding dyes **III** and **IV**. With the latter, a noticeable increment of $-\Delta\mu$ is observed only for 0·2 mol/litre of carrier concentration.

Consideration of the solubility and affinity values shows that the carrier activity has a greater influence on the equilibrium dye uptake than anything else. In fact, the changes of $-\Delta\mu$ values mainly depend on the changes of D_F (dye adsorbed) values, as in eqn (2):

$$-\Delta\mu = RT \ln D_F/D_S \qquad (2)$$

Actually, the carrier favours both solubility in the dyebath and the penetration of the dye into the fibre. However, steric hindrance by *ortho*-substituents, as in **I** and **II**, probably interferes with the desorption process of dyes from the fibre, resulting in a higher thermodynamic affinity.

The dyeing rate constants (k) of dyes **I**–**IV** together with the apparent diffusion coefficients were also measured at 85 °C in the presence of various concentrations of phenol (Table 3). The less soluble dyes (**I** and

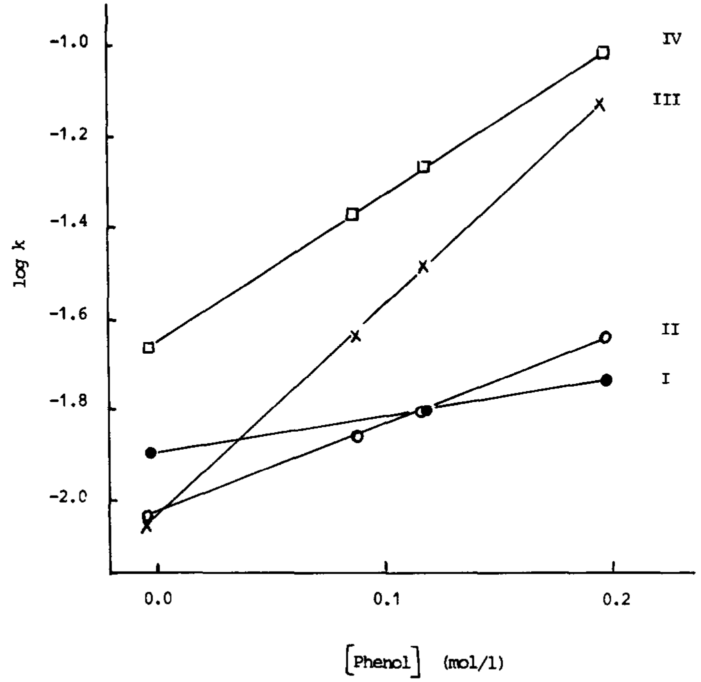

Fig. 2. Plot of log*k* versus phenol concentrations.

IV) show *k* values higher than those of more soluble hydrophilic dyes (**II** and **III**). The addition of the carrier always increases the dyeing rates. The phenol is more effective with dye **III**, in which a hydrophilic group and no *ortho*-groups are present (Fig. 2). On the contrary, minor effects are observed with dye **I**, which has two *ortho*-substituents and no hydrophilic group. An intermediate trend is observed with dye **II** because of balance of the hydrophilic and *ortho*-groups.

The influence of carrier on the diffusion coefficients appears to be different. In fact, the *D* values of the dyes **I** and **II** clearly decrease on passing from 0 to 0·2 mol/litre of phenol, whereas for the dyes **III** and **IV** small variations are observed. The different behaviour may be ascribed to steric effects of substituents in the dyes **I** and **II**.

Therefore, the carrier effects on the dyeing rate clearly depend on the dye structure.

Some structural correlation can be pointed out from the results obtained. In fact the least soluble dye **I** shows the smallest increment of *k* and the highest increments of $-\Delta\mu$ and T_D values, passing from pure water to 0·2 mol/litre of added phenol. On the other hand, dye **III** has the highest Δk and the smallest increases in $-\Delta\mu$ and T_D values. Dyes **II** and **IV** show intermediate behaviour. Therefore, all parameters studied, including T_D values, appear to correlate with the structure of the dye, i.e. size, shape and dye–polymer interactions.

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