Dyes and Pigments **18** (1992) 199–206

Kinetic and Thermodynamic Characteristics of Azo Dyes for Polyester Fibre in the Presence of Phenol as a Carrier

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(Received 9 August 1991; accepted 19 September 1991)

ABSTRACT

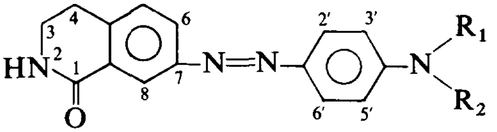
This paper reports the synthesis of some new basic azo dyes obtained by coupling diazotized 7-amino-3,4-dihydro-iso-carbostyril with N,N-disubstituted anilines. The effects of phenol, as carrier, on the dye solubilities and on the kinetics, diffusion coefficients, and thermodynamics of the dyeing of polyester (PET) fibre are also investigated.

At lower concentrations ($<0{\cdot}2$ mol/kg), phenol acts as a dispersant of the dye in the dye bath, whereas, at higher concentrations ($>0{\cdot}2$ mol/kg), it has a greater influence on the desorption process.

INTRODUCTION

We have previously reported[1,2] data on the kinetic and thermodynamic properties of azo disperse dyes for poly(ethylene terephthalate) (PET) fibre. The presence of phenol as carrier allows dyeing to be effected at lower temperatures owing to increase in the solubility of the dye and also because of its influence on the fibre structure.

In continuation of this work, we now report the synthesis and the dyeing properties on PET of some new basic dyes (I–IV) derived from 7-amino-3,4-dihydro-isocarbostyril:



Dyes and Pigments 0143-7208/92/$05.00

(I) $R_1 = C_2H_5$; $R_2 = H$

(II) $R_1 = R_2 = C_2H_5$

(III) $R_1 = C_2H_4OH$; $R_2 = C_2H_5$

(IV) $R_1 = R_2 = C_2H_4OH$

The kinetics of the dyeing process, thermodynamic affinities, and diffusion coefficients have been measured at 75°C and 90°C at various concentrations of phenol in the dyebath. Phenol was selected as a carrier because its Hildebrand solubility parameter[3] ($\delta = 14{\cdot}5$) is similar to that of PET ($\delta = 10{\cdot}7$). The solubility of dyes I–IV in aqueous solutions has also been determined for comparison purposes.

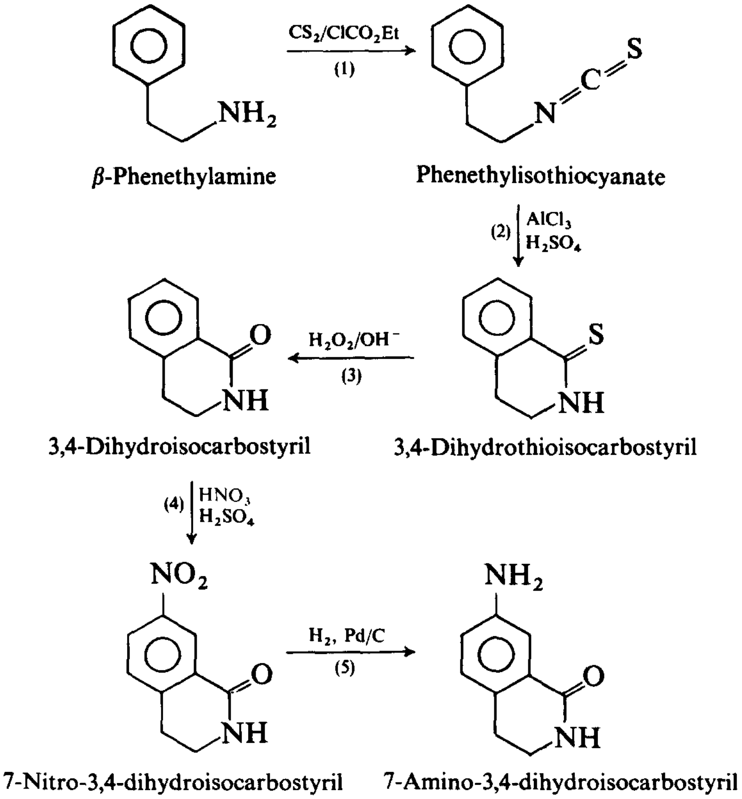
EXPERIMENTAL

Synthesis of the dyes

Dyes I–IV were prepared by diazotization of 7-amino-3,4-dihydroisocarbostyril (V) and coupling with the *N,N*-substituted anilines (VI). V was synthesized by using the reaction sequence outlined in the Scheme, i.e. involving:

(i) preparation of phenethylisothiocyanate (b.p. 95°C/0·5 mm Hg) by reaction of β-phenethylamine with carbon disulphide and ethylchloroformate in aqueous solution of KOH;[4]
(ii) cyclization of phenylisothiocyanate to 3,4-dihydrothioisocarbostyril (m.p. 98–99°C) by $AlCl_3$ and conc. H_2So_4;[4]
(iii) oxidation of 3,4-dihydrothioisocarbostyril to 3,4-dihydroisocarbostyril (m.p. 65–66°C) by H_2O_2 in alkaline medium;[5]
(iv) nitration of 3,4-dihydroisocarbostyril to the 7-nitro derivative (m.p. 229–230°C);[5]
(v) reduction to the 7-amino derivative by H_2 on Pd/C (m.p. 124–125°C).[5]

Diazotization of V was carried out with $NaNO_2/HCl$. The appropriate VI (0·01 mol) was dissolved in an aqueous solution (100 ml) containing 0·015 mol of 96% H_2SO_4. After two hours, this solution was neutralized with 10% aqueous NaOH, cooled at 0°C, and slowly stirred into the solution of the diazonium salt. The resultant dye was filtered, washed with water, and dried. After dissolution in aqueous acid (pH 1) and reprecipitation with saturated $NaHCO_3$ to a neutral pH value, dyes I–IV were finally crystallized from absolute ethanol.



Scheme I

Dye I ($R_1 = C_2H_5$; $R_2 = H$). M.p. 232–235°C. IR (KBr) (cm^{-1}): 3360, amide NH stretching; 3200, amine NH stretching; 1660, CO stretching; 1600, *p*-disubstituted aromatic ring. Visible spectrum in *N*,*N*-dimethylformamide (DMF) [λ_{max} (nm); ε]: 420; 19 800 ^{1}H NMR, DMSO-d_6, (δ, ppm): 8·30 d, (H_8) $J_{8,6}$ = 2 Hz; 8·01 s (NHCO); 7·9–8·01 dd (H_6) $J_{6,5}$ = 8·3 Hz; $J_{6,8}$ = 2 Hz; 7·7–7·75 d ($H_{2'}$, $H_{6'}$), $J_{2'6'}$ = 9 Hz; 7·45 d (H_5) $J_{5,6}$ = 8·3 Hz; 6·7 d ($H_{3'}$, $H_{5'}$) $J_{3'5'}$ = 9 Hz; 3·40 (CH_2 diethylamino group); 3·20 t ($CH_{2(3)}$); 3·0 t ($CH_{2(4)}$); 1·20 t (CH_3).

Dye II ($R_1 = R_2 = C_2H_5$). M.p. 232–234°C. IR (KBr) (cm^{-1}): 2190, amide NH stretching; 1660, CO stretching; 1600, *p*-disubstituted aromatic ring. Visible spectrum in DMF [λ_{max} (nm); ε]: 440; 20 600. ^{1}H NMR, DMSO-d_6, (δ, ppm): 8·20 d (H_8) $J_{8,6}$ = 1 Hz; 8·07 s (NHCO); 7·89–7·86 dd (H_6) $J_{6,5}$ = 8·3 Hz, $J_{6,8}$ = 2·1 Hz; 7·80–7·77 d ($H_{2'}$, $H_{6'}$) $J_{2'6'}$ = 9 Hz; 7·47–7·44 d (H_5) $J_{5,6}$ = 8·3 Hz; 6·83–6·79 d ($H_{3'}$, $H_{5'}$) $J_{3'5'}$ = 9 Hz; 3·45 m($CH_{2(3)}$ and $2CH_2$ of diethylamino group); 2·97 t ($CH_{2(4)}$); 1·15 t ($2CH_3$).

Dye III ($R_1 = C_2H_4OH$; $R_2 = C_2H_5$). M.p. = 222–224°C. IR (KBr) (cm^{-1}):

3430 amide NH stretching; 3180 OH stretching; 1660 CO stretching; 1600 *p*-disubstituted aromatic ring. Visible spectrum in DMF [λ_{max} (nm); ε]: 445; 19 600. ^{1}H NMR, DMSO-d$_6$, (δ, ppm): 8·20 d (H_8) $J_{8,6}=2{\cdot}1$ Hz; 8·07 s (NHCO); 7·89–7·86 dd (H_6) $J_{6,5}=8{\cdot}3$ Hz; $J_{6,8}=2{\cdot}1$ Hz; 7·80–7·77 d ($H_{2'}, H_{6'}$) $J_{2'6'}=9$ Hz; 7·47–7·44 d (H_5) $J_{5,6}=8{\cdot}3$ Hz; 6·85–6·81 d ($H_{3'}, H_{5'}$) $J_{3'5'}=9$ Hz; 3·45 m ($CH_{2(3)}$ and 3CH$_2$ of diethylamino group); 2·97 t ($CH_{2(4)}$); 1·14 t (CH_3).

Dye IV ($R_1=R_2=C_2H_4OH$). M.p. 225–226°C. IR (KBr) (cm^{-1}): 3360 diethylamino OH stretching; 3200 amino NH stretching; 1660 CO stretching; 1600 *p*-disubstituted aromatic ring. Visible spectrum in DMF [λ_{max} (nm); ε]: 445; 21 700. ^{1}H NMR, DMSO-d$_6$, (δ, ppm): 8·20 d (H_8) $J_{8,6}=1{\cdot}8$ Hz; 8·08 s (NHCO); 7·89–7·86 dd (H_6) $J_{6,5}=8{\cdot}13$ Hz; $J_{6,8}=1{\cdot}8$ Hz; 7·80–7·76 d ($H_{2'}, H_{6'}$) $J_{2'6'}=9{\cdot}14$ Hz; 7·48–7·44 d (H_5) $J_{5,6}=8{\cdot}13$; 6·88–6·84 d ($H_{3'}, H_{5'}$) $J_{3'5'}=9{\cdot}14$ Hz; 3·59 m ($CH_{2(3)}$) and 4CH$_2$ of diethylamino group); 2·97 t ($CH_{2(4)}$).

Kinetic and thermodynamic measurements

The dyebath contained 0·02 g of dye dispersed in 25 ml of H_2O and 1 g of a commercial sample of PET in the form of continuous-filament yarn (30 tex, T_g 77°C). The amount of phenol (laboratory-reagent grade) used was 0·1–0·4 mol/kg of fibre.

Dyeing kinetics at 75°C and 90°C were performed as previously described.[6] At suitable intervals, the quantity of dye adsorbed on the fibre was determined spectrophotometrically after extraction with DMF. The rate constants (k) were calculated by the rate law by using the least-squares method:[6]

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

where C_D is the concentration of the dye on the fibre at time t. All the runs were carried out in duplicate; the maximum error did not exceed 7%.

The values of thermodynamic affinity were calculated by the Vickerstaff equation, eqn (2):[7]

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

where D_F is the amount of dye adsorbed on the fibre and D_S is the amount of dye dissolved in the dyebath. The $-\Delta\mu$ values (kcal mol^{-1}) were measured after 24 h of dyeing at 75°C and 90°C.

The diffusion-coefficient values of the dyes on PET fibre were calculated by Hill's equation, eqn (3):[7]

$$C_t/C_\infty = 4(D_t/\pi r^2)^{1/2} \qquad (3)$$

where C_t and C_∞ are the quantities of dye adsorbed at time t and at equilibrium, and r is the radius of the filament measured under the microscope ($r = 0{\cdot}109$ mm).

The solubilities[8] of I–IV were determined at 75°C and 90°C in water, with and without phenol. The precision of the measurements varies within ±6%.

RESULTS AND DISCUSSION

The solubility values (S) of dyes I–IV in aqueous solution at 75°C and 90°C are reported in Table 1, together with the corresponding rate constants of dyeing (k), thermodynamic affinities ($-\Delta\mu$), and diffusion coefficients (D).

Solubility is clearly related to the presence of hydrophilic groups in the dye structure. In fact, dye IV, which contains two OH groups, is the most soluble, while dye II is the least soluble owing to the lack of hydrophilic groups; dye III (one OH group) and dye I (one NH group) show intermediate values. The solubility of each dye increases on increasing the phenol concentration. The presence of carrier therefore, facilitates the dyeing process, since only dissolved dye participates in the process:

$$\text{Dye}_{(\text{solid})} \rightleftharpoons \text{Dye}_{(\text{solution})} \xrightleftharpoons[\text{Desorption}]{\text{Absorption}} \text{Dye}_{(\text{fibre})}$$

Figure 1 shows the correlation between the solubility and the thermodynamic affinity at 75°C without phenol and at 90°C with 0·4 mol/kg of phenol. The greater the solubility of the dye, the smaller is its affinity towards PET fibre.

Nevertheless, the affinity values also increase on increasing the bath temperature, because of a plasticizing effect on the fibre, in spite of the increased solubility. When the solubility goes beyond a limiting value, dye desorption from the fibre counteracts the absorption process, so that $-\Delta\mu$ values tend towards a limit (Fig. 2).

The dyeing-rate constants are also inversely correlated with the solubilities. The dye with lowest affinity is the β,β-dihydroxy derivative, dye IV, at both 75°C and 90°C, and dyes with greater affinity are dye II and dye III, depending on the temperature of the dyebath. The k values increase with increasing temperature and show a maximum at 0·2 mol/kg of phenol (Fig. 3). This trend, already noted in the kinetic studies carried out in the presence of carrier, may be ascribed to the competition of the desorption process.

The diffusion coefficients behave similarly to the k values. In fact, the D values increase with increasing temperature and show a maximum at 0·2 mol/kg of phenol. This indicates that the macromolecules of the fibre

TABLE 1

Solubilities (*S*), Rate Constants (*k*), Thermodynamic Affinities ($-\Delta\mu$), and Diffusion Coefficients (*D*) of Dyes I–IV at 75°C and 90°C at Various Phenol Concentrations in the Dyebath

Dye	*Phenol* ($mol\,kg^{-1}$)	*75°C*				*90°C*			
		S (*mol/litre*)	*k. 10²* ($mmol\ kg^{-1}\,min^{-1/2}$)	$-\Delta\mu$ (*kcal/mol*)	*D* ($mm^2\,s^{-1}$)	*S* (*mol/litre*)	*k. 10²* ($mmol\ kg^{-1}\,min^{-1/2}$)	$-\Delta\mu$ (*kcal/mol*)	*D* ($mm^2\,s^{-1/2}$)
I	0·0	4·3	3·1	2·19	1·1	6·0	3·4	3·42	3·1
	0·1	—	4·3	2·39	1·8	—	5·2	2·43	3·2
	0·2	4·4	6·1	2·41	3·1	6·3	9·8	2·64	3·2
	0·3	—	4·6	2·42	1·4	—	6·2	2·66	1·2
	0·4	5·2	2·4	2·49	0·2	11·8	5·0	2·70	0·4
II	0·0	0·6	5·6	2·71	25·4	0·8	6·3	2·99	25·8
	0·1	—	6·0	2·76	20·4	—	6·5	3·16	7·6
	0·2	0·6	11·4	3·28	16·2	1·1	13·1	3·29	7·4
	0·3	—	9·1	3·29	8·0	—	11·7	3·29	6·8
	0·4	0·6	2·8	3·30	0·8	1·4	7·1	3·31	3·2
III	0·0	10·4	3·5	0·63	42·8	14·4	8·7	0·68	138·0
	0·1	—	4·0	0·86	22·2	—	10.6	0·91	105·0
	0·2	10·7	6·9	1·43	11·1	18·8	21·7	1·45	95·9
	0·3	—	6·1	1·43	8·1	—	21·2	1·45	90·4
	0·4	11·3	4·9	1·44	5·2	20·3	16·0	1·52	42·8
IV	0·0	65·0	1·6	0·01	1·2	116·0	1·7	0·04	0·6
	0·1	—	1·8	0·02	1·4	—	2·0	0·06	0·8
	0·2	85·9	2·9	0·06	1·9	155·0	3·8	1·03	2·5
	0·3	—	2·4	0·07	1·3	—	2·8	1·37	1·2
	0·4	90·1	2·3	0·14	0·9	182·0	2·6	0·15	1·0

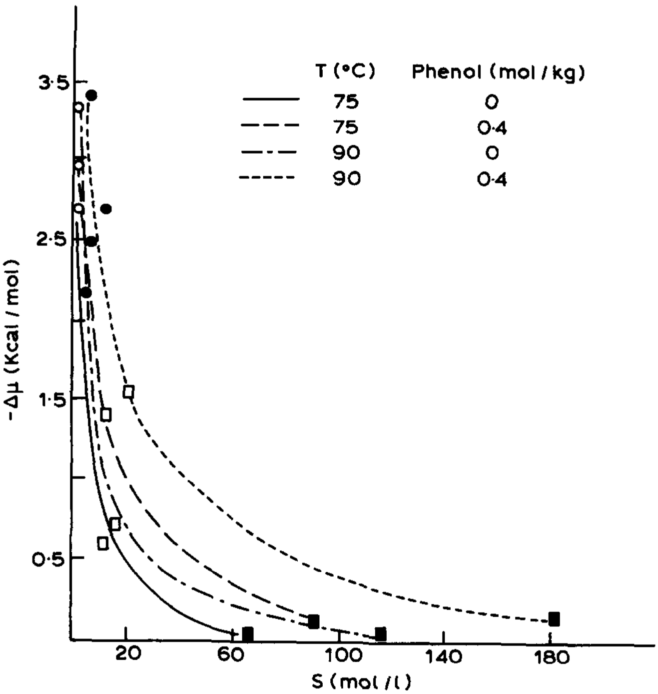


Fig. 1. Correlation between solubility and thermodynamic affinity at 75°C and 90°C without and with 0·4 mol/kg of phenol. Dyes: I (●), II (○), III (□), IV (■).

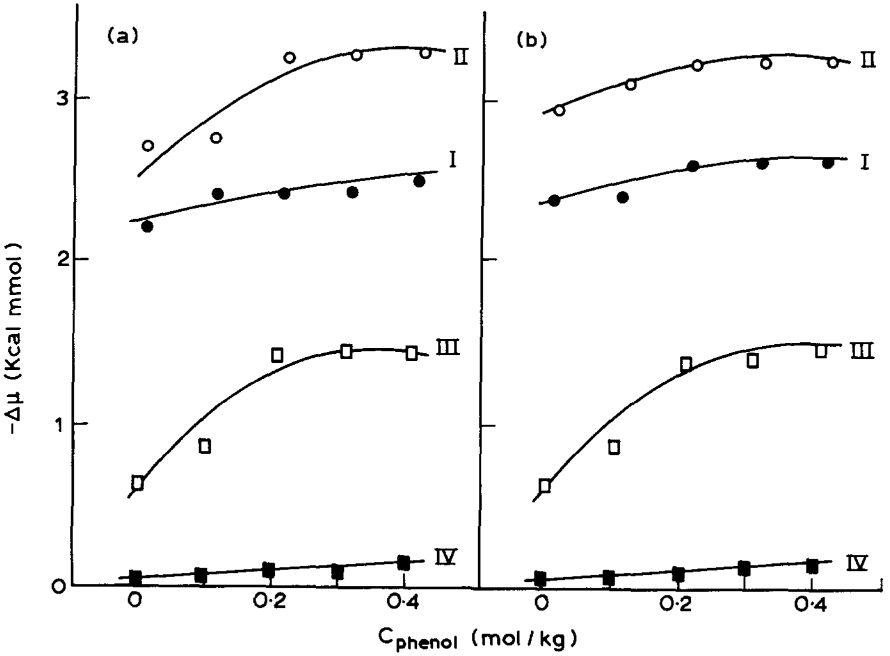


Fig. 2. Plot of thermodynamic affinity of dyes I–IV versus phenol concentration: (a) at 75°C, (b) at 90°C. Dyes: I (●), II (○), III (□), IV (■).

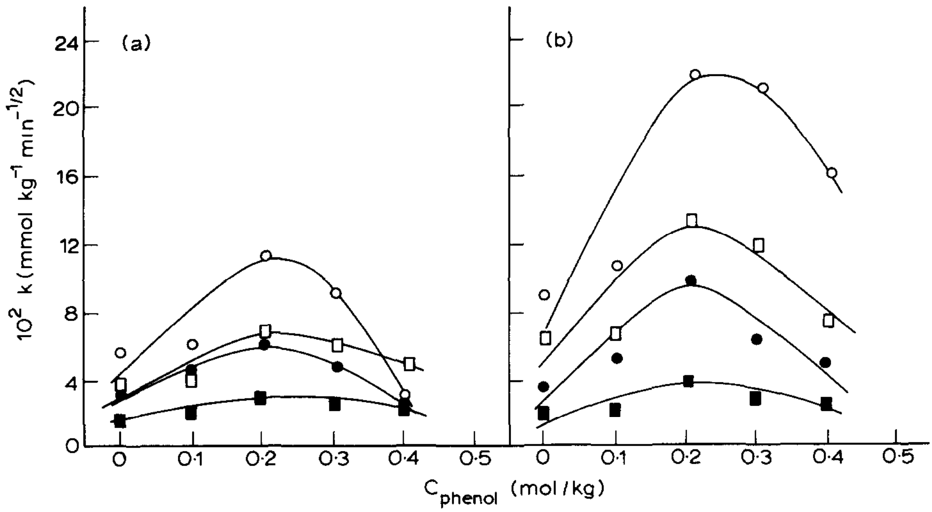


Fig. 3. Plot of rate constants versus phenol concentration: (a) at 75°C, (b) at 90°C. Dyes: **I** (●), **II** (○), **III** (□), **IV** (■).

become more plastic and thus more suitable for an irreversible absorption of the dye molecule up to a limiting value.

The dyeing process for PET fibre with dyes I–IV is thus strongly influenced by the carrier. Phenol has a double effect, namely, at concentrations below 0·2 mol/kg it is beneficial to the dyeing process owing to solubilization of the dye and to its plasticizing effect on the fibre; at concentrations above 0·2 mol/kg, it has a negative effect, favouring desorption of the dye from the fibre.

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