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Dyeing Properties of Basic Azo-Dyes from 2-Amino Thiadiazole*

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ABSTRACT

Some new basic azo-dyes derived from thiadiazole were synthesized to evaluate the dyeing parameters on polyester fibre (PET) for optimizing the dyeing process.

The kinetics of dyeing were performed at various temperatures (80°, 90° and 100°C) in the absence and in the presence of phenol, benzoic acid and salicylic acid as carriers. Thermodynamic affinities were also measured.

The dyeing rate constants increase on increasing the concentration of carrier, while low affinity values were observed for the dyes bearing hydroxyl groups, owing to increased solubility of the dye in the dyebath. This behaviour is less evident in the dyes bearing a methyl group in the thiadiazole ring.

The dyes show good fastness to light, perspiration and dry cleaning.

1 INTRODUCTION

We have previously investigated some factors which determine the dyeing properties of various basic azo-dyes for polyester fibre (PET).[1-3] Following this work, we now report the synthesis of some new basic azo-dyes derived

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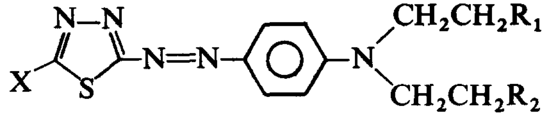
from 2-amino thiadiazole (I) together with the kinetics and thermodynamics of dyeing on PET:

(I)



(1) X = H — $R_1 = R_2 = H$
(2) X = H — $R_1 = H$ $R_2 = OH$
(3) X = H — $R_1 = R_2 = OH$
(4) $X = CH_3$ — $R_1 = R_2 = H$
(5) $X = CH_3$ — $R_1 = H$ $R_2 = OH$
(6) $X = CH_3$ — $R_1 = R_2 = OH$

The data were obtained at various temperatures (80°C, 90°C and 100°C) and in the absence and presence of some carriers in the dyebath, viz., phenol (Ph), benzoic acid (B) and salicylic acid (S). The wet- and light-fastness properties of the dyes on PET were also measured.

2 EXPERIMENTAL

The azo-dyes 1–6 were prepared by diazotization of 2-amino-1,3,4-thiadiazole, and of the corresponding 5-methyl derivative, and coupling with N,N-substituted anilines.

The dyes were purified by recrystallization from ethanol–ligroin and gave satisfactory microanalysis data. Melting points (m.p.), visible absorption maxima and absorptivities are: [m.p. (°C), λ_{max} (nm), log ε]: (1) 154–6, 504, 4·53; (2) 159–61, 505, 4·59; (3) 195–6, 503, 4·52; (4) 167–8, 500, 4·62; (5) 198–9, 498, 4·67; (6) 217–8, 500, 4·62.

The carriers used were 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 solubilities of dyes I were determined at 80°C, 90°C and 100°C in water in the absence and presence of carriers (0·4 M) according to the procedures described by Bird *et al.*[4] From the saturation solubilities of the dyes, measured in the range 80–100°C, the heats of solution were calculated using the Van't Hoff relationship:[5]

$$\Delta H = -R\frac{\mathrm{d}\ln S_T}{\mathrm{d}(1/T)}$$

where S_T is the solubility (mmol/litre) at T (K).

The kinetic data and the thermodynamic affinities were measured as previously described.[6]

The dyed fibres were tested for wet- and light-fastness according to the literature,[7] using LINITEST and XENOTEST apparatus.

3 RESULTS AND DISCUSSION

The solubility values (S) of the dyes 1–6 in the absence and presence of carriers (0·4 M) at 80°C, 90°C and 100°C together with the corresponding rate constants of dyeing (k) and thermodynamic affinities ($-\Delta\mu$) are reported in Table 1.

TABLE 1

Solubilities (S), Rate Constants (k), Thermodynamic Affinities ($-\Delta\mu$) and Heats of Solution (ΔH) of Dyes I at 80°C, 90°C and 100°C in the Absence and in the Presence of Carriers (0·4 M) in the Dyebath

Dye	*Carrier*	S^a	*80°C* ($k \times 10^2$)^b	$-\Delta\mu^c$	S^a	*90°C* ($k \times 10^2$)^b	$-\Delta\mu^c$	S^a	*100°C* ($k \times 10^2$)^b	$-\Delta\mu^c$	ΔH^d
1	—	0·30	1·0	1·94	0·37	1·5	2·18	0·87	4·0	2·87	11·7
	Ph	0·31	1·7	2·03	0·59	4·8	2·79	0·89	5·4	2·90	12·3
	B	0·36	1·6	2·12	0·51	4·4	2·82	1·01	4·4	2·87	12·1
	S	0·30	1·1	2·38	0·46	3·6	2·79	0·87	6·2	3·37	12·2
2	—	1·70	0·4	−0·12	2·20	0·7	0·19	2·97	1·8	1·29	8·3
	Ph	2·08	0·4	−0·10	2·80	0·7	0·81	3·01	2·0	1·47	7·0
	B	2·21	0·4	0·03	3·12	0·7	0·97	5·39	2·0	1·55	10·8
	S	1·75	0·5	0·37	2·32	0·7	0·56	3·01	2·1	1·18	7·0
3	—	3·04	0·1	−0·68	4·00	0·2	−0·64	3·76	0·2	−0·30	3·1
	Ph	2·79	0·2	−0·65	3·07	0·2	−0·39	3·77	0·3	−0·14	3·9
	B	3·59	0·2	−0·22	5·59	0·2	0·16	6·46	0·2	0·40	7·7
	S	2·77	0·3	−0·14	3·60	0·4	0·11	4·30	0·4	0·24	5·8
4	—	0·17	1·0	2·69	0·27	1·1	2·85	0·31	3·8	3·08	7·9
	Ph	0·18	1·0	2·90	0·29	1·7	3·37	0·40	4·8	3·41	10·5
	B	0·20	1·2	3·16	0·29	2·5	3·41	0·39	3·9	3·64	8·7
	S	0·21	1·5	3·00	0·32	2·6	3·53	0·45	5·8	3·90	10·0
5	—	0·35	0·3	0·69	0·58	0·6	1·07	0·86	1·0	1·61	11·8
	Ph	0·45	0·3	0·68	0·59	0·6	1·15	0·87	1·2	1·62	8·6
	B	0·39	0·3	0·87	0·62	0·7	1·31	1·21	1·0	1·87	14·4
	S	0·41	0·4	1·01	0·54	1·1	1·30	0·85	1·1	1·84	9·5
6	—	2·28	0·2	−1·17	2·84	0·2	−0·05	3·27	0·3	−0·25	4·7
	Ph	2·12	0·2	−1·11	3·00	0·2	−0·52	3·38	0·6	−0·22	6·1
	B	2·09	0·2	−0·85	3·72	0·2	0·50	5·17	0·3	0·78	11·9
	S	2·37	0·2	−0·49	3·00	0·3	0·42	3·50	0·4	0·47	5·1

[a] S = mmol/litre.
[b] $k \times 10^2$ = mmol/(kg s).
[c] $-\Delta\mu$ = kcal/mmol.
[d] ΔH = kcal/mmol.

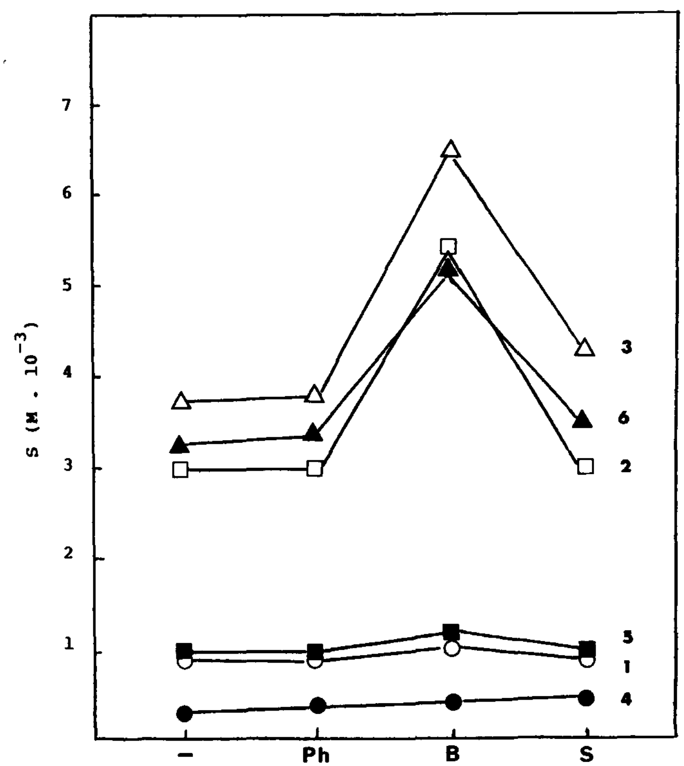


Fig. 1. Solubility values of dyes I at 100°C in the absence and in the presence of carriers (0·4 M) in the dyebath.

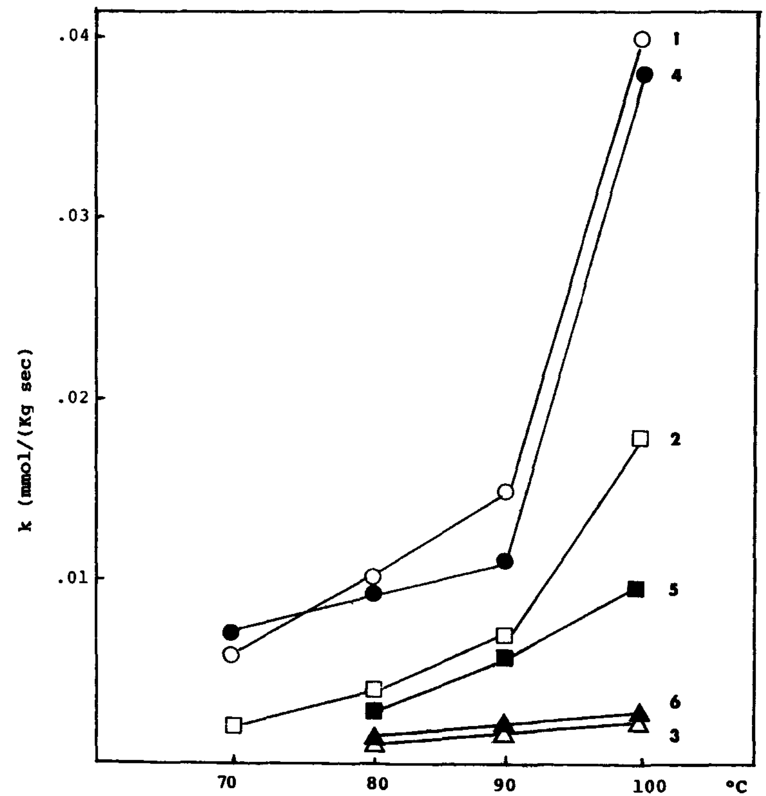


Fig. 2. Temperature effects on the dyeing rate constants of dye I in absence of carriers.

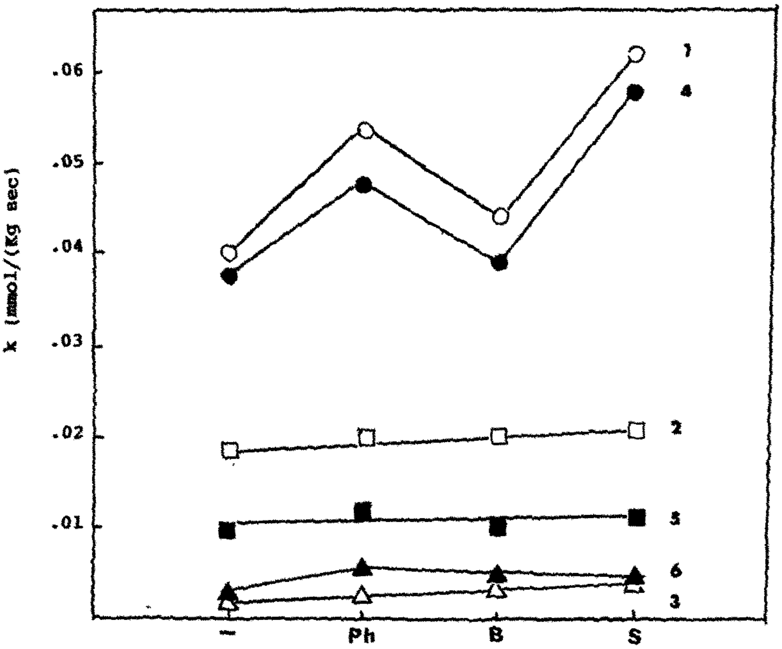


Fig. 3. Carrier effects (0·4 M) on the dyeing rate constants of Dyes I at 100°C.

The solubilities increase on increasing the temperature; the dyes which contain two OH groups are the most soluble, whereas the presence of a methyl group in the thiadiazole ring decreases the solubility. The effect of carriers (0·4 M) is generally negligible, except for benzoic acid which increases the solubility of the dyes with hydroxyl groups (Fig. 1).

The heats of solution depend on the difference between the heat generated by the separation of dye molecules in the crystalline state and that needed for the formation of the dye–water bond. They vary in the range 3–14 kcal/mmol (Table 1). The lowest heats of solution were observed for the derivatives containing hydroxyl groups.

The dyeing rate constants also increase on increasing the bath temperature (Fig. 2). The influence of temperature is more effective with dyes 1 and 4 where the OH groups are absent, whereas only minor effects are observed with dyes 3 and 6 containing two OH groups. An intermediate behaviour is observed with dyes 2 and 5.

The influence of carriers on the dyeing rate constant becomes effective above 90°C, especially for dyes 1 and 4 (Fig. 3).

The affinity values ($-\Delta\mu$) also increase on increasing the bath temperature (Fig. 4); the presence of a methyl group in the thiadiazole ring, and of carriers, also increases the dye affinity for PET (Fig. 5).

The wet- and light-fastness values are reported in Table 2. Dyes 1–6 have

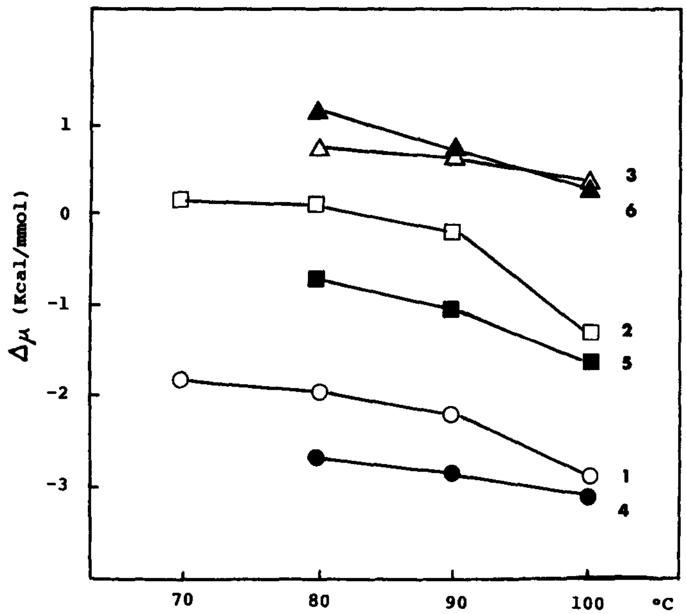


Fig. 4. Temperature effects on the thermodynamic affinity of Dyes I in the absence of carriers.

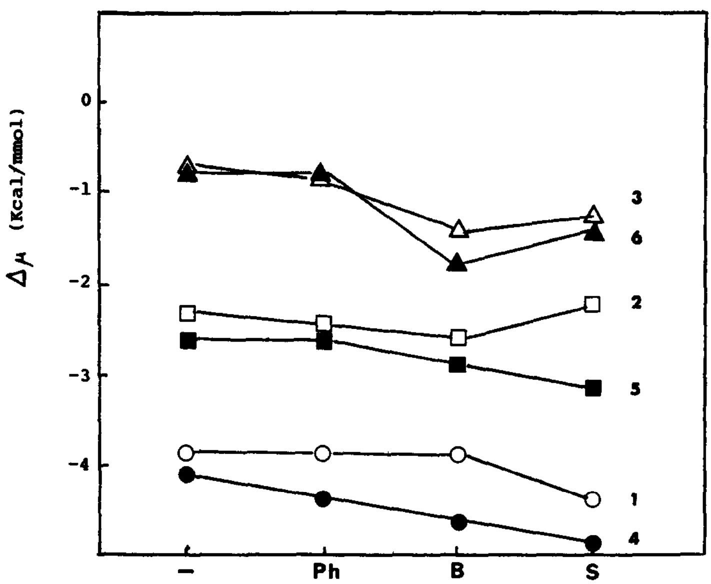


Fig. 5. Carrier effects (0·4 M) on the thermodynamic affinity of Dyes I at 100°C.

TABLE 2
Colour Fastness of Dyes I on the PET at 100°C in the Absence and in the Presence of Carriers (0·4 M) in the Dyebath

Dye	*Carrier*	*Washing*			*Perspiration*		*Light*
		Mild	*Medium*	*Strong*	*Acid*	*Alkali*	
1	—	5	5	4–5	5	5	7
	Ph	5	5	4–5	5	5	7
	B	5	5	5	5	5	7
	S	5	5	5	5	5	6
2	—	5	5	4–5	5	4–5	6
	Ph	5	5	5	5	5	6
	B	5	4	3–4	4	4	5
	S	5	4–5	4	4–5	4–5	5
3	—	5	4–5	4	4–5	4	5
	Ph	5	4–5	4	4	4	5
	B	5	4–5	4	4–5	4	5
	S	5	4–5	4	4–5	5	4
4	—	5	5	4–5	5	5	7
	Ph	5	5	4–5	5	5	7
	B	5	5	5	5	5	7
	S	5	5	4–5	5	5	6
5	—	5	5	4–5	5	5	6
	Ph	5	5	5	5	5	6
	B	5	5	4–5	4–5	4–5	6
	S	5	5	4–5	4–5	5	5
6	—	5	5	5	5	5	5
	Ph	5	5	5	5	5	5
	B	5	5	3–4	4	4	5
	S	5	4–5	4–5	4	4–5	4

good fastness to light, perspiration and cleaning. The colour fastness is lower for dyes with hydroxyl groups,[8] since it depends on the affinity values towards bath and fibre.

In conclusion, dyes bearing two OH groups (3 and 6) show the lowest affinity towards PET because they are more strongly solvated in the aqueous bath. The most hydrophobic dyes (1 and 4) show the highest rates of dyeing and affinity values.

The presence of phenol as carrier increases the rate of dyeing of the less soluble dyes, but it does not influence the affinity values.

An opposite trend is shown by benzoic acid, since it improves the affinity of the dyes for the fibre, but does not increase the kinetics.

Salicylic acid favours the carriage on the fibre of the less soluble dyes, both from a kinetic and thermodynamic point of view.

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