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Carrier Dyeing of Polyester Fibre with some Disperse Azo Dyes

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ABSTRACT

This paper reports the effects of phenol, as a carrier, on the kinetics and thermodynamics of the dyeing of polyester fibre with some substituted benzothiazolyl azo dyes. The dyeing rate constants, the thermodynamic affinity and the apparent diffusion coefficients depend on the carrier concentration and on the dye structure, i.e. the presence of hydroxy groups in the N,N-diethylamino moiety of the coupler and of the phenyl ring between the thiazole and azo group. The results indicate the phenol does not behave by plasticizing the fibre, but it mainly acts as dispersant of the dye in the dyebath.

INTRODUCTION

Polyester fibre is difficult to dye with many disperse azo dyes because of the low rate of dye sorption at temperatures lower than the glass transition temperature ($T_g = 333$–353 K); however, the presence in the dyebath of certain low-molecular-weight compounds (carriers), which are rapidly adsorbed by the fibre, markedly accelerates the dyeing rate.

The chemical structure of the carrier has only slight influence on the glass transition temperature of the fibre, since equimolecular amounts of different carriers cause similar decrements of the T_g values.[1–3] The carrier effect on the dyeing rate thus depends on the dye structure.[2,4–6]

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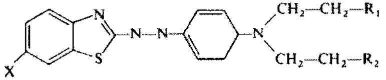
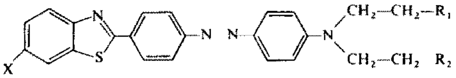
TABLE 1
Chemical Structure and Physical Data of the Disperse Azo Dyes

Dye	*X*	*R*$_1$	*R*$_2$	*M.p.* (°*C*)	*Crystallization solvent*	*Colour*	*Molecular formula*	*Analysis (%)*						*Ref.*
								C		*H*		*N*		
								Found	*Calcd*	*Found*	*Calcd*	*Found*	*Calcd*	
														
1	H	H	H	156–158	Ligroin	Bordeaux	—	—	—	—	—	—	—	10
2	H	H	OH	206–207	Chlorobenzene	Violet	—	—	—	—		—	—	10
3	H	OH	OH	208–209	Chlorobenzene	Violet	—	—		-	—	—	—	10
4	Me	H	H	172–173	Ligroin	Red–bordeaux	—	—			—	-	—	11
5	Me	H	OH	204–206	Toluene	Dark violet	$C_{18}H_{20}N_4OS$	63·58	63·50	5·83	5·92	16 43	16·46	
6	Me	OH	OH	206–208	Chlorobenzene	Violet		—	—					12
7	OMe	H	H	146–147	Toluene	Bordeaux		-						12
8	OMe	H	OH	174–176	Toluene	Dark	—	—	—	—	-	—	—	12
9	OMe	OH	OH	199–201	Chlorobenzene	Dark green	—	—	—	—	—	—	—	12
10	Cl	H	H	162–164	Ligroin	Dark bordeaux	—	—	—	—	—	—	—	11
11	Cl	H	OH	214–215	Toluene	Dark	$C_{17}H_{17}N_4ClOS$	56·50	56·58	4·60	4·75	15 78	15 53	
12	Cl	OH	OH	220–221	Chlorobenzene	Dark violet	—	—	—	—	—	—	—	12
														
13	Me	H	H	214–215	Chlorobenzene	Red–orange	$C_{24}H_{24}N_4S$	71·64	71·97	6·00	6·04	14·09	13·99	
14	Me	H	OH	214–216	Toluene	Red	$C_{24}H_{24}N_4OS$	69·44	69·20	6·00	5 81	13 29	13 45	
15	Me	OH	OH	215–216	Chlorobenzene	Red–bordeaux	—	—	—	—	—	—		13

We have previously reported the effect of carriers on the kinetic and thermodynamic affinities of some disperse dyes in polyester and acrylic fibres,[7–9] and we now report the effects of phenol on the dyeing of polyester with the disperse azo dyes shown in Table 1.

EXPERIMENTAL

The dyes were obtained by diazotization of 6-X-substituted-2-aminobenzothiazoles (X = H, Me, OMe, Cl) and of 6-methyl-2-*p*-aminophenylbenzothiazole followed by coupling with *N*,*N*-diethylaniline, *N*-ethyl-*N*-(2-hydroxyethyl)aniline and *N*,*N*-di(2-hydroxyethyl)aniline. All dyes were purified by crystallization and relevant physical data are reported in Table 1.

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, $T_g = 77°C$).

Carrier application and dyeing kinetics were performed as previously described.[9] At suitable intervals, the amount of dye adsorbed on the fibre was determined spectrophotometrically after extraction with *N*,*N*-dimethylformamide. The rate constants (k) were calculated by the rate law (1), using the least-squares method:

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

where C_D is the concentration of the dye on the fibre at time t.

The values of thermodynamic affinity were calculated by the Vickerstaff equation (2):

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

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 90°C, 100°C and 110°C.

The diffusion coefficient values (D) in polyester fibre were calculated using eqn (3):[7]

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

where C_t and C_∞ are the quantities of dye adsorbed at time t and at equilibrium, respectively, and r is the radius of the filament, measured under the microscope; the value found for r was 0·109 mm. Thus, over the period of time during which the substrate may be regarded as being a semi-infinite cylinder, the relationship obtained when plotting C_t/C_∞ against $\sqrt{t}$ is linear with a slope equal to $4r(D/\pi)^{1/2}$.

RESULTS AND DISCUSSION

The dyeing rate constants (*k*) of the azo dyes **1**–**15**, measured in the absence and in the presence of phenol at different concentrations, increase on increasing the carrier concentration and temperature (Table 2).

The greatest effect is observed for **3**, which contains two OH groups. In the absence of phenol, this dye shows a dyeing rate lower than that of the analogous dyes **1** and **2**, probably because of its higher solubility in the aqueous dyebath.

The presence of Me, OMe and Cl substituents (dyes **4**–**12**) does not noticeably modify the dyeing rate at 100°C in the absence of the carrier. However, *k* values markedly vary with 0·3 mol litre^{-1} of phenol, following the rate order: OMe > Me > H > Cl. The greatest acceleration is always observed for the dyes containing two OH groups.

The dyeing rate constants of the azo dyes **13**–**15**, which have a phenyl ring between the thiazole and azo groups, are lower than those observed for the corresponding dyes **4**–**6**. The presence of the carrier accelerates the kinetics as expected. For these dyes the rate constants increase on increasing the number of OH groups, both in the absence and presence of phenol.

The values of thermodynamic affinity of the dyes **1**–**15** for the polyester fibre are reported in Table 3. The $-\Delta\mu$ values increase on increasing the carrier concentration. Consideration of the affinity values shows that the carrier activity has a greater influence on the equilibrium dye uptake than any other factor. Actually, the carrier would favour both solubility in the dyebath and penetration of the dye into the fibre.

Among the dyes **1**–**12**, the lowest affinity values are associated with dyes bearing two OH groups, which display also the lowest dyeing rates. On the contrary, in the series **13**–**15**, dye **15** which bears two OH groups, shows the highest affinity value.

The highest thermodynamic affinity values reflect the highest dye concentrations on the fibre. Such concentrations result from the balance between the dye absorption (which is proportional to the amount of dye dissolved in the dyebath) and desorption processes.

In dyes **13**–**15** the affinity seems to be ruled by their solubility in the dyebath (in the order **15** > **14** > **13**), probably because the desorption process plays a minor role, due to the greater bulkiness of the hydrophobic moiety compared with that in the series **1**–**12**.

The diffusion coefficients of dyes **1**–**15** on the polyester fibre are reported in Table 4. A small variation is observed for dyes **1**–**12**, but generally the diffusion increases on increasing temperature. The greatest effect occurs in those dyes which bear two OH groups. The X-substituted dyes **4**–**12** also show little variation, but the presence of the phenyl ring in dyes **13**–**15**

TABLE 2

Dyeing Rate Constants (10^2k, mmol kg^{-1} min$^{-1/2}$) of Polyester with Dyes **1–15** in Absence and Presence of Phenol

Dye	*T* (°*C*)	*Phenol concentration*			
		0·0M	0·1M	0·2M	0·3M
1	90	5·70	6·70	9·30	15·50
1	100	12·30	24·10	28·20	29·40
1	110	29·00	31·70	36·60	43·00
2	90	7·00	10·10	13·10	47·20
2	100	9·00	18·70	28·50	54·00
2	110	12·10	36·10	41·90	58·60
3	90	4·00	8·80	15·80	30·00
3	100	6·50	19·20	27·30	50·00
3	110	11·70	21·90	40·10	71·50
4	90	18·80	21·97	23·49	24·50
4	100	23·10	31·88	37·01	42·20
4	110	24·18	37·14	43·50	49·74
5	90	8·80	22·21	37·89	51·25
5	100	21·60	25·50	56·01	99·60
5	110	23·01	30·65	80·23	132·40
6	90	12·50	16·12	41·28	65·20
6	100	21·00	23·80	66·03	99·80
6	110	31·20	38·22	73·15	134·10
7	100	15·80	16·80	23·91	52·30
8	100	23·40	31·45	71·32	113·00
9	100	19·7	25·29	89·88	114·00
10	100	13·70	16·81	20·14	25·50
11	100	14·50	34·38	35·18	37·20
12	100	29·90	30·79	35·31	39·50
13	90	0·18	0·24	0·70	1·10
13	100	0·20	0·29	1·00	1·40
13	110	1·60	1·80	2·10	2·70
14	90	0·36	0·44	0·80	1·60
14	100	0·60	0·90	1·50	2·30
14	110	3·60	4·30	5·20	6·90
15	90	3·00	7·30	9·60	10·10
15	100	6·20	9·30	18·60	19·20
15	110	16·40	18·10	20·20	24·10

TABLE 3

Thermodynamic Affinities (kcal mol^{-1}) of Dyes **1–15** for Polyester in Absence and Presence of Phenol

Dye	*T* (°*C*)	*Phenol concentration*			
		0·0M	0·1M	0·2M	0·3M
1	90	4·11	4·84	5·76	6·06
1	100	4·97	6·09	6·32	6·40
1	110	5·57	6·14	6·48	7·13
2	90	4·16	4·55	4·66	4·78
2	100	5·03	5·46	5·63	6·84
2	110	5·05	5·62	5·73	5·90
3	90	2·90	3·32	3·56	3·63
3	100	2·96	3·44	3·70	4·03
3	110	3·08	3·51	3·81	4·05
4	90	2·01	4·20	4·21	4·23
4	100	3·97	4·43	4·89	5·07
4	110	4·45	4·56	5·01	5·42
5	90	3·49	4·08	4·12	4·15
5	100	4·23	4·32	4·77	5·68
5	110	4·36	4·67	5·23	5·54
6	90	2·67	2·93	3·30	3·41
6	100	3·34	3·45	3·60	3·77
6	110	3·48	3·55	3·71	3·89
7	100	4·17	6·85	6·87	7·06
8	100	3·80	4·06	6·93	4·60
9	100	2·17	3·13	3·20	3·41
10	100	3·07	3·88	4·50	4·95
11	100	3·50	4·62	5·03	5·30
12	100	1·40	3·21	3·78	3·90
13	90	2·19	3·14	4·05	4·14
13	100	2·37	3·21	4·38	5·47
13	110	3·32	4·11	4·49	5·54
14	90	2·48	2·84	4·16	4·57
14	100	3·04	3·64	4·61	5·23
14	110	3·35	4·48	4·87	5·95
15	90	3·08	4·59	5·01	5·52
15	100	3·73	4·92	5·76	6·51
15	110	3·76	5·06	5·87	6·62

TABLE 4

Diffusion Coefficients ($10^2 D$, mm^2 min^{-1}) of Dyes **1–15** into Polyester in Absence and Presence of Phenol

Dye	*T* (°*C*)	*Phenol concentration*			
		0·0M	0·1M	0·2M	0·3M
1	90	3·0	2·7	2·9	2·9
1	100	3·4	3·4	3·4	3·2
1	110	3·8	3·8	3·4	3·3
2	90	2·7	2·5	2·4	1·9
2	100	3·5	3·2	3·0	2·9
2	110	4·1	3·9	3·7	3·5
3	90	8·1	7·8	7·6	4·7
3	100	8·4	8·1	7·8	7·5
3	110	12·4	12·1	11·7	11·4
4	90	6·0	5·5	4·4	3·8
4	100	6·8	5·9	4·8	3·9
4	110	7·2	6·0	5·0	4·1
5	90	10·2	10·0	10·0	9·9
5	100	11·4	11·2	10·7	10·5
5	110	12·3	11·4	11·0	10·4
6	90	10·8	10·5	10·0	9·5
6	100	11·1	10·9	10·7	10·2
6	110	11·6	11·0	11·0	11·0
7	100	6·3	6·0	4·9	3·4
8	100	19·7	16·6	14·1	12·8
9	100	42·5	35·7	22·0	14·6
10	100	7·3	6·3	4·7	4·9
11	100	13·5	12·0	7·2	8·1
12	100	16·2	15·0	11·6	10·2
13	90	0·6	0·5	0·3	0·2
13	100	1·8	0·8	0·5	0·5
13	110	7·8	4·7	1·6	1·6
14	90	0·7	0·5	0·3	0·1
14	100	0·8	0·8	0·5	0·2
14	110	11·1	4·1	2·2	0·3
15	90	13·3	4·1	3·2	1·3
15	100	15·2	6·3	3·5	2·0
15	110	25·7	14·6	4·7	2·2

markedly decreases the coefficients because of the more difficult diffusion of these dyes into the fibre due to their greater molecular volume.

The overall results (kinetics, thermodynamic affinities and diffusion coefficients) indicate that phenol does not behave by plasticizing the fibre, but it acts mainly as dispersant of the dye in the dyebath.

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