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Note

Thin-layer chromatographic investigation of the interaction between dispersed dyes and hydrotropic agents

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When dyeing and printing polyester material, auxiliary agents are added so as to render the dyes more dispersive and more soluble in water, for the purpose of fixing a greater quantity of dyes in the textile substrate. Salts, alcohols, acids and carbonyl compounds, in particular, have been widely used for this purpose[1]. Flow fixation of dispersed dyes at 180–210°C is a prerequisite for interaction between the dyes and the hydrotropic agents: the dyes possess –X (halogen), –OH or NH_2 groups, while hydrotropic agents at high temperatures decompose into products which are reactive towards the dyes. For instance, urea, which is a hydrotropic agent universally applied in the textile industry at high temperatures, decomposes into melamine, cyanuric acid, biuret, ammonium isocyanate, etc., and reacts itself with organic halogenides, alcohols, fatty and aromatic amines[2]. Another hydrotropic agent, urotropin, which is the object of the present study, forms complexes with organic halogenides, while with many aromatic compounds it interacts as a formative agent; at high temperatures it decomposes into ammonia and formaldehyde, which is capable of binding dye molecules having methylene bridges at the –OH and NH_2 groups[3].

The aim of this study was to use thin-layer chromatography (TLC) to establish whether dispersed dyes interact with the hydrotropic additives caprolactam and urotropin, which can be used as intensifiers in dyeing baths and printing pastes with dispersed dyes[4,5]. The well-known hydrotropic substances urea and ethylene carbonate have been included in this investigation for the sake of comparison.

EXPERIMENTAL

The dyes investigated were CI Disperse Yellow 48005, CI Disperse Red 54, CI Disperse Orange 30, CI Disperse Red 167 and CI Disperse Blue 73.

Melts or purified dyes only and of their mixtures with hydrotropic agents were subjected to TLC. The melts were prepared by annealing physical mixtures of both components in the air at a rate of 50°C/min to 210°C. The gravimetric ratio between the components was analogous to that employed in practice: in this case, urea and urotropin were mixed with the dye pigment in the ratio 10:4, and caprolactam and ethylene carbonate in the ratio 1:1. The melts with ethylene carbonate remained liquid at room temperature. The melts were dissolved in acetone and were separated

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on a silica gel G layer (Merck) applied in the form of a suspension of 10 g silica gel G + 21.7 ml water with a 0.5-mm thickness on 100 × 140 mm glass plates. The following organic solvent systems were used[6]: S_1 = *n*-hexane–ethyl acetate–acetone (5:4:1); S_2 = light petroleum–tetrahydrofuran–acetone (6:2:1); S_3 = benzene–methanol–acetone (20:2:1); S_4 = benzene–ethyl acetate (1:1).

RESULTS AND DISCUSSION

Melts of the pure hydrotropic substances gave no coloured spots. Twenty chromatograms (of five dyes in four solvent systems) were obtained: of these 12 were

TABLE I

R_F VALUES OF THE SPOTS OF THE CHROMATOGRAMS SHOWN IN FIGS. 1–5

Spot colours: y = yellow; o = orange; v = violet; b = blue; r = red; i = indefinite.

Fig. No.	*Dye and solvent system*	*R_F values and spot colours*								
1a	Disperse Yellow 48005, S_1	0.12 o-y	0.20 y	0.37 y	0.45 y	0.59 y	0.68 y	0.72 y		
1b	Disperse Yellow 48005, S_2	0.09 i	0.15 o-y	0.21 i	0.28 o-y	0.40 y	0.47 y			
1c	Disperse Yellow 48005, S_4	0.09 o-y	0.14 o-y	0.29 o-y	0.47 y	0.73 y				
2a	Disperse Red 54, S_1	0.05 o	0.18 y	0.26 r	0.38 o	0.46 y	0.65 r	0.82 r		
2b	Disperse Red 54, S_4	0.15 o-y	0.29 o-y	0.35 o-y	0.65 o-y	0.72 r	0.84 r			
3a	Disperse Orange 30, S_1	0.10 o	0.38 o	0.67 o	0.71 v					
3b	Disperse Orange 30, S_3	0.06 o	0.21 o	0.34 o	0.43 o	0.50 o	0.54 o	0.68 v	0.74 o	
3c	Disperse Orange 30, S_4	0.10 o	0.25 o	0.42 y	0.48 v	0.63 i	0.75 o	0.87 v		
4a	Dispersed Red 167, S_1	0.10 o	0.22 y	0.28 o	0.31 r	0.38 i	0.44 i	0.52 r	0.60 r	0.69 i
4b	Disperse Red 167, S_3	0.11 r	0.14 o	0.22 r	0.40 r	0.69 r				
4c	Disperse Red 167, S_4	0.07 r	0.25 i	0.34 r	0.60 r	0.68 r	0.75 r	0.80 y		
5	Disperse Blue 73, S_3	0.09 i	0.16 i	0.35 i	0.52 v	0.63 v	0.70 i	0.87 b	0.97 i	

selected, where the dyes separated into more spots and yielded more information (Figs. 1–5). The R_F values and spot colours are given in Table I.

As can be seen from Fig. 1, the dye reacts with ethylene carbonate. The main part of the dye gives spots with R_F values of 0.59, 0.47 and 0.47 in Fig. 1a, 1b and 1c respectively. In the presence of ethylene carbonate a new spot with an R_F value of 0.37 appears in Fig. 1a, two spots with R_F values of 0.15 and 0.28 in Fig. 1b and two spots with R_F values of 0.14 and 0.29 in Fig. 1c. In contrast to the spots of the starting dye CI Disperse Yellow 48005, the products of its interaction with ethylene carbonate are orange-yellow and yellow. It may be assumed that the ethylene carbonate decarboxylates and that the ethylene residue binds two dye molecules or joins itself to one molecule. This means that, under favourable interaction conditions with some dispersed dyes, ethylene carbonate may produce a change in the shade of the dyed or printed textile material. As can be seen in Fig. 1, the CI Disperse Yellow 48005 dye also reacts with urotropin; the interaction product remains at the start, with a modified deep orange shade.

The CI Disperse Red 54 dye reacts with urotropin, the orange-yellow product remaining at the start. The intensity of the spots at the start is very strong, while the intensity of the two main spots into which the dye separates, with R_F values of 0.26 and 0.65 in Fig. 2a and of 0.35 and 0.72 in Fig. 2b, decreases.

In the case of CI Disperse Orange 30 (Fig. 3) it can categorically be stated that urotropin interacts with a part of the dye. This is borne out by the new violet spot observed, whose respective R_F values are 0.68 (3a), 0.71 (3b) and 0.87 (3c); the mobility of this spot is close to that of the starting spot with corresponding R_F values of 0.67, 0.74 and 0.75. A number of spots of undefined products also appear in the form of a broken up tail. The chromatograms obtained do not permit us to claim that this dye interacts with the other hydrotropic substances.

The CI Disperse Red 167 dye, too, interacts with urotropin and its disintegration products to give compounds of varying composition, which move like a tail

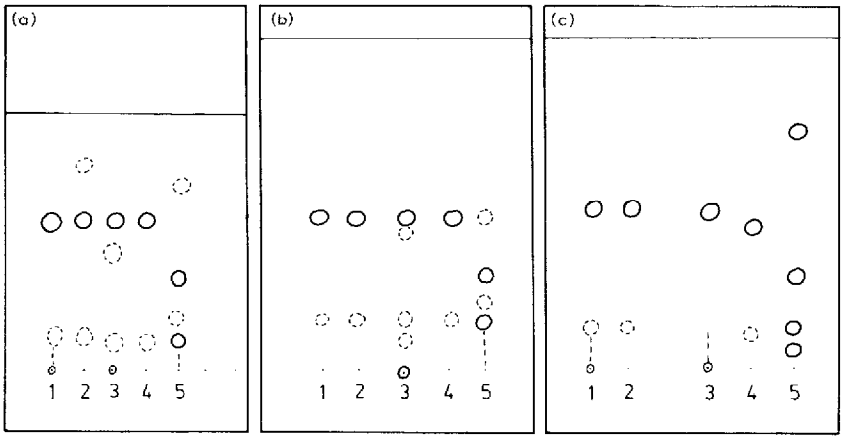

Fig. 1. TLC chromatograms of melts of CI Disperse Yellow 48005. Solvent systems: a, S_1; b, S_2; c, S_3. 1, Melt of purified dye; 2, melt of dye + urea; 3, melt of dye + urotropin; 4, melt of dye + caprolactam; 5, melt of dye + ethylene carbonate.

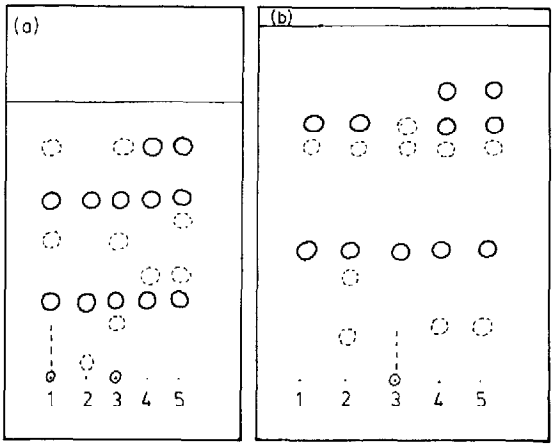

Fig. 2. TLC chromatograms of melts of CI Disperse Red 54. Solvent systems: a, S_1; b, S_4. Melts as in Fig. 1.

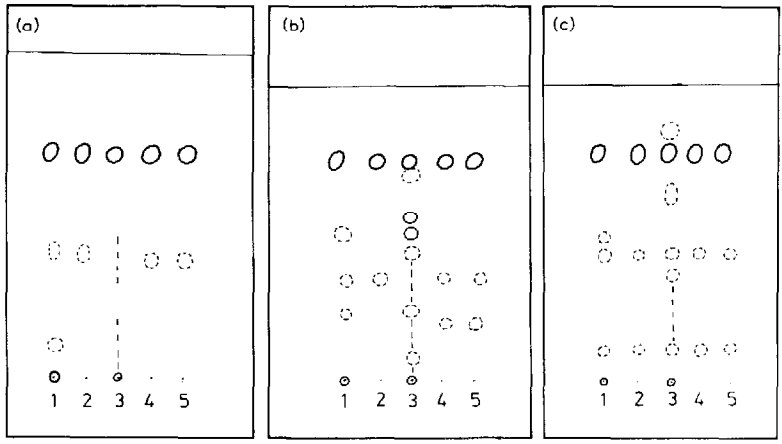

Fig. 3. TLC chromatograms of melts of CI Disperse Orange 30. Solvent systems: a, S_1; b, S_3; c, S_4. Melts as in Fig. 1.

containing orange and yellow spots (Figs. 4). The dye itself moves with one main intense spot having R_F 0.60 (4a), 0.69 (4b) and 0.68 (4c).

With all solvent systems the CI Disperse Blue 73 dye gave two main spots, a violet and a blue one, the latter being the more intense and the former probably belonging to a by-product of dye synthesis. The chromatograms do not suggest any interaction of the dye with the investigated hydrotropic substances (Fig. 5).

None of the five investigated dispersed dyes showed an interaction with caprolactam. The same cannot be said for urea, as in Fig. 2b with the CI Disperse Red 54 dye there appears, where the melt breaks up into urea and dye, an additional orange-yellow spot with an R_F value of 0.29, which is not encountered in the other samples.

Among the investigated combinations of dye and hydrotropic substance, uro-

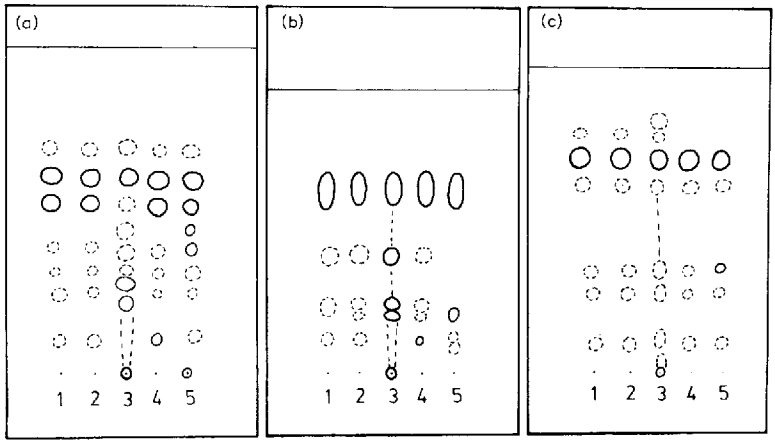

Fig. 4. TLC chromatograms of melts of CI Disperse Red 167. Solvent systems: a, S_1; b, S_3; c, S_4. Melts as in Fig. 1.

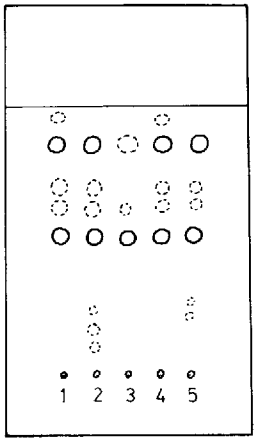

Fig. 5. TLC chromatogram of melts of CI Disperse Blue 73. Solvent system: S_3. Melts as in Fig. 1.

tropin interacts most frequently and ethylene carbonate to a lesser degree. The interaction product may be obtained on the fibre's surface or in the textile's substrate. A precipitation at the surface would tend to get the ruberfastness worse, while in the substrate interaction products would migrate and do not sublimate easily. Changes in shade are, of course, undesirable.

In conclusion, the TLC method can be recommended for investigating the interaction of dyes with auxiliary agents under the conditions of textile manufacture. Of the four hydrotropic substances investigated, urea, caprolactam, urotropin and ethylene carbonate, only the first two can be recommended as intensifiers of dispersed dye fixation, when dyeing and printing polyester textiles. Experience has shown that the purity of the colour is often dulled, when using urea. Bearing in mind the quantity of hydrotropic substance necessary for a maximal intensification effect (*ca.* 100 g/kg)

or for high-temperature fixation methods, the use of caprolactam is preferred because the optimal amount added is 5–10 g per kg dyeing bath or printing paste.

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