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# Thin-layer chromatographic separation of new direct dyes

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The direct dyes belong to the most diverse and heterogeneous group of azo dyes. They continue to be of interest, regardless of the low values of some of their dye fastness indices, mainly because of the easily achievable process of dyeing, the possibility of covering a greater colour scale in comparison with other classes of dyes and the applicability of comparatively simple techniques for their production. Generally, the methods for the production of direct dyes involve multi-stage syntheses and use technical-grade initial products, so that account the dyestuffs obtained contain intermediate compounds or isomeric dyes as admixtures. The latter affect the quality of the ultimate toning and lead to demands for constant compositions of dyestuffs by dye consumers. Thin-layer chromatography is very suitable for rapid and highly effective laboratory quality control of materials in individual stages during dye production and in the textile industry.

This work was aimed at establishing appropriate conditions for the application of thin-layer chromatography in the characterization of direct dyes obtained on the basis of terephthaloylaminonaphtholsulphonic acids.

## EXPERIMENTAL

The chromatographic systems reported in the literature[1–5] did not give satisfactory results when applied to the dyes, which led us to seek new systems that would separate the investigated mixtures into the maximum number of well outlined spots. The following solvents were investigated: methanol, ethanol, *n*-propanol, isopropanol, *n*-butanol, isobutanol, isoamyl alcohol, acetone, ammonia ($NH_3$), pyridine, dimethylformamide (DMF) and water in different proportions and combinations. All solvents are purified in advance[6].

Standard Kieselgel 60 silica gel plates (Merck) deposited on aluminium foil with a layer thickness of 0.2 mm were used as carriers. The dyes were introduced as 0.1% solutions. Thin-layer chromatographic separation of nine direct dyes (Table I) was carried out.

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TABLE I

RESULTS OF CHROMATOGRAPHIC STUDY OF THE DYES

| *Dye* | *Initial products* | | | | | | *Dyes* | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | *Azo component* | | *Diazo component* | | | *Degree of attachment (%)* | *Colour of spot** | $R_F$ | | $\lambda$ | |
| | *Compound* | $R_F$ | *Amino compound* | $R_F$ | $R_F$ *of diazonium salt* | | | $S_1$ | $S_2$ | *In water* | *In* $S_1$ *and* $S_2$ |
| 1 | Terephthaloyl I-acid | 0.51 | Anthranilic acid | 0.66 | 0.86 | 77.4 | Orange | 0.59 | — | 485; 500 | 490; 510 |
| | | | | | | | Orange-red | 0.67 | — | 480; 500 | 485; 510 |
| 2 | | 0.51 | *p*-Nitroaniline | 0.85 | 0.85 | 88.4 | Orange | 0.70 | — | 485 | 485 |
| | | | | | | | Brown | 0.75 | — | — | — |
| | | | | | | | Red | 0.78 | — | 405; 495 | 405; 515 |
| | | | | | | | Light brown | 0.82 | — | — | — |
| | | | | | | | Orange-red | 0.86 | — | 480 | 505 |
| | | | | | | | Red | 0.89 | — | 405; 495 | 415; 525 |
| 3 | | 0.51 | Sulphanilic acid | 0.86 | 0.59 | 73.8 | Light brown | 0.59 | — | — | — |
| | | | | | 0.71 | | Orange-red | 0.61 | — | 400; 488 | 400; 500 |
| | | | | | | | Orange-red | 0.66 | — | 400;490 | 400; 490 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 4 | | 0.51 | 4-Chloro-2-Aminophenol | 0.82 | 0.75 | 85.0 | Brown | 0.60 | – | – | – |
| | | | | | | | Light brown | 0.71 | – | – | – |
| | | | | | | | Red-violet | 0.84 | – | 480 | 510 |
| 5 | | 0.51 | 4-Nitroaniline-2-sulphonic acid | 0.81 | 0.59 | 76.6 | Brown | 0.59 | – | – | – |
| | | | | | 0.81 | | Orange | 0.64 | – | 455 | 610 |
| | | | | | | | Orange | 0.72 | – | 455 | 570 |
| | | | | | | | Red-violet | 0.80 | – | 510 | 515 |
| 6 | Terephthaloyl H-acid | 0.48 | Anthranilic acid | 0.66 | 0.76 | 78.9 | Red-violet | – | 0.12 | 500; 530 | 520;550 |
| | | | | | | | Red-violet | – | 0.41 | 500; 530 | 520; 550 |
| | | | | | | | Red-violet | – | 0.46 | 510; 540 | 520; 550 |
| 7 | | 0.48 | *p*-Nitroaniline | 0.89 | 0.95 | 75.3 | Violet | – | 0.31 | 530; 580 | 520; 550 |
| | | | | | | | Red-violet | – | 0.36 | 525 | 540 |
| | | | | | | | Brown | – | 0.40 | – | – |
| 8 | | 0.48 | *p*-Toluidine | 0.94 | 0.62 | 73.3 | Red-Violet | – | 0.51 | 508; 540 | 510; 550 |
| | | | | | 0.67 | | Red-violet | – | 0.54 | 508; 540 | 508; 540 |
| 9 | | 0.48 | 4-Nitroaniline-2-sulphonic acid | 0.78 | 0.81 | 78.4 | Light brown | – | 0.08 | – | – |
| | | | | | | | Brown | – | 0.24 | – | – |
| | | | | | | | Red-violet | – | 0.50 | 525 | 540; 555 |
| | | | | | | | Red-violet | – | 0.52 | 510 | 530; 555 |

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* The change in the colour of these spots on the plates is due to the variations in the pH of the medium during the process of their drying.

The best chromatographic behaviour was observed with systems $S_1$ (*n*-butanol–DMF–25% $NH_3$, 4:2:3.5) for dyes 1–5 and $S_2$ (*n*-propanol–acetone–25% $NH_3$, 1.5:1.5:1) for dyes 1–6.

A change in the polarity of the system varied the solubility of the dyes. The movement of the spots was delayed and tailing was observed on increasing the proportion of DMF in system $S_1$ and a decrease led to a decrease in the separating ability of the system. The poor chromatographic behaviour of dyes 6–9 in system $S_1$ and of dyes 1–5 in system $S_2$ is explained by the higher polarity of system $S_1$ compared with $S_2$ and the higher solubility of dyes 6–9 in system $S_1$ compared with dyes 1–5.

An increase in the content of *n*-propanol in system $S_2$ delayed and deformed the spots whereas an increase in the ammonia content moved the spots with the front and reduced the separating ability of the system.

The very good chromatographic behaviour obtained for the studied dye mixture allow systems $S_1$ and $S_2$ to be used for the preparative quantitative isolation of the compounds of interest to us.

The direct dyes studied have very good solubility in water and DMF and hence these two solvents were tried as eluents. Water did not give satisfactory results although it apparently has a better eluting ability than DMF owing to its ability to form colloidal systems with silica gel, which prevents its complete separation from the eluate.

The presence of silica gel in the isolated compounds led to errors. For example, the presence of silica gel shielded the absorption bands in the range 1100–1200 cm$^{-1}$ when recording IR spectra and varied the absorptivity when recording visible spectra because the spectrophotometric solutions became turbid.

In view of the above, was chosen as the eluent regardless of its comparatively high boiling point. The used was purified by azeotropic distillation with benzene followed by fractional vacuum distillation[6].

Silica gel was removed by filtration using a Nutsche filter. The complete removal of fine particles of silica gel was achieved using the method of Székely[7] and Amos[8].

The isolated compounds were investigated by visible and IR spectrophotometry. Distilled water and the chromatographic systems $S_1$ and $S_2$ for dyes 1–5 and 6–9, respectively, were used as solvents when recording the visible range absorption spectra as it is observed that some of the compounds showed variations in their colour on drying the chromatographic plates.

Textile samples of 100% cotton were dyed with the synthesized dyes using the classical method and the degree of attachment was determined (Table I). The visible spectra of the dye batch before and after dyeing of the samples were also recorded.

## RESULTS AND DISCUSSION

The results presented in Table I and Figs. 1 and 2.

The chromatographic results show that the investigated direct dye derivatives of terephthaloylaminonaphtholsulphonic acids are not homogeneous products. The characterization of the individual components in this instance cannot be entirely based on the chromatographic results because preliminary information about the

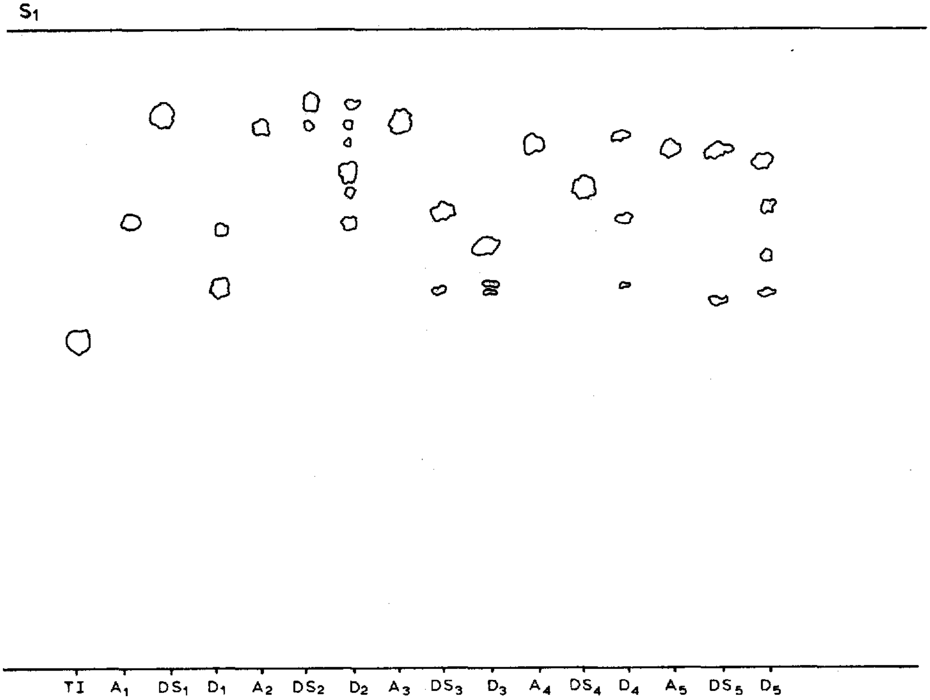

Fig. 1. Chromatograms of dyes 1–5 and their initial products in system $S_1$. $A_n$ = Initial amine; $DS_n$ = diazonium salt; TI = azo component; $D_n$ = dye.

compounds obtained is lacking. The presence of spots with identical $R_F$ values (Fig. 1) was observed with dyes 1–6 on comparing the chromatographic behaviour of the initial and end products. The suggestion that the dye mixtures obtained contain chemically unchanged initial products is not justified because they give spots differing in colour when used as standards. This conclusion was confirmed by the chromatographic investigations carried out here.

The behaviour of dye 1 in system $S_1$, which gives two spots, can be considered as an example. The spectral curves of the two components recorded in the visible region are identical in both instances. The high degree of attachment and the correspondence between the visible spectra of the dye bath before and after the dyeing indicate that both compounds behave like direct dyes. The presence of two components can be explained by the formation of isomeric dyes by comparing the results given here. This suggestion can explain the shift of the absorption maxima in the longwave region when visible-range spectrophotometry is carried out in systems $S_1$ and $S_2$. Analogous reasoning and assumptions can be applied to dyes 3, 6 and 8.

The heterogeneity of dye mixtures, based on the experimental data, can be explained by the occurrence of side reactions and with the formation of intermediate products. For example, the compounds with $R_F$ = 0.64 and 0.72 that appear when dye 5 is considered do not behave like direct dyes and are probably low-molecular-weight coloured compounds. The dyeing of the sample is due to the presence of the component with $R_F$ = 0.80. The reasoning is based on the visible spectra of the

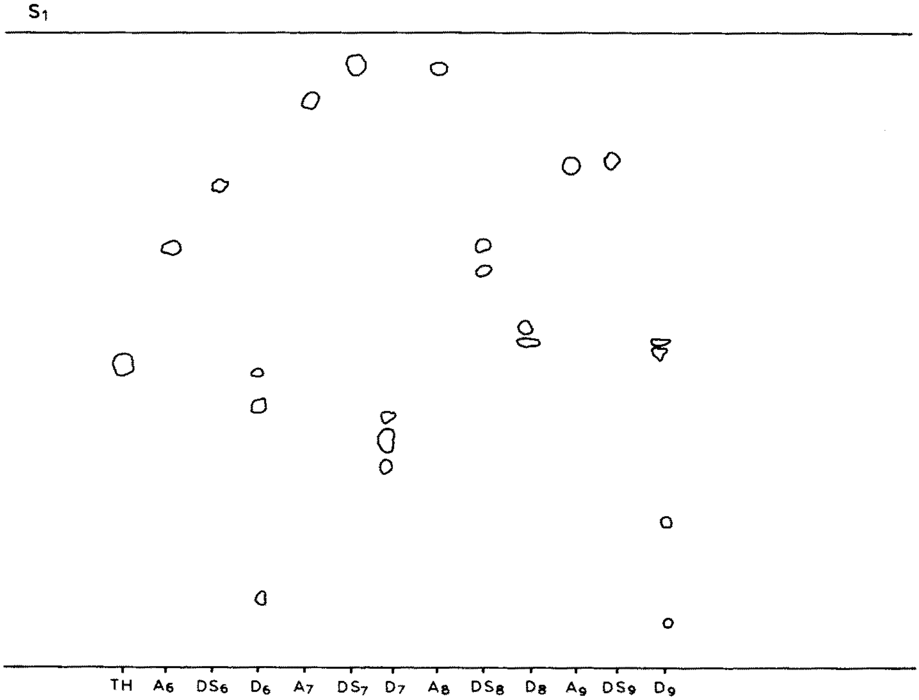

Fig. 2. Chromatograms of dyes 6–9 and their initial products in System $S_2$. $A_n$ = Initial amine; $DS_n$ = diazonium salt; TH = azo component; $D_n$ = dye.

individual spots and of the dye bath before and after the process of dyeing. Analogous reasoning can be applied to dyes 2, 4, 7 and 9.

The spectral data obtained and the results of other physico-chemical methods (NMR spectroscopy, elemental analysis) would have allowed definite conclusions to be drawn about the kind of isomerization of the dyes and the structures of the intermediate and side products. The elucidation of the structure of each compound in a given dye mixture will provide, by the application of the TLC method reported here, rapid and detailed information about the direction of the reactions involved in their synthesis.

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