PAPER CHROMATOGRAPHY OF DYES
IV. PAPER CHROMATOGRAPHY OF WATER-SOLUBLE DYES

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INTRODUCTION

In previous reports paper chromatography of water-insoluble dyes, namely, disperse dyes[1], vat and sulphur dyes[2], was described, and the subject of the chromatography of indigosols[3] was discussed. Although the latter are water-soluble, they are prepared by solubilizing insoluble vat dyes.

In the present paper, a chromatographic method suitable for water-soluble dyes is described. These dyes represent some 50 % of the total volume of the annual world production of coal tar dyestuffs, amounting to about 200,000 tons. Water-soluble dyes are manufactured practically by all dye producers and the number of trade products at present on the market reaches several thousand. Individual trade products of the various dye manufacturers are frequently identical, a fact easily shown by paper chromatography. The individual dyes, however, differ from each other in purity. The reaction mechanism of dye synthesis is of a complicated and manifold nature. For this reason the impurities occurring in the dye very frequently consist of other dyes or intermediates formed during the course of the reaction. The non-uniformity of the dye mostly depends on the degree of purity of the intermediates and on the tautomerism of the products likely to form isomers. Unreacted intermediates, isomers and other impurities, must be regarded as the main cause of the non-uniformity of dyes. Dyes are either pure homogeneous, *i.e.* they are free from any secondary dye impurities which might have been formed in the course of the dye synthesis itself, or shaded, *i.e.* they contain a small amount of another dye so that the desired shade is obtained, or lastly miscellaneous, these are formed by intentional mixing of several fundamental dyes.

In the selection of dyes for purposes of industrial application, purity of the dye is of great importance, influencing the dyeing technology. For the purity estimation of dyes and of their dyeing behaviour, paper chromatography is of paramount importance.

Water-soluble dyes are represented by a number of organic compounds with typical properties, either derivatives of aromatic hydrocarbons or of heterocyclic compounds of aromatic character. The chromatographic behaviour of these dyes depends generally on the complexity, shape and size of the dye molecule; its functional groups, their nature and positions, the nature of the bonds, and the ionic as well as electrostatic character of the molecules (*e.g.* on polarity and polarizability).

The subject of paper chromatography of water-soluble dyes has already been dealt with by numerous authors[4-12]. A check of the methods described revealed their unsuitability for a comprehensive systematic analysis of dyes of all chemical classes. In most cases, the results of the separation did not confirm the relation between the structure of the dye and its chromatographic behaviour and were not in accordance with the laws of partition chromatography.

In view of the technological importance of these dyes, we have turned our attention to the development of a chromatographic method, by means of which it should be possible, under equal chromatographic conditions, to compare the properties of water-soluble dyes of all chemical classes[13-16].

EXPERIMENTAL

For a systematic analysis of water-soluble dyes of all chemical classes a descending chromatographic technique using Whatman No. 1 paper and a solvent system composed of pyridine–isoamyl alcohol–25% ammonia (1.3:1:1) has proved to be most suitable. This system also gives satisfactory results with a solvent ratio of 1:1:1; its effectiveness remaining the same even when the ratio of pyridine is increased up to 1.9:1:1. Increasing the quantity of pyridine increases the sharpness of the zones, but this is already optimal when the ratio of the components is 1.3:1:1. This solvent system possesses sufficient sensitivity to detect differences in chemical composition and structure of dyes of individual manufacturers and permits chromatographic separation of very complex mixtures of dyes.

The separating properties of the isoamyl alcohol solvent system are also evident with a butan-1-ol–pyridine–water (1:1:1) system. For the determination of the purity of highly substantive azo dyes a butan-1-ol–pyridine–water (0.5:1:1) solvent system was used.
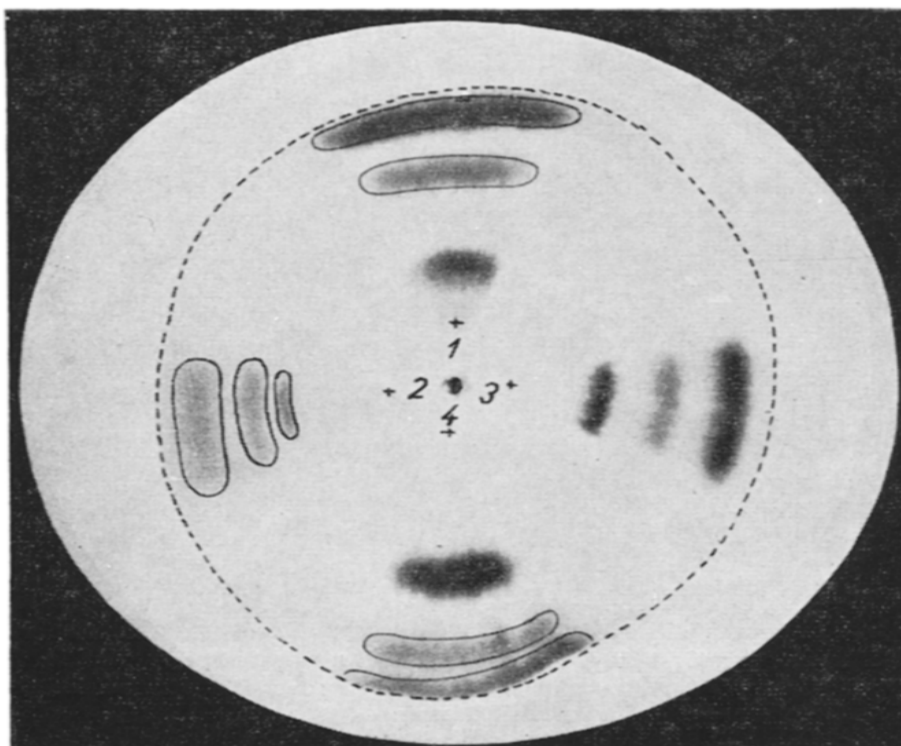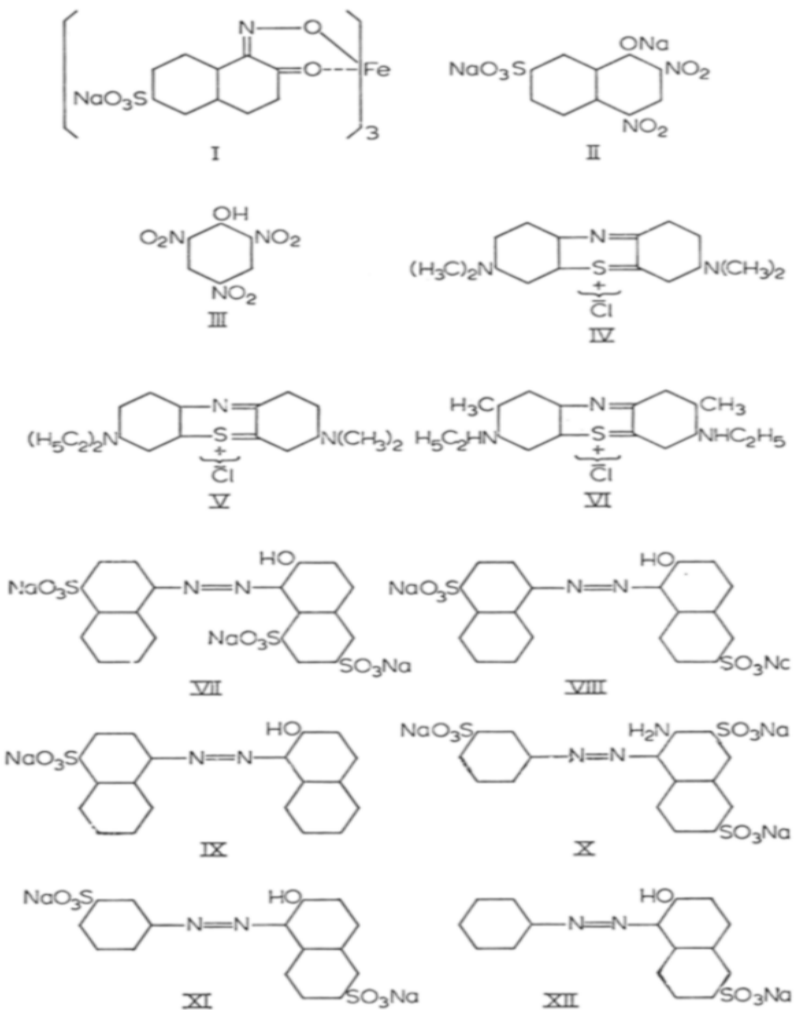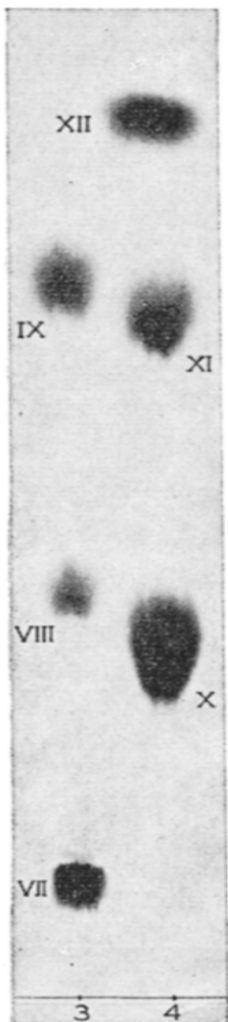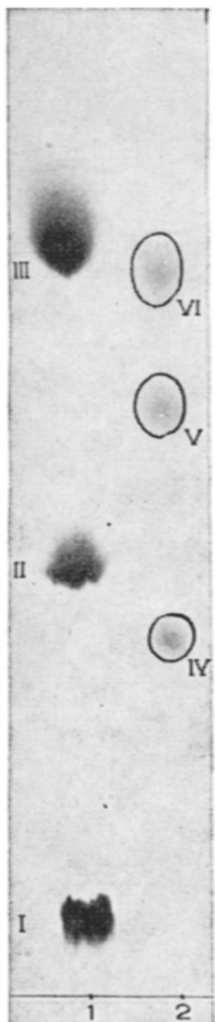
Method

0.1 µl samples of 1% aqueous solution of water-soluble dye are applied as spots on the start of the chromatogram by means of a micro-pipette. The size of the chromatogram is 160 × 470 mm, the distance of the start from the edge of the paper being 70 mm. The dyes are spotted on the start at intervals of 20 mm from each other. Development of the chromatogram takes place at a temperature of 20–22° for 12 h (preferably overnight) and the length of the run is 400 mm.

RESULTS AND DISCUSSION

Water-soluble dyes of all chemical classes were chromatographed by the method described above, employing an isoamyl alcohol system.

This isoamyl alcohol system is compatible with the conditions of partition chromatography and particularly distinguishes between differences in the partition

Fig. 1. The influence of the flow rate of the isoamyl alcohol solvent system on the quality of separation. A. Descending technique. B. Centrifugal technique. 1. Mixture of nitroso and nitro dyes (I, II, III). 2. Mixture of thiazine dyes (IV, V, VI). 3. Mixture of monoazo dyes (derivatiives of azonaphthalene, VII, VIII, IX). 4. Mixture of monoazo dyes (derivatives of benzeneazo-naphthalene, X, XI, XII).

III
VI
V
II
IV
I
1 2

XII
IX
XI
VIII
X
VII
3 4

I

II

III

IV

V

VI

VII

VIII

IX

X

XI

XII

+
1
+2 3+
4
+

Fig. 2. An example of the separation of a mixture of eight pyrazolone dyes. Methyl derivatives have higher R_F values than carboxy derivatives. A. Descending technique. B. Centrifugal technique.

coefficients and in the solubility of the dyes. For instance, the rate of flow of the solvent system through the paper, which with most systems not compatible with the conditions of partition chromatography, influences the reproducibility of results, fails here to exert any effect whatsoever. This was shown by applying this solvent system in chromatography in a centrifugal field, where the rate of flow of the solvent system through the paper increases many times. Results obtained with chromatograms in a centrifugal field and by the normal descending method were identical. Figs. 1 and 2 show the influence of the flow rate of the isoamyl alcohol solvent system on the quality of separation, the descending and centrifugal chromatographic techniques being compared.

Centrifugal chromatography was carried out with the pressureless apparatus with central spot development described previously by PAVLÍČEK, ROSMUS AND DEYL[17, 18]. The chromatograms were cut from Whatman No. 3 paper and the separa-

TABLE I

MEAN R_F VALUES OF WATER-SOLUBLE DYES

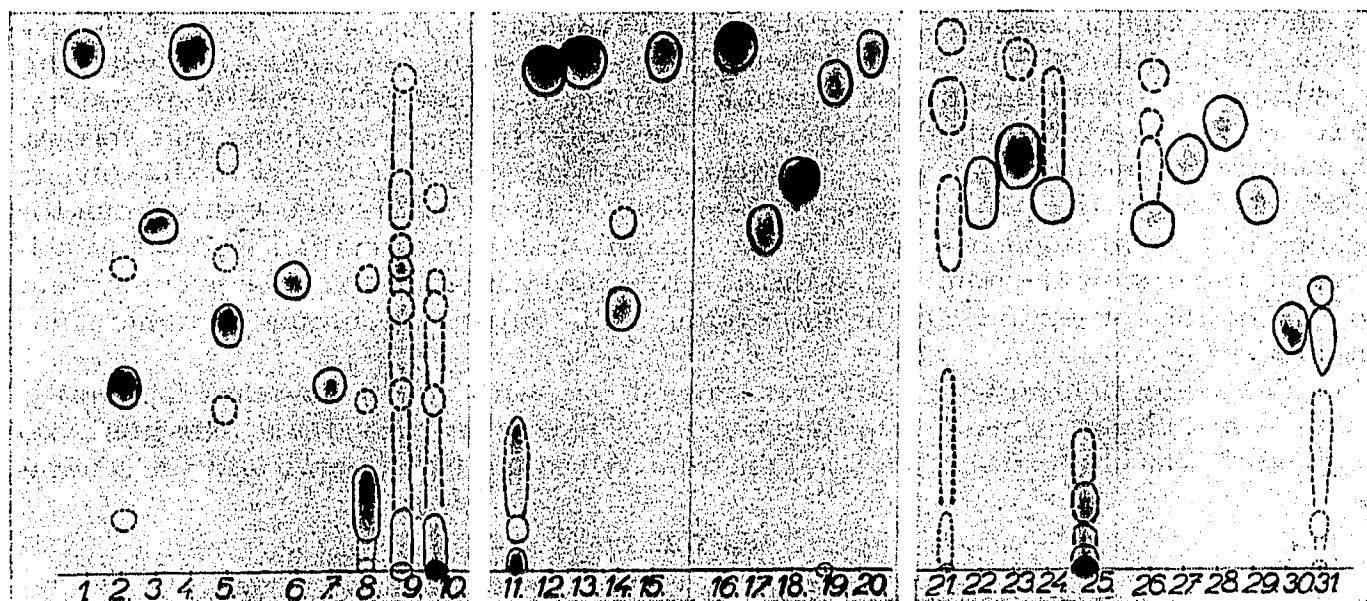Acid dyes ————— Basic dyes ··········· Substantive dyes —·—··—·—·
Mordant dyes —··——··——

Fig. 3. Example of a chromatographic separation of water-soluble dyes.

1. Picric Acid (nitro), CI 10305
2. Green PLX (nitroso), CI 10020
3. Brilliant Geranine B (monoazo – substantive), CI 15080
4. Cellit Fast Yellow R (monoazo – acid), CI 13145
5. Chloramine Red 8BS (bisazo – substantive), CI 23050
6. Wool Black 6BG (bisazo – acid), CI 20350
7. Sirius Blue 6G (trisazo – substantive), CI 34230
8. Sirius Supra Grey R (tetrakisazo), CI 35870
9. Diamine Catechine G (pentakisazo), CI 36030
10. Diamine Nitrazol Fast Brown BD (hexakisazo), CI 36310
11. Chlorantine Supra Orange T4RLL (stilbene), CI 40265
12. Auramine G (diphenylmethane – basic), CI 41005
13. Malachite Green (triphenylmethane – basic), CI 42000
14. Carbinol Fast Green G (triphenylmethane – acid), CI 42165
15. Victoria Blue R (diphenylnaphthylmethane – basic), CI 44040
16. Victoria Blue 4R (diphenylnaphthylmethane – basic), CI 44045

17. Naphthaline Green V (diphenylnaphthylmethane – acid), CI 44025
18. Methylene Red (xanthene – basic), CI 45006
19. Phosphine E (acridine – basic), CI 46045
20. Astrazone Orange G (methine – basic), CI 48035
21. Thioflavine S (thiazine – substantive), CI 49010
22. Toluylene Blue (indophenol – basic), CI 49410
23. Induline Scarlet (azine – basic), CI 50080
24. Rhoduline Sky Blue 3G (monooxazines – basic), CI 51005
25. Sirius Supra Blue F3GL (dioxazines – substantive), CI 51310
26. Thionine Blue GO (thiazine – basic), CI 52025
27. Brilliant Sulpho Flavine FF (aminoketone – acid), CI 56205
28. Anthralan Blue B (anthraquinone – acid), CI 62130
29. Alizarine Chrome Blue FFG (anthraquinone – mordant), CI 62120
30. Alizarine Rubinol 3 G (anthraquinone – acid), CI 68205
31. Sirius Supra Turquoise Blue GL (phthalocyanine), CI 74180

tion process was carried out for 45 min at 600 r.p.m. The chromatograms were always developed with the same solvent system as that used for the descending technique.

Table I shows mean R_F values of the individual groups of water-soluble dyes obtained by compilation of minimum and maximum R_F values of several hundred dyes of known chemical constitution. The R_F values refer to the isoamyl alcohol solvent system and Whatman No. 1 paper. Fig. 3 shows an example of a chromatographic separation of water-soluble dyes.

Although the establishment of correlation between the structure and chromatographic behaviour of a dye is rather complicated, we have been able to set up some general rules:

(1) Structurally simple dyes, with low physico-chemical activity, have a high R_F, as seen in Table I. With increasing complexity of the dye molecule, its physical and chemical tendency for reaction between the phases and phase-carrier increases proportionally, this being most pronounced with the azo dyes.

The substantive dyes have the lowest R_F values, the acid dyes come next and the basic dyes have the highest R_F values.

(3) The polarizability, substantivity and adsorption affinity increase with increasing number of conjugated double bonds traversing the entire dye molecule, the R_F values decreasing in proportion. If the chain of conjugated double bonds is interrupted, the R_F increases, even though a decrease of the R_F would be expected owing to the number of $-N=N-$ bonds. The greater the number of the azo groups, the lower the R_F. Carbamide and amide conjugated double bond systems replacing the $-N=N-$ bond cause a decrease of the R_F value.

(4) With dyes where the formation of internal hydrogen bonds is possible, the adsorption affinity decreases and the R_F value increases.

(5) With compounds of the same fundamental skeleton the R_F is decreased by $-SO_3H$, $-COOH$, $-NH_2$ and $-NO_2$ groups. The influence of these groups on the R_F is additive. Halogens and heterocyclic compounds act in the same way. A conductive connection of these groups with a conjugated system of double bonds decreases the R_F value.

(6) With the increase of the total dipole moment of the dye molecule, with compounds of the same fundamental skeleton, the R_F diminishes depending on the position and character of the substituents.

(7) Symmetric dyes have a lower R_F than unsymmetric dyes.

(8) Generally, the R_F value is dependent on the molecular weight. With its increase the R_F value diminishes proportionally with growing capillary adhesion.

Results obtained by the chromatography of various individual industrial important classes of water-soluble dyestuffs will be described in subsequent papers.

SUMMARY

A descending paper chromatographic method for water-soluble dyes is described in which a pyridine–isoamyl alcohol–ammonia solvent system is used. The relationship between dye constitution and chromatographic behaviour has been investigated.

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