Journal of Chromatography, 81 (1973) 181–186

CHROM. 6711

Note

Thin-layer chromatography of basic dyes

A. M. ARSOV, B. K. MESROB and A. B. GATEVA
Institute of Chemical Technology, Sofia 56 (Bulgaria)
(First received December 12th, 1972; revised manuscript received March 21st, 1973)

The importance of basic dyes is increasing rapidly with the development of the production of polyacrylonitrile fibres. The control of the synthesis and commercial production of these dyes requires more rapid and effective analytical methods to be used, such as thin-layer chromatography (TLC) on different carriers. A particular advantage of this method is its simple application on a preparative scale, so that different dyes can be purified if determination of their structure is required. In this way, the side-reactions that occur in the industrial synthesis of dyes can also be followed. There has been little mention of the use of TLC for the separation of basic dyes[1–8]. Different solvent systems have been used on silica gel[2–8], aluminium oxide[2,3,8] and polyamide powder[1] as carriers. However, the methods usually applied were tested on particular groups of dye and were not so effective with other dyes. The purpose of the present work was to study the behaviour of different new basic dyes on silica gel in order to find more suitable solvent systems for their TLC separation.

EXPERIMENTAL

Materials

We studied 23 basic dyes (Table I) obtained from Bayer AG, G.F.R. (Astrazons), Geigy, Switzerland (Maxilons), Sandoz, Switzerland (Sandocryls), BASF, G.F.R. (Basacryls) and the U.S.S.R. (cation dyes). Data on the chemical structures were found only for the Astrazons. Thus, the yellow Astrazons are of the methine type, the blue BG and B of the triphenylmethane type, the red dyes of the monoazo type and the blue 3RL of the anthraquinone type.

The solvents were treated as follows. Chloroform (puriss) was washed with a 10% solution of $NaHCO_3$, dried over $CaCl_2$ and distilled through a column (the fraction boiling in the range 57–58° was used), pyridine (puriss) was boiled for 24 h with CaO and distilled through a short column (the fraction boiling in the range 113.5–114.5° was used). The other solvents were purified by distillation of the commercial p.a. products.

Chromatography

Thin-layer chromatography was performed according to the method of Stahl[9] on 10 × 14 cm plates coated with Kieselgel G für DC (Merck). The dyes were applied

on the start as 2–3 μl volumes of 0.1 % aqueous solutions. The front line was run to a distance of 11 cm from the start and photographs were taken of the chromatograms obtained. Here we give the results for the solvent systems which produced the best separations and which proved to be better than the systems described in the literature. Some of the well separating systems were tested in two-dimensional chromatography on 10 × 10 cm plates.

RESULTS AND DISCUSSION

The results of the chromatographic separations in different systems are shown in Table I.

TABLE I

R_F VALUES OF DYES IN DIFFERENT SOLVENT SYSTEMS ON KIESELGEL G

Solvent systems: S1 = Chloroform–ethyl methyl ketone–glacial acetic acid–formic acid (8:6:1:1)
S2 = Chloroform–*n*-propanol–pyridine–glacial acetic acid–water (8:6:1:1:2)
S3 = Chloroform–ethyl methyl ketone–formic acid (6:8:1)
S4 = Chloroform–isopropanol–pyridine–glacial acetic acid–water (6:12:3:1:1)
S5 = Chloroform–isopropanol–pyridine–glacial acetic acid–water (6:8:3:1:2).

No.	*Dye*	*Type, Colour Index (C.I.) No. and structure*	*Colour of spots*	*Solvent system**				
				S1	*S2*	*S3*	*S4*	*S5*
1	Astrazon gelb 7GLL	Basic yellow 21; polymethine	Lemon yellow	0.64	0.63	0.76	0.45	0.50
2	Cation-yellow 4G		Lemon yellow	0.62	0.76	0.69	0.72	0.67
			Pink	0.69	0.68	0.77	0.96	0.56
3	Maxilon gelb 4GL	Basic yellow 17	Yellow	0.35dt	0.18	0.23dt	0.05	0.29
			Yellow	–	–	0.88	0.85	0.85
4	Astrazon gelb GRL	Basic yellow 29; methine	Yellow	0.53	0.30	0.53	0.17	0.37
			Orange	0.64	0.80	0.77	0.69	0.62
5	Maxilon gelb 2RL	Basic yellow 19	Yellow	0.36t	0.18t	0.29t	0.05	0.31
			Yellow	–	–	–	–	0.95
6	Astrazon goldgelb GL	Methine	Gold yellow	0.50	0.27	0.49	0.15	0.35
7	Sandocryl orange B3RLE		Orange	0.25	0.13	0.18	0.05	0.33
			Orange	–	0.39	–	0.15	0.43
			Orange	–	–	–	–	0.95
8	Sandocryl brill. rot BF200%		Pink	0.56t	0.39t	0.53t	0.18t	0.43
9	Cation-pink 2B		Pink	0.46t	0.42t	0.47t	0.41t	0.46
			Pink	–	0.59	0.68	0.55t	0.55
			Pink	0.65d	–	0.74	–	–
10	Sandocryl rubin BRLE		Ruby	0.20	0.12	0.15	0.04	0.29
			Ruby	–	0.35	–	0.15	0.38
			Ruby	–	–	–	–	0.95
11	Astrazon blau BG	Basic blue 3; C.I. 51005 triphenylmethane	Turkish	0.59	0.56	0.64	0.37	0.45
			Blue	0.55	0.45	0.58	0.47	0.49
			Dark blue	0.49	0.43	0.53	–	–
			Dark blue	0.46	–	0.45	–	–
			Violet	0.40	0.32	–	–	–
			Pink	0.28	0.84	–	–	–

TABLE I *(continued)*

No.	Dye	Type, Colour Index (C.I.) No. and structure	Colour of spots	Solvent system				
				S1	*S2*	*S3*	*S4*	*S5*
12	Cation-blue G		Blue	0.70t	0.87t	0.77t	0.68	0.70
			Blue	–	–	–	0.78t	0.87
13	Astrazon blau B	Basic blue 5; C.I. 42140; triphenylmethane	Pink	0.81	0.99	0.85	0.92	0.95
			Blue	0.68	0.61	0.77	0.36	0.46
			Blue	0.65	0.79	0.70	0.77	0.55
			Blue	–	0.86	–	0.95	0.76
			Violet	–	–	0.76	–	0.69
14	Sandocryl blau BFE		Violet	0.03	0.03	0.03	0.01	0.12
			Violet	–	–	–	0.12	0.15
			Dark blue	–	–	–	–	0.37
			Pink	0.84	0.98	0.79	0.84	0.91
15	Maxilon blau RL	Basic blue 40	Blue–violet	0.49t	0.25t	0.17t	0.06	0.30t
			Violet	–	0.49t	0.36t	0.26	0.46
			Pink	0.66	0.56	0.58	0.45	0.57
			Pink	0.84	0.98	0.82	0.89	0.96
16	Cation-blue R		Blue	0.68t	0.83t	0.68dt	0.42	0.49
			Blue	–	–	–	0.73	0.70
			Pink	0.76	0.99	0.76	0.90	0.95
17	Cation-blue 2R		Dark blue	0.27t	0.14t	0.28dt	0.07	0.19t
			Violet	0.48t	0.49t	0.38dt	0.38t	0.47
			Violet	–	0.56t	0.56dt	–	–
			Pink	0.76t	0.98t	0.73dt	0.90	0.95
18	Basacryl blau 3RL		Blue	0.69	0.70t	0.64t	0.43t	0.61
			Blue	–	0.82	–	0.74	–
			Pink	–	–	–	0.89	–
19	Astrazon blau 3RL	Basic blue 47; anthraquinone	Blue–grey	0.05	0.15	0.05	0.15	–
			Violet	0.16	0.22	0.14	–	0.32
			Violet	0.88	0.29	0.89	–	0.39
			Blue–violet	–	0.98	–	–	–
20	Sandocryl schwarz BBL		Orange	0.25	0.13	0.18	0.05	0.34
			Blue	0.70	0.74	0.65	0.35	0.58t
21	Astrazon rot GTL	Basic red 18; monoazo	Orange–red	0.12	0.11	0.08	0.04	0.24
			Orange	0.94	–	–	0.90	–
22	Astrazon rot BBL	Basic red 23; monoazo	Red	0.09	0.08	0.06	0.04	0.23
			Pink	0.94	–	–	0.90	–
23	Astrazon rot 5BL	Basic red 24; monoazo	Red	0.10	0.04	0.06	0.04	0.24
			Pink	0.94	0.08	0.12	0.90	0.97
Time for 11 cm run (min)				35	65	35	70	70

* t = tailing; d = diffuse spot.

Beside the solvents shown in Table I, for the optimum separation of the 23 dyes studied we also used methanol, ethanol, *n*-butanol, isoamyl alcohol, *tert.*-butanol, ethyl acetate, methyl acetate, benzene, light petroleum and 25% ammonia solution. The best results with respect to separation and reproducibility were obtained with eight of the combinations tested and the R_F values of the coloured spots obtained with five of them are given in Table I. The three remaining systems have the same constituents as S5 (chloroform–isopropanol–pyridine–glacial acetic acid–water) but with the following slightly different ratios: S6, 6:8:4:1:2; S7, 6:12:3:1:2; and

S8, 6:12:4:1:2. The separation in these systems is similar to that in S5. S6 and S7 separate the dyes Nos. 11, 19 and 20 into three constituents, while from Nos. 21 and 22 a very fast pink spot with $R_F = 0.95$ was obtained. S8 gives the same results as S5, S6 and S7. As can be seen from Table I, only three of the dyes showed homogeneity in all of the chromatographic systems tested, while the others can be separated in different compounds, some of them being present only as negligible impurities. An unsatisfactory result was obtained in the experiments with the three red dyes (not shown on the figures), Astrazon rot GTL, Astrazon rot BBL and Astrazon rot 5BL, which could not be separated from one another, while in all the recommended systems they can be separated from the remaining dyes. The instances in which some of the dyes demonstrated bad chromatographic behaviour are given in Table I. The separation of the tested dyes in solvent systems S1 and S2 is shown in Figs. 1 and 2.

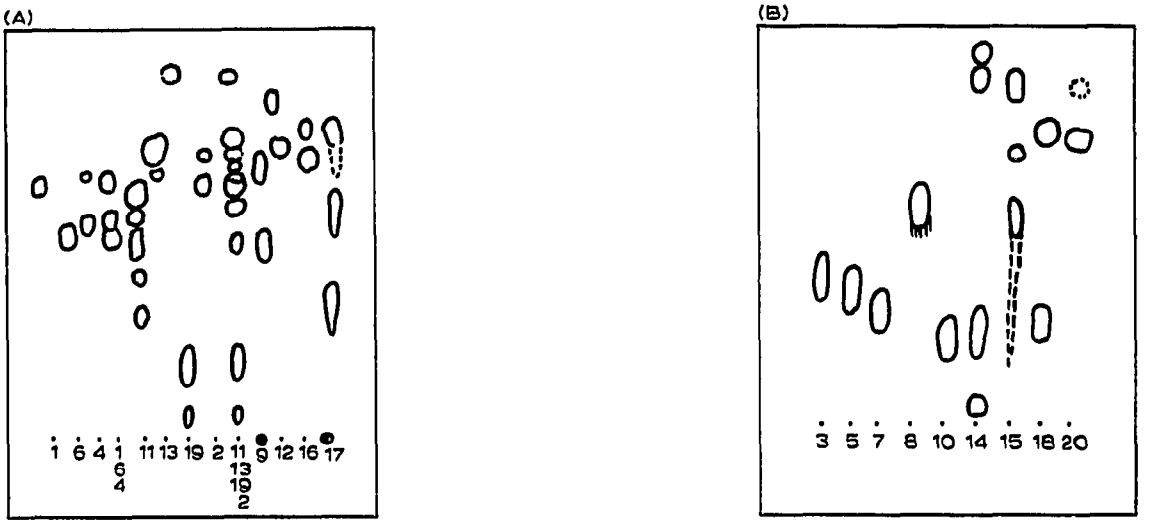

Fig. 1. Thin-layer chromatograms on Kieselgel G in solvent system S1 of the dyes mentioned in Table I.

It can be seen that in S1 the run of the dyes is longer, while in S2 they are distributed along the whole distance of the chromatogram. It can also be seen that the insoluble and strongly adsorbed dye material is present in very small amounts and is characteristic of only some of the dyes.

The different systems were tested in three combinations of two-dimensional chromatography:

(a) first run in S8 and second run in S1;
(b) first run in S6 and second run in S2;
(c) first run in S8 and second run in S2.

The map of the spots for (b) is shown in Fig. 3, which demonstrates that the mixture of 11 dyes is clearly separated into 14 coloured components. In this instance, the lesser components in the main mixture of dyes present in the composition are lost owing to the stronger diffusion. It can be seen that on the starting line for the second run there is a red component, which is a typical result for this dye adsorption on dried silica gel.

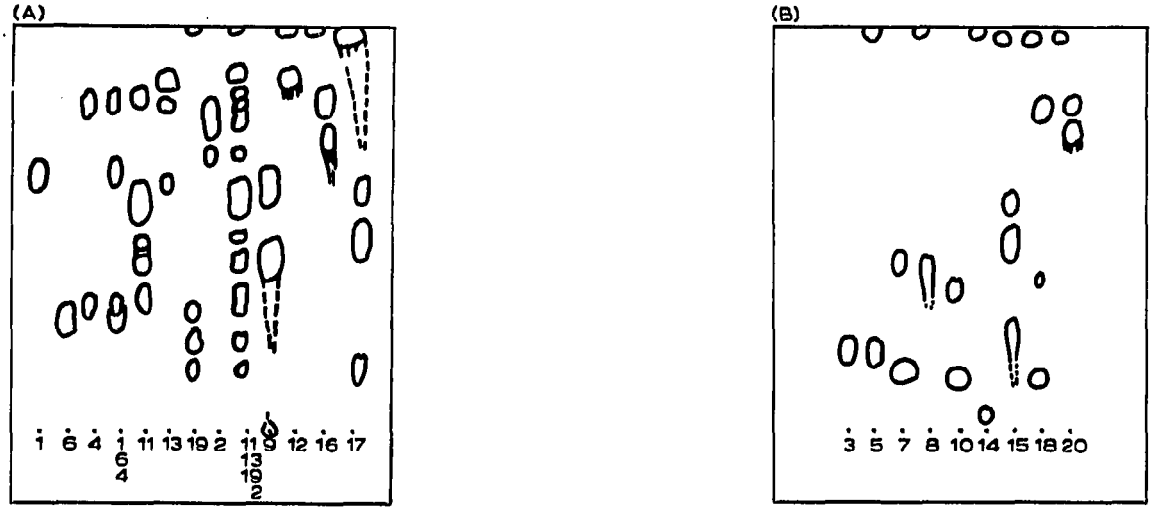

Fig. 2. Thin-layer chromatograms in Kieselgel G in solvent system S2 of the dyes mentioned in Table I.

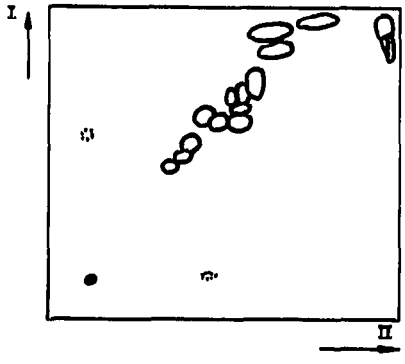

Fig. 3. Two-dimensional TLC on Kieselgel G of mixture of 11 basic dyes (Nos. 1, 2, 4, 6, 9, 11, 12, 13, 16, 17 and 18 according to Table I). Solvent systems: S6 for the first run and S2 for the second run. After the first run, the plate was activated at 110° for 15 min and after reaching room temperature was run in the second direction.

The results in Table I and Figs. 1–3 show the possibilities of the proposed chromatographic systems for determining the purity of commercial dyestuffs and for comparing the constituents present in the different products. It was proved, for example, that the orange component of Sandocryl schwarz BBL with $R_F = 0.25$ in system S1 (or $R_F = 0.33$ in S6) behaves in an identical manner to the main orange component in Sandocryl orange B3RLE, because their R_F values were the same in the corresponding solvent systems. A final conclusion, however, can be drawn only if these dyes are isolated by preparative TLC and their spectra are shown to be identical in the visible region. As only commercial products and not raw, unstandard dyes have been studied, an example of the difference in the chromatograms of the two batches of synthetic dyes cannot be given. Nevertheless, some dyes, such as Sandocryl blau

BFE, Cation-blue R and Cation-blue 2R, give very fast and pale-coloured spots, which could represent some intermediate stage of transformation of the reaction products which have not been well purified.

The systems described can also be used for the preparative isolation of dye components in order to study their chemical structures.

REFERENCES

1 R. Takeshita, N. Itoh and Y. Sakagami, *J. Chromatogr.*, 57 (1971) 437.
2 S. Logar, J. Perkavec and M. Perpar, *Microchim. Acta*, (1967) 496.
3 G. H. Rettie and C. G. Haynes, *J. Soc. Dyers Colour.*, 80 (1964) 629.
4 J. S. L. Ruiz and C. Laroch, *Bull. Soc. Chim. Fr.*, (1963) 1594.
5 G. R. Jamieson, *Symposium of Scottish Section of the Society for Analytical Chemistry on Modern Aspects of Chromatography, Dublin, Sept. 1963.*
6 N. B. Naff and A. S. Naff, *J. Chem. Educ.*, 40 (1963) 534.
7 A. Stier and W. Specht, *Naturwissenschaften*, 50 (1963) 549.
8 J. W. Copius Peereboom, *Chem. Weekbl.*, 57 (1961) 625.
9 E. Stahl, *Dünnschicht Chromatographie*, Springer, Berlin, 1962.