Journal of Chromatography, 207 (1981) 29–36
Elsevier Scientific Publishing Company, Amsterdam — Printed in The Netherlands

CHROM. 13,492

THIN-LAYER CHROMATOGRAPHY OF AROMATIC AMINES ON AMMONIUM MOLYBDOPHOSPHATE AND TUNGSTOPHOSPHATE

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(Received October 30th, 1980)

SUMMARY

The use of ammonium tungstophosphate in the thin-layer chromatography of 35 primary aromatic amines was investigated, with respect to the influences of the exchanger concentration in the layer, the acidity and salt concentration in the eluent and the kind of the organic solvent. Many interesting separations among the amines have been carried out. On ammonium molybdophosphate layers the amines are oxidized, giving rise to blue spots, and sample amounts ten times as large as on ammonium tungstophosphate must be employed.

INTRODUCTION

Recently, two synthetic inorganic exchangers have been used in the thin-layer chromatography (TLC) of organic compounds. Thus, ammonium molybdophosphate (AMP) was employed for the separation of sulphonamides[1], while ammonium tungstophosphate (AWP) showed great advantages with respect to AMP in the separation of amino acids[2] owing to its lower redox potential and lack of colour. In comparison with organic exchangers[3] and with silanized silica gel impregnated with anionic and cationic detergents[4], on ammonium tungstophosphate a different affinity sequence of the amino acids and a higher sensitivity was found. Layers of silica gel impregnated with small amounts of pyridinium tungstoarsenate have also allowed an improvement in the separation of some nitrogenous organic compounds with respect to silica gel alone[5,6].

We have now examined the behaviour of 35 primary aromatic amines on AWP and AMP layers. This class of compounds is very suitable for the study of the retention mechanism on these exchangers and for comparison with the results achieved on layers of organic exchangers[7–9] and with the soap TLC[10,11].

EXPERIMENTAL

Standard solutions of amines were prepared by dissolving the compounds in methanol– 1 *M* hydrochloric acid (1:1) and stored in dark bottles. Fresh solutions were used for those amines which decompose easily, *i.e.*, phenylenediamines. The amines were detected with a solution of 5% N,N-dimethyl-*p*-aminobenzaldehyde (*p*-DAB) in ethanol–glacial acetic acid (5:1, v/v).

0021-9673/81/0000–0000/$02.50

Ammonium tungstophosphate was prepared by dissolving 50 g of phosphotungstic acid (E. Merck, Darmstadt, G.F.R.) in 200 ml of 2 *M* nitric acid; 200 ml of 2 *M* ammonium nitrate were added with stirring. The suspension was filtered and the solid was rinsed with water and air-dried. The layers (thickness 300 μm) were prepared with a Chemetron automatic apparatus by mixing the desired amount of AMP (Bio-Rad Labs., Richmond, CA, U.S.A.) or AWP (0.5–8 g) in 50 ml of water. To the suspension, shaken with a magnetic stirrer, were added 2 g of calcium sulphate hemihydrate (first passed through a 200-mesh sieve). After 10 min the aqueous slurry was sprayed on the plates.

The measurements were carried out at 25°C. The migration distance was 10 cm unless otherwise stated.

RESULTS AND DISCUSSION

Layers of ammonium tungstophosphate

Influence of the AWP concentration. In order to examine the influence of the exchanger concentration on the retention of the aromatic amines, the R_F values of 35 compounds were determined on layers of calcium sulphate hemihydrate mixed with increasing amounts of AWP, by eluting with water.

The development time increases from 30 to 70 min with increasing proportion of AWP in the layer. On layers of calcium sulphate hemihydrate alone most amines run with the solvent front giving rise, in some cases, to elongated spots. In the presence of small amounts of AWP, *i.e.*, AWP:$CaSO_4 \cdot \frac{1}{2}H_2O$ ratio = 0.5:2, the retention of the amines, particularly of those without acid groups, is increased; under these conditions, the spots are diffuse even when spherical, and for this reason some amines cannot be detected at the amounts reported in Table I. As the AWP concentration in the layer is increased a sharp increase in the retention of all compounds and more compact spots are observed. For most amines a limiting R_F value is not reached even at high percentages of exchanger, as observed in the case of amino acids[2].

The sequence of the R_F values for the aromatic amines does not change with increasing AWP concentration in the layer, except for the data in the first column in Table I where the chromatographic behaviour of the compounds is only slightly affected by the exchanger owing to its small concentration in the layer.

The influence of the substituent groups on the chromatographic behaviour of the amines can be discussed in relation to aniline. The introduction of a $-CH_3$, $-Br$, $-Cl$ group and of a second $-NH_2$ group in the ring involves an increase in the affinity towards the stationary phase. The opposite behaviour is observed in the presence of a sulphonic group or (except for the *meta* isomers) of carboxylic and nitro groups in the molecule. The last result is peculiar to these exchangers since neither organic exchangers[7–9] nor silanized silica gel impregnated with detergents[10,11] exhibited this behaviour. The presence of a second aromatic nucleus in the molecule, *e.g.* α-naphthylamine, results a sharp decrease in the R_F value. As regards the influence of the substituent group position on the chromatographic characteristics, the *para* isomers are more strongly retained in the case of toluidines and of arsanilic acids, and the *meta* isomers in the case of bromo-, chloro- and nitroanilines and aminobenzoic acids. Such behaviour could be useful in the separation of isomers.

Another peculiar characteristic is the high sensitivity in the detection of

TABLE I

R_F VALUES OF PRIMARY AROMATIC AMINES ON THIN LAYERS OF CALCIUM SULPHATE HEMIHYDRATE MIXED WITH INCREASING AMOUNTS OF AWP

Eluent: water. n.d. = Not determined; e.s. = elongated spot.

Amine	*AWP:$CaSO_4 \cdot \frac{1}{2}H_2O$ ratio*				*Amount (μg)*
	0.5:2	*2:2*	*4:2*	*8:2*	
Aniline	0.50	0.21	0.15	0.12	0.02
o-Toluidine	0.45	0.20	0.14	0.11	0.02
m-Toluidine	0.43	0.19	0.12	0.09	0.02
p-Toluidine	0.37	0.19	0.10	0.08	0.02
o-Bromoaniline	n.d.	0.18	0.11	0.09	0.02
m-Bromoaniline	0.29	0.11	0.07	0.07	0.02
p-Bromoaniline	0.33	0.13	0.08	0.07	0.02
o-Chloroaniline	n.d.	0.18	0.11	0.09	0.03
m-Chloroaniline	0.40	0.17	0.10	0.08	0.02
p-Chloroaniline	0.45	0.20	0.12	0.09	0.03
2,4-Dichloroaniline	n.d.	0.18	0.11	0.08	0.4
o-Nitroaniline	0.82	0.62	0.52	0.41	0.3
m-Nitroaniline	0.50	0.20	0.14	0.08	0.02
p-Nitroaniline	0.78	0.55	0.45	0.35	0.03
o-Aminobenzoic acid	0.68	0.45	0.35	0.20	0.04
m-Aminobenzoic acid	0.46	0.23	0.15	0.10	0.02
p-Aminobenzoic acid	0.72	0.48	0.36	0.23	0.04
4-Amino-3,5-dimethylbenzoic acid	0.68	0.48	0.37	0.24	0.05
3,4-Diaminobenzoic acid	0.37	0.22	0.15	0.11	0.3
3,5-Diaminobenzoic acid	0.14	0.07	0.04	0.02	0.05
o-Aminophenylarsonic acid	0.80	0.70	0.65	0.56	0.2
p-Aminophenylarsonic acid	0.75	0.65	0.59	0.50	0.1
o-Aminophenylsulphonic acid	0.90	0.77	0.73	0.60	0.1
m-Aminophenylsulphonic acid	0.90	0.78	0.74	0.61	0.1
p-Aminophenylsulphonic acid	0.91	0.85	0.84	0.75	0.1
1,3,6-Xylidene-4-sulphonic acid	0.90	0.77	0.75	0.62	0.2
2-Aminotoluene-5-sulphonic acid	0.90	0.82	0.80	0.69	0.2
4-Aminotoluene-3-sulphonic acid	0.90	0.73	0.68	0.55	0.2
6-Amino-4-chloro-3-toluenesulphonic acid	0.90	0.74	0.70	0.58	0.2
o-Phenylenediamine	0.02	0.01	0.01	0.00	0.5
m-Phenylenediamine	0.02	0.01	0.01	0.00	0.03
p-Phenylenediamine	0.01	0.01	0.01	0.00	0.01
α-Naphthylamine	e.s.	0.04	0.03	0.03	0.05
1-Naphthylamino-7-sulphonic acid	0.85	0.69	0.60	0.45	0.1
1-Naphthylamino-4-sulphonic acid	0.88	0.78	0.70	0.55	0.1

aromatic amines. The sensitivity on AWP layers is 3–100 times higher than on cellulose-based organic exchangers[7–9] and on silanized silica gel impregnated with detergents[10,11].

Besides water, 1 *M* nitric acid was also employed as eluent. This resulted in a greater compactness of the spots even at low AWP concentrations in the layer so that all the amines could be detected. Aminophenylarsonic acids and α-naphthylamine, however, give rise to elongated spots on the layer with 50% AWP. On the basis of the results achieved on eluting with water, or 1 *M* nitric acid, a layer with a 4:2 ratio of AWP:$CaSO_4 \cdot \frac{1}{2}H_2O$ was chosen for further investigations.

Influence of salt concentration and eluent acidity. Table II lists the R_F values of the aromatic amines obtained on layers of AWP:$CaSO_4 \cdot \frac{1}{2}H_2O$ in the ratio 4:2 with changing acidity and salt concentration in the eluent. On eluting with 1 *M* nitric

TABLE II

R_F VALUES OF PRIMARY AROMATIC AMINES ON LAYERS OF AWP:$CaSO_4 \cdot \frac{1}{2}H_2O$ IN THE RATIO 4:2 (w/w)

n.d. = Not determined.

Amine	*Eluent*					*1 M* NH_4NO_3*
	1 M HNO_3	*1 M* HNO_3 + *0.25 M* NH_4NO_3	*1 M* HNO_3 + *0.5 M* NH_4NO_3	*1 M* HNO_3 + *1 M* NH_4NO_3	*1 M* HNO_3 + *2 M* NH_4NO_3	
Aniline	0.35	0.47	0.51	0.61	0.67	0.63
p-Toluidine	0.33	0.44	0.49	0.59	0.66	0.61
o-Toluidine	0.29	0.41	0.47	0.57	0.64	0.59
m-Toluidine	0.25	0.39	0.45	0.55	0.63	0.57
p-Bromoaniline	0.20	0.31	0.38	0.44	0.54	0.46
o-Bromoaniline	0.18	0.30	0.38	0.46	0.56	0.48
m-Bromoaniline	0.15	0.27	0.35	0.43	0.53	0.45
p-Chloroaniline	0.32	0.43	0.49	0.56	0.63	0.58
o-Chloroaniline	0.22	0.37	0.44	0.51	0.62	0.54
m-Chloroaniline	0.21	0.34	0.41	0.49	0.59	0.52
2,4-Dichloroaniline	0.20	0.30	0.38	0.47	0.56	n.d.
p-Nitroaniline	0.30	0.37	0.42	0.47	0.55	0.53
o-Nitroaniline	0.30	0.36	0.39	0.43	0.51	0.52
m-Nitroaniline	0.19	0.26	0.31	0.36	0.48	0.39
p-Aminobenzoic acid	0.48	0.50	0.56	0.63	0.70	0.66
o-Aminobenzoic acid	0.32	0.38	0.46	0.54	0.64	0.60
m-Aminobenzoic acid	0.30	0.36	0.44	0.51	0.62	0.55
4-Amino-3,5-dimethylbenzoic acid	0.31	0.34	0.42	0.50	0.58	0.55
3,4-Diaminobenzoic acid	0.35	0.38	0.46	0.55	0.63	0.55
3,5-Diaminobenzoic acid	0.05	0.13	0.20	0.30	0.44	0.33
p-Aminophenylarsonic acid	0.44	0.52	0.56	0.66	0.73	0.75
o-Aminophenylarsonic acid	0.36	0.40	0.45	0.56	0.64	0.75
p-Aminophenylsulphonic acid	0.81	0.81	0.82	0.85	0.86	0.82
o-Aminophenylsulphonic acid	0.68	0.66	0.67	0.72	0.73	0.72
m-Aminophenylsulphonic acid	0.72	0.70	0.71	0.77	0.77	0.75
1,3,6-Xylidene-4-sulphonic acid	0.71	0.70	0.71	0.75	0.76	0.75
2-Aminotoluene-5-sulphonic acid	0.76	0.75	0.78	0.81	0.83	0.79
4-Aminotoluene-3-sulphonic acid	0.63	0.60	0.64	0.68	0.70	0.68
6-Amino-4-chloro-3-toluene-sulphonic acid	0.63	0.60	0.64	0.64	0.64	0.66
p-Phenylenediamine	0.02	0.10	0.20	0.34	0.51	0.35
o-Phenylenediamine	0.02	0.13	0.23	0.36	0.52	0.37
m-Phenylenediamine	0.02	0.12	0.22	0.36	0.52	0.37
α-Naphthylamine	0.08	0.13	0.19	0.26	0.36	0.28
1-Naphthylamino-4-sulphonic acid	0.70	0.65	0.67	0.70	0.72	0.68
1-Naphthylamino-7-sulphonic acid	0.62	0.59	0.60	0.62	0.63	0.61

* R_F value of the first solvent front = 0.75.

acid the compounds with sulphonic or arsonic groups and some of those with nitro or carboxylic groups were similarly or more retained than with water. This behaviour indicates that the presence of a positive charge in the molecule, related to the protonation of the $-NH_2$ group, results in a greater affinity of the compounds towards the exchanger as is the case with a decrease in their anionic characteristics[2]. In the case of the remaining amines, which are more weakly retained than with water and which are in the cationic form at the pH of the eluent, the lower retention with respect to the non-ionized form can be ascribed to the influence of the hydrogen ion as counter ion rather than to a lower affinity towards the exchanger of the protonated form with respect to the free-base form. In fact, as the nitric acid concentration in the eluent is increased, *i.e.*, to 2 *M*, the R_F values of these amines increase remarkably.

Plots of the R_M values as a function of the nitric acid activity in the 0.5–2 *M* concentration range were linear and almost parallel to the abscissa for most sulphonated amines and *o*-nitroaniline, with slopes between 0.3 and 0.5 for the other monoamines and between 0.9 and 1.1 for the diamines. This shows that most sulphonated amines and *o*-nitroaniline are not affected by the nitric acid concentration in the eluent, and that for the other monoamines the occurrence in the retention mechanism of an ion-exchange process must be considered. Such a process, however, is not predominant since the values of the slopes are smaller than those predicted theoretically[12]. In the case of the diamines, the ion-exchange process seems more important.

The replacement of 1 *M* nitric acid with the same concentration of ammonium nitrate as eluent results in a remarkable increase in the R_F values of the amines, except for the sulphonated ones. With this eluent the appearance on the layer of two fronts, the first of which has $R_F = 0.75$, is observed. On eluting with solutions of constant nitric acid content (1 *M*) but increasing concentration of ammonium nitrate, it is observed that nitric acid affects the retention of the amines less than does ammonium nitrate. The chromatographic behaviour resembles more that obtained on eluting with 1 *M* ammonium nitrate than that with 1 *M* nitric acid.

From the above results and keeping in mind that, on eluting with 1 *M* ammonium nitrate, many amines (nitroanilines, 2,4-dichloroaniline, etc.) are in the free-base form, it seems that the protonation of the amines does not determine their retention by the layer and that the effect of the ammonium ions as counter ions is surprisingly different from that of hydrogen ions. This can be explained by assuming that ammonium nitrate is more strongly adsorbed by the exchanger than nitric acid, thus decreasing the adsorption of the amines both in the protonated and in the free-base form. This "desorption" of the amines seems, therefore, to be the determining factor in the chromatographic behaviour of most amines, at least in the presence of significant amounts of ammonium nitrate in the eluent.

The different affinity of many isomers towards the exchanger on eluting with 1 *M* nitric acid compared with elution with water is very interesting from an analytical point of view. The reversal of the sequence of the two aminophenylarsonic acids is of note in this context. Such characteristics can be used for the separation of groups of isomers with two-dimensional development.

Aqueous–organic eluents. Elution with aqueous–organic mixtures (water–methanol, water–ethanol, water–acetic acid and 1 *M* nitric acid in water–methanol) resulted in the following differences with respect to elution with water or with aqueous

salt solutions: (1) a longer elution time; (2) a greater compactness of the spots. The elution time increased with increasing percentage of the organic solvent in the eluent and it was about 2 h (for a migration distance of 10 cm) when eluting with a 7:3 (v/v) mixture of water–methanol or water–acetic acid. The elution time also increased when methanol or acetic acid was replaced with ethanol.

The percentage of organic solvent in the eluent must not be higher than 50% in order to avoid both high elution time and diffuse spots. The affinity sequence was almost the same when eluting with water–methanol, water–ethanol or water–acetic acid (7:3, v/v). Aniline, α-naphthylamine, amines containing $-CH_3$, –Br and –Cl groups, *m*-nitroaniline, *m*-aminobenzoic acid, 3,4- and 3,5-diaminobenzoic acids, which are strongly retained with the above eluents ($R_F \leqslant 0.10$), can be separated from all the other amines. The addition of methanol to the nitric acid solutions generally yields an improvement in the separation of the amines.

Decomposition products. The high sensitivity of the AWP layers towards aromatic amines can be used to detect the presence of decomposition products in the standard amine solutions. Some aromatic amines, whose solutions are generally considered stable over long periods, give rise, after few days, to a secondary spot other than the main one obtained with a fresh solution. We deemed it useful, therefore, to report in Fig. 1 the chromatographic behaviour of standard solutions of nitroanilines and *p*-aminobenzoic acid, 10 days after their preparation, on layers of AWP:$CaSO_4 \cdot \frac{1}{2}H_2O$ in the ratio 4:2 eluted with 1 *M* nitric acid. The presence of the two spots is observed also when eluting with water.

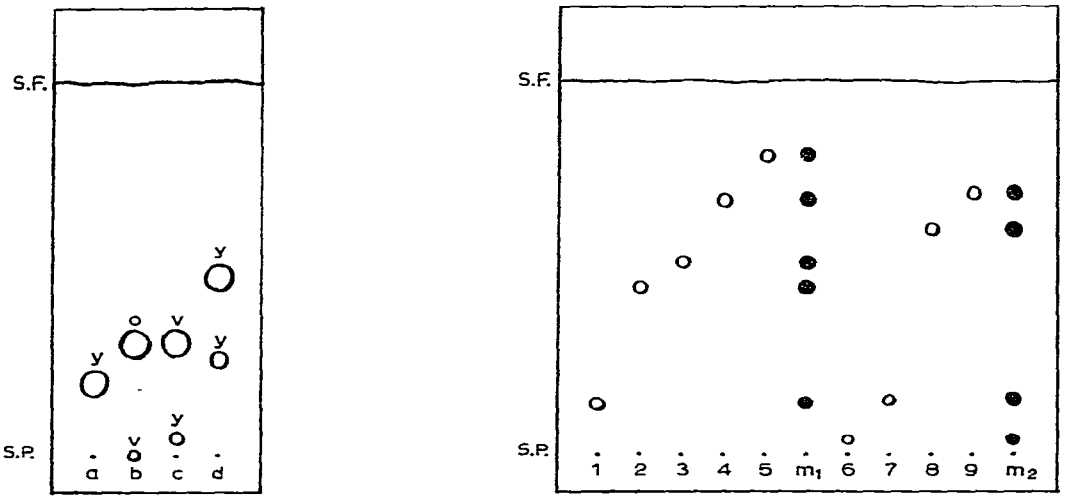

Fig. 1. Thin-layer chromatogram of standard solutions of amines, 10 days after their preparation, on AWP:$CaSO_4 \cdot \frac{1}{2}H_2O$ in the ratio 4:2. Eluent: 1 *M* nitric acid. Amines (1 μg): a = *m*-nitroaniline; b = *p*-nitroaniline; c = *o*-nitroaniline; d = *p*-aminobenzoic acid. Colours after spraying with *p*-DAB: y = yellow; o = orange; v = violet. S.P. = Starting point; S.F. = solvent front.

Fig. 2. Thin-layer chromatogram of some isomers on AWP:$CaSO_4 \cdot \frac{1}{2}H_2O$ in the ratio 4:2. Eluent: water. Amines: 1 = *m*-nitroaniline; 2 = *p*-nitroaniline; 3 = *o*-nitroaniline; 4 = 4-aminotoluene-3-sulphonic acid; 5 = 2-aminotoluene-5-sulphonic acid; m_1 = mixture of 1–5; 6 = 3,5-diaminobenzoic acid; 7 = 3,5-diaminobenzoic acid; 8 = 1-naphthylamino-7-sulphonic acid; 9 = 1-naphthylamino-4-sulphonic acid; m_2 = mixture of 6–9. Other details as in Fig. 1.

From these data, the stability of *m*-nitroaniline, with respect to the other isomers, can be determined. *p*-Aminobenzoic acid was found to be the compound decomposing most quickly, since the second spot appeared 2 days after the preparation of the standard solution. A chromatogram of these compounds 3 weeks after preparation of the standard solutions is similar to that in Fig. 1.

It should be noted that the stability of the solutions of these amines depends on the kind of solvent used. For instance, solutions of nitroanilines in methanol are more stable than those in a 1 *M* hydrochloric acid–methanol (1:1, v/v) (to which Fig. 1 refers).

Layers of ammonium molybdophosphate

Ammonium molybdophosphate exhibits more marked oxidizing properties than ammonium tungstophosphate and for this reason most amines are oxidized when deposited on the layer, giving blue spots. The amines which are more easily oxidized, *i.e.*, phenylenediamines, aniline, toluidines, etc., give rise to blue elongated spots which start from the application point, showing that their oxidation by the exchanger is not complete at the starting point but continues during their migration. An amine which is not yet oxidized reacts with *p*-DAB to give an orange colour.

The oxidation process is dependent on the pH of the eluent and its extent may be decreased with strong acid eluents. Amines containing $-NO_2$ or sulphonic groups are less readily oxidized and do not give rise to blue elongated spots.

The chromatographic behaviour of the amines on layers of ammonium molybdophosphate is similar to that obtained on ammonium tungstophosphate under the same elution conditions, apart from the lower sensitivity of detection.

Analytical applications

On the basis of the R_F values of Tables I and II and of those obtained on eluting with aqueous–organic mixtures, many separations among the different amines and, particularly, among isomers can be effected. In Fig. 2 are illustrated the separations of nitroanilines, of aminotoluenesulphonic, diaminobenzoic and naphthylaminosuphonic acids on layers of AWP:$CaSO_4 \cdot \frac{1}{2}H_2O$ in the ratio 4:2 eluted with water. The three nitroanilines were separated also with 2 *M* nitric acid on layers of AWP:$CaSO_4 \cdot \frac{1}{2}H_2O$ in the ratios 4:2 and 8:2. On both these layers, with this eluent, the affinity sequence (*meta* > *ortho* > *para*) obtained was different from that obtained on eluting with water (*meta* > *para* > *ortho*) or with 1 *M* nitric acid (*meta* > *para* = *ortho*). For instance, on layers with a exchanger:binder ratio of 4:2, the R_F values of nitroanilines are: 0.25 (*meta*), 0.32 (*ortho*) and 0.39 (*para*). The use of 2 *M* nitric acid as eluent allows the separation of the three aminobenzenesulphonic acids on the same layers since the *ortho* and *meta* isomers are well separated from them.

With aqueous–organic eluents, the separation of the three nitroanilines and of nine compounds in total on AWP:$CaSO_4 \cdot \frac{1}{2}H_2O$ in the ratio 4:2 has been achieved (see Fig. 3). This separation involves the three isomers of aminobenzoic acid and demonstrates the different behaviour among amines with a carboxylic, arsonic or sulphonic group. The other compounds containing a sulphonic group exhibit R_F values between those of 4-aminotoluene-3-sulphonic and *p*-aminobenzenesulphonic acids, which are shown in Fig. 3.

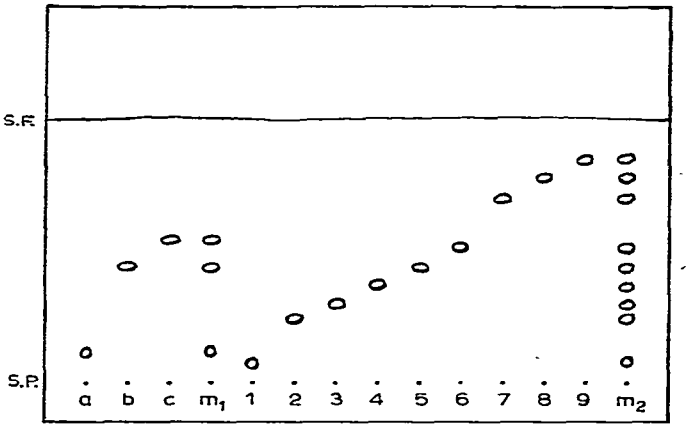

Fig. 3. Thin-layer chromatogram of aromatic amines on AWP:$CaSO_4 \cdot \frac{1}{2}H_2O$ in the ratio 4:2. Eluent: water–ethanol (7:3, v/v). Migration distance: 7 cm. Amines: a = *m*-nitroaniline; b = *p*-nitroaniline; c = *o*-nitroaniline; m_1 = mixture of nitroanilines; 1 = *m*-aminobenzoic acid; 2 = *o*-aminobenzoic acid; 3 = *p*-aminobenzoic acid; 4 = 4-amino-3,5-dimethylbenzoic acid; 5 = *p*-aminophenylarsonic acid; 6 = *o*-aminophenylarsonic acid; 7 = 4-aminotoluene-3-sulphonic acid; 8 = *o*-aminophenylsulphonic acid; 9 = *p*-aminophenylsulphonic acid; m_2 = mixture of 1–9. Other details as in Fig. 1.

The peculiar compactness of the spots and their flat shape allow the separation of compounds that differ only by 0.04 retention units, notwithstanding the short migration distance (7 cm), in an elution time of about 2 h. The best separations among the amines containing $-CH_3$, –Cl and –Br groups have been achieved by eluting with 1 *M* nitric acid in 30% methanol. Aniline ($R_F = 0.30$) is separated from the three toluidines, *meta* (0.28), *ortho* (0.33), *para* (0.33) and from the bromoanilines, *meta* (0.17), *ortho* (0.21), *para* (0.26). The behaviour of the bromoanilines allows the separation of the *para* isomer from the other two isomers. The difference in retention is more marked in the case of chloroanilines where the *para* isomer ($R_F = 0.38$) is much less strongly retained than the *meta* ($R_F = 0.26$) and *ortho* ($R_F = 0.29$) isomers.

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