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THIN-LAYER AND HIGH-SPEED LIQUID CHROMATOGRAPHY OF THE DERIVATIVES OF 1,4-PHENYLENEDIAMINE*

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SUMMARY

The conditions for the thin-layer and liquid column chromatography of aromatic diamines were studied. It was found that tailing and sorption of these compounds can be suppressed by adding a small amount (0.1%, v/v) of triethylamine to the mobile phase, so that the compounds can also be analyzed by using liquid chromatography. The sorption of both diamines and triethylamine on silica gel is a reversible process. Comparison of the R_F values of diamines for the system ethanol–*n*-hexane containing triethylamine with the same system not containing triethylamine revealed that triethylamine in this concentration suppresses the sorption of diamines without influencing the R_F values.

INTRODUCTION

The chromatographic aspects of derivatives of 1,4-phenylenediamine have been widely studied for the purpose of using them in the photographic or plastics industry. Owing to their low volatility, the compounds were mainly studied by paper[1–4] or thin-layer[5,6] chromatography, and only recently have gas[7–11] and gel[12] chromatography been used. The application of analytical liquid chromatography has so far been limited to aromatic amines that contain only one nitrogen atom[13], which are not sorbed on a silica gel carrier. This paper deals with the conditions used for the analytical investigation of the derivatives of 1,4-phenylenediamine by thin-layer chromatography (TLC) and high-speed liquid chromatography.

EXPERIMENTAL

Thin-layer chromatography

Commercial Silufol plates (Kavalier, Votice, Czechoslovakia), 15 × 15 cm, were activated at 100° for 1 h in a drying box. On adding 1 μl of a sample containing 1 mg of the compound in 1 ml of tetrahydrofuran, the plate was exposed to the solvent vapour for 2 min, and the compounds thus deposited were chromatographed over a length of 10 cm in the systems ethanol–*n*-hexane or ethanol–*n*-hexane–0.1% triethylamine in varying ratios.

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Detection. The detection of amines was based on the readily formed and intensely coloured ion radicals produced by oxidizing agents (iodine vapour in this work). The literature reports detection with bromine vapour[14]. However, the disadvantage of the latter type of detection is that prolonged treatment with bromine vapour leads to further oxidation of the cation radicals formed and thus to the disappearance of the spots. With iodine, which is a weaker oxidizing agent, no such reaction takes place; moreover, a number of further compounds that are not subject to oxidation develop colour owing to iodine absorption.

The detection was carried out by placing a dried Silufol plate into a closed cell with several iodine crystals for *ca.* 10–15 min. The spots of aniline, diphenylamine and phenyl-2-naphthylamine, which develop colour with iodine only through adsorption, disappeared after some time because of the desorption of iodine.

Liquid chromatography

The apparatus used for analytical liquid chromatography was of our own design. It consisted of storage vessels for ethanol and *n*-heptane, a degassing unit for *n*-heptane, an MC-100 micro-pump (Mikrotechna, Prague, Czechoslovakia) for ethanol, an MC-300 micro-pump for *n*-heptane, a mixing cell, a manostat, a column with an adapter for introducing samples, a UV detector (Development Works of the Czechoslovak Academy of Sciences, Prague, Czechoslovakia) operating at 254 nm and connected with a recorder, and a device monitoring the volume of the effluent.

The columns used for liquid chromatography were made of glass (I.D. 2.6 mm, O.D. 7.6 mm), provided with stainless-steel adapters of our own design (Fig. 1). They were dry-filled by a standard technique[15]. The flow-rate of the solvent was 1.5 ml/min.

Materials. Silpearl (Kavalier), of 10–30 μm particle size, was used as the packing in liquid chromatography. The mobile phase consisted of analytical grade *n*-heptane (Lachema, Brno, Czechoslovakia) and ethanol denatured with 5% of methanol (United Distilleries, National Enterprise, Prague, Czechoslovakia), with 0.1% of redistilled triethylamine added. No significant absorption of the UV radiation at 254 nm could be detected for any of the components of the mobile phase.

Samples

The compounds employed are listed in Table III. They were either pure commercially available products or were synthesized by us[16].

RESULTS AND DISCUSSION

A considerable problem in the chromatography of amines is their basicity. The aromatic diamines are chemisorbed on active hydroxyl groups on the surface of silica gel, forming very long spots that are frequently elongated so much that they reach the start, which greatly distorts or even makes impossible the determination of R_F values. Such tailing often cannot be suppressed even by using very polar mixtures[18]. As a consequence, for the separation of antioxidants some workers have used either carriers other than silica gel (paper chromatography[1,2,4,18]), or systems that contain a large amount of base[6], or they modified the surface of silica gel with other compounds[19,20], even for the derivatives of aliphatic amines[20].

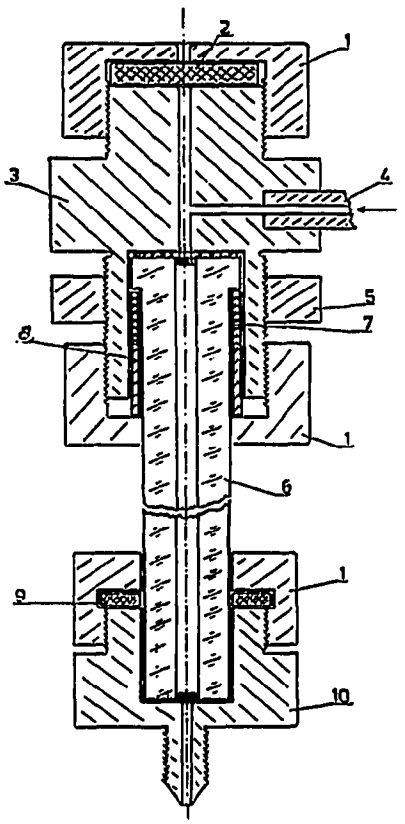

Fig. 1. Cross-section of the liquid chromatographic column: (1) nut; (2) silicone rubber packing of the adapter head; (3) body of the adapter; (4) solvent inlet; (5) nut for fixing on the supporting structure; (6) glass column; (7) PTFE packing; (8) brass tube; (9) silicone rubber packing of the lower adapter; (10) body of the lower adapter.

A phenomenon analogous to the tailing of aromatic diamines on silica gel was also observed in column chromatography on Silpearl. In the system ethanol–*n*-hexane or ethanol–*n*-heptane, very strong chemisorption of 1,4-phenylenediamine and of other diamines takes place at the top of the column, accompanied by the formation of a very intense red colour, which can be explained by the known reaction of 1,4-phenylenediamine with acids in the presence of trace amounts of oxygen, leading to the formation of a cation radical.

The considerable chemisorption of amines on silica gel has been explained by the presence of trace amounts of acids[21] remaining in the silica gel after the precipitation of silicic acid with mineral acids and insufficient washing out. However, this cannot occur with Silufol chromatographic plates or Silpearl packing, as in this case silicic acid is precipitated by pouring sodium silicate through a layer of an ion exchanger. The only suitable explanation is therefore the reaction of the amines with active hydroxyl groups on the surface of the silica gel.

The chemisorption described above can be suppressed by adding a small amount of triethylamine (0.1%, v/v) to the mobile phase, which has virtually no effect

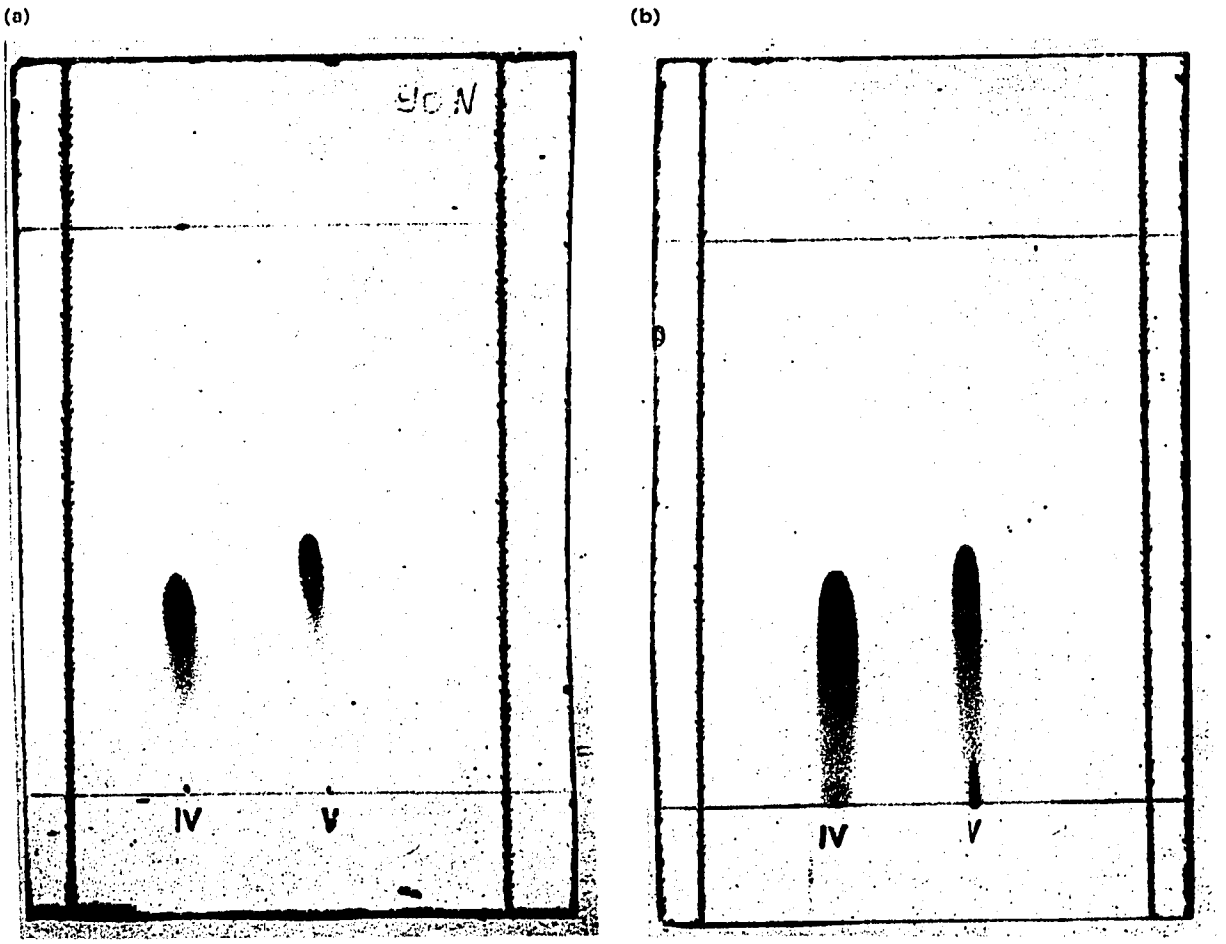

Fig. 2. Thin-layer chromatograms of 1,4-phenylenediamine (IV) and 2-methyl-1,4-phenylenediamine (V) in the systems (a) ethanol–*n*-hexane–triethylamine (90:10:0.1) and (b) ethanol–*n*-hexane (90:10).

on the R_F (or R_M) values, but removes the tailing of the compounds (*cf.*, Fig. 2a and 2b) and makes it possible to analyze the mixture of amines by liquid chromatography (see Fig. 3).

Such chemisorption of bases on silica gel is not the usual neutralization reaction that would be required in the presence of a trace amount of a mineral acid. If in liquid chromatography a mobile phase that does not contain triethylamine begins to flow through a silica gel column that has been in equilibrium with a system containing triethylamine, before long the latter is displaced and a new chemisorption of diamines takes place. The formation of such complexes was also assumed in the adsorption of aromatic amines on both alumina[22,23] and silica gel[24].

The effect of 0.1% triethylamine on elution behaviour in the systems ethanol–*n*-hexane and ethanol–*n*-heptane was tested by comparing the difference in R_F values with the same elution systems that did not contain triethylamine. Snyder[21] and later,

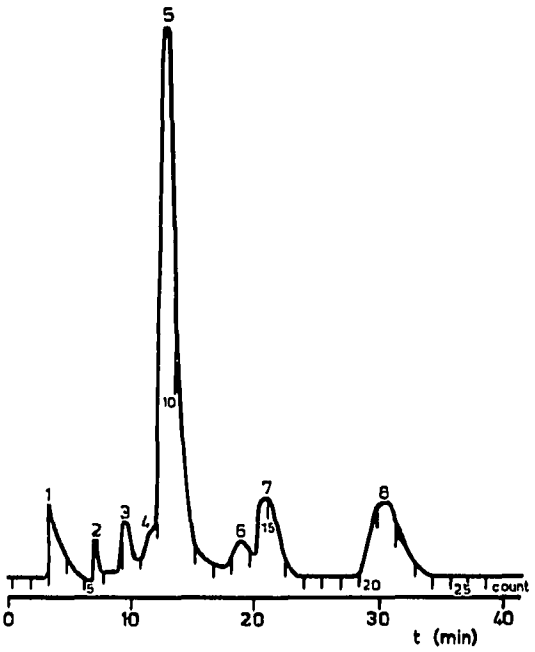

Fig. 3. A typical liquid chromatogram of a mixture from the reaction between N,N'-dimethyl-1,4-phenylenequinodiimine and methyl-lithium[16]. Solvent system: ethanol–*n*-heptane–triethylamine (5.5:94.5:0.1). Mobile phase flow-rate: 1.5 ml/min. Each count represents 1.95 ml. Peaks Nos. 1, 2, 3, 4 and 7 are reaction by-products. Peaks 5, 6 and 8 are compounds IX, X, VIII, respectively.

in a much simpler way, Soczewinski and Golkiewicz[25] derived the following relationship for the dependence of R_M on the solvent in thin-layer chromatography:

$$R_M = \log\left(\frac{1}{R_F} - 1\right) = \text{constant} - n \cdot \log x_S \qquad (1)$$

where n is the number of molecules of the solvent displaced from the active centre by one molecule of the substrate and x_S is the molar fraction of the polar solvent in the binary elution mixture. This dependence is represented by a straight line with a slope n, depending on the number of molecules of the solvent displaced from the active centre[25].

Eqn. 1 was correlated only for concentrations of ethanol ranging from 5 to 50% (v/v). In the range of medium concentrations, the dependence is represented by a straight line, identical in most cases for the systems with and without triethylamine (*cf.*, Fig. 4); the small differences observed for some compounds in Tables I and II may be explained by an inaccurate determination of R_F for systems that did not contain triethylamine. In some instances, at a concentration of ethanol of about 20% (v/v), the slope of the straight line changed (*cf.*, Fig. 5). This sudden change may be explained by multilayer adsorption of the polar solvent in the vicinity of the packing surface, which is then displaced by molecules of the substrate according to its basicity

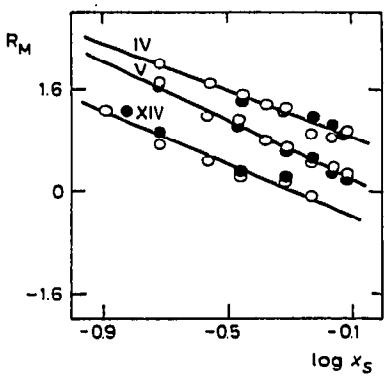

Fig. 4. Dependence of R_M on the molar fraction (x_S) of ethanol in the mobile phase in the system ethanol–*n*-hexane–0.1% triethylamine (open circles) and in the system ethanol–*n*-hexane (closed circles) for 1,4-phenylenediamine (IV), 2-methyl-1,4-phenylenediamine (V) and N-phenyl-N'-isopropyl-1,4-phenylenediamine (XIV).

TABLE I

$R_F \times 100$ VALUES OF AROMATIC DIAMINES ON SILUFOL PLATES IN THE SOLVENT SYSTEM ETHANOL–*n*-HEXANE

*Compound**	*Composition of the mobile phase (vol.-% ethanol)***					
	5 (0.151)	*10 (0.192)*	*20 (0.357)*	*30 (0.488)*	*40 (0.595)*	*50 (0.685)*
I	16	20	74	81	77	76
II	79	82	88	–	96	95
III	0	14	35	80	89	–
IV	0	1	4	5	7	9
V	0	2	9	20	27	35
VI	8	8	17	21	21	25
VII	0	1	3	6	8	7
VIII	0	2	4	6	8	8
IX	0	4	8	11	10	9
X	0	3	6	7	8	8
XI	0	1	2	2	3	3
XII	0	2	4	6	8	8
XIII	0	1	2	2	3	3
XIV	5	11	36	40	34	28
XV	16	28	68	83	81	72
XVI	25	29	68	97	97	96
XVII	2	13	60	95	96	95
XVIII	18	21	76	98	96	96

* See Table III for identification.
** Molar fractions are given in parentheses.

TABLE II

$R_F \times 100$ VALUES OF AROMATIC DIAMINES ON SILUFOL PLATES IN THE SOLVENT SYSTEM ETHANOL–*n*-HEXANE–0.1% TRIETHYLAMINE

*Compound**	*Composition of the mobile phase (vol.-% ethanol)***							
	5 (0.128)	*10 (0.192)*	*15 (0.279)*	*20 (0.352)*	*25 (0.422)*	*30 (0.490)*	*40 (0.594)*	*50 (0.689)*
I	15	22	34	65	80	79	78	75
II	75	82	84	89	94	95	94	94
III	40	49	68	68	85	94	–	–
IV	0	1	3	3	5	7	14	21
V	0	2	6	7	14	19	28	32
VI	6	11	25	34	38	45	52	54
VII	0	2	4	5	7	14	24	24
VIII	1	2	6	7	10	14	27	20
IX	4	5	9	10	12	18	26	20
X	2	3	6	8	11	17	24	23
XI	1	1	2	3	3	4	7	8
XII	0	0	1	2	3	5	10	13
XIII	3	12	13	21	39	39	31	30
XIV	5	15	27	39	43	55	44	42
XV	19	32	45	69	84	84	82	78
XVI	20	32	37	67	94	96	96	96
XVII	2	12	29	61	92	94	93	93
XVIII	13	22	34	68	94	98	97	96

* See Table III for identification.
** Molar fractions are given in parentheses.

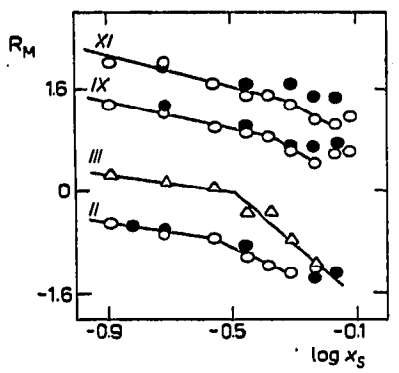

Fig. 5. Dependence of R_M on the molar fraction (x_S) of ethanol in the mobile phase in the system ethanol–*n*-hexane–0.1% triethylamine (open circles) and in the system ethanol–*n*-hexane (closed circles) for diphenylamine (II), N-phenyl-2-naphthylamine (III), N,N,N′-trimethyl-1,4-phenylenediamine (IX) and N,N′-diethyl-1,4-phenylenediamine (XI).

TABLE III

SLOPES OF THE DEPENDENCE OF R_M ON ETHANOL CONCENTRATION ACCORDING TO EQN. 1

No.	*Compound*	n_1	n_2
I	Aniline*	1.72	4.62
II	Diphenylamine*	0.73	1.55
III	Phenyl-2-naphthylamine*	0.60	4.55
IV	1,4-Phenylenediamine*	1.8	—
V	2-Methyl-1,4-phenylenediamine**	2.35	—
VI	N,N-Diethyl-1,4-phenylenediamine*	1.38	2.3
VII	2-Methylamino-5-aminotoluene**	2.62	3.7
VIII	N,N'-Dimethyl-1,4-phenylenediamine**	2.23	—
IX	N,N,N'-Trimethyl-1,4-phenylenediamine**	0.97	2.2
X	2,5-Bis(methylamino)toluene**	1.45	2.77
XI	N,N'-Diethyl-1,4-phenylenediamine*	1.12	2.44
XII	N,N'-Diisopropyl-1,4-phenylenediamine***	2.9	—
XIII	N,N'-Di-*sec.*-butyl-1,4-phenylenediamine§	2.2	—
XIV	N-Phenyl-N'-isopropyl-1,4-phenylenediamine§§	2.38	—
XV	N-Phenyl-N'-*sec.*-butyl-1,4-phenylenediamine§§	2.45	—
XVI	N,N'-Diphenyl-1,4-phenylenediamine§§§	2.34	7.95
XVII	N-Phenyl-N'-tosyl-1,4-phenylenediamine§§§	4.33	6.92
XVIII	N,N'-Di-2-naphthyl-1,4-phenylenediamine†	1.63	8.2

* Lachema, Brno, Czechoslovakia.
** *Cf*, ref. 16.
*** See ref. 17.
§ I.C.I., Macclesfield, Great Britain.
§§ Arnold & Hoffmann, Providence, R.I., U.S.A.
§§§ U.S. Rubber Co., Naugatuck Chemical Division, New York, N.Y. U.S.A.
† Monsanto, St. Louis, Mo., U.S.A.

and size. Similar deviations were also observed by Lesiak and Orlikowska[5] in the mixtures benzene–acetone with ratios from 3:1 to 3:4. The slopes n for the compounds investigated are summarized in Table III, together with some more detailed data on the substrates; n_1 is the slope of the original straight line and n_2 is the slope of the straight line in the range of higer ethanol concentrations.

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