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THIN-LAYER CHROMATOGRAPHY OF SOME AROMATIC AMINO COMPOUNDS

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SUMMARY

A series of amines has been chromatographed on silica gel thin layers and on layers of cellulose impregnated with bis(2-ethylhexyl)phosphate, the latter system being investigated with hydrochloric acid mobile phases and with mixed aqueous perchlorate–chloride mobile phases. The hydrochloric acid mobile phases failed to resolve the model compounds. Resolution occurred in the mixed perchlorate–chloride systems. The chromatographic mechanism governing the resolution was considered to be uptake of the solutes by molecular association between the hydrocarbon residue of the stationary phase and the aromatic skeleton of the solutes followed by their removal from the stationary phase as a consequence of the solvation of the amino groups by the aqueous mobile phases. The modification of these effects by steric factors is considered.

INTRODUCTION

The recent interest shown in the use of various organophosphorus compounds and long-chain amines as liquid ion exchangers has led to the development of several new methods for the separation of inorganic ions by reversed-phase chromatography. These have been extensively reviewed by CERRAI[1]. The application of amines to reversed-phase thin-layer chromatography has been investigated by BRINKMAN and co-workers[2–4] and also by GRAHAM *et al.*[5–7]. Little use has as yet been made of liquid ion exchangers for the reversed-phase chromatography of organic ions although the possibilities of success in such systems appear equally viable. For example, SOCZEWIŃSKI AND ROJOWSKA[8] have reported the reversed-phase chromatography of some organic electrolytes including several heterocyclic nitrogen bases on papers impregnated with bis(2-ethylhexyl)phosphate (HDEHP) and eluted with citric acid solutions.

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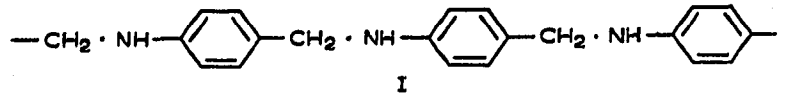
Similarly, the thin-layer chromatography of aniline derivatives on cellulose impregnated with HDEHP is presently being investigated by GRAHAM and the results of this work will be reported shortly.

The present work describes the application of normal thin-layer chromatography and reversed-phase thin-layer chromatography to the separation of several aromatic polyamines produced as a result of the condensation reaction between aniline and formaldehyde under acidic conditions. The products obtained in this reaction depend to a large extent on the ratio of formaldehyde–aniline in the reaction mixture.

(a) High formaldehyde–aniline ratio

When the formaldehyde is in excess, long-chain amines result, *i.e.*



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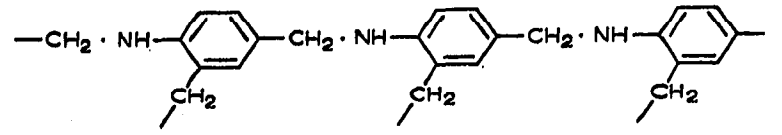
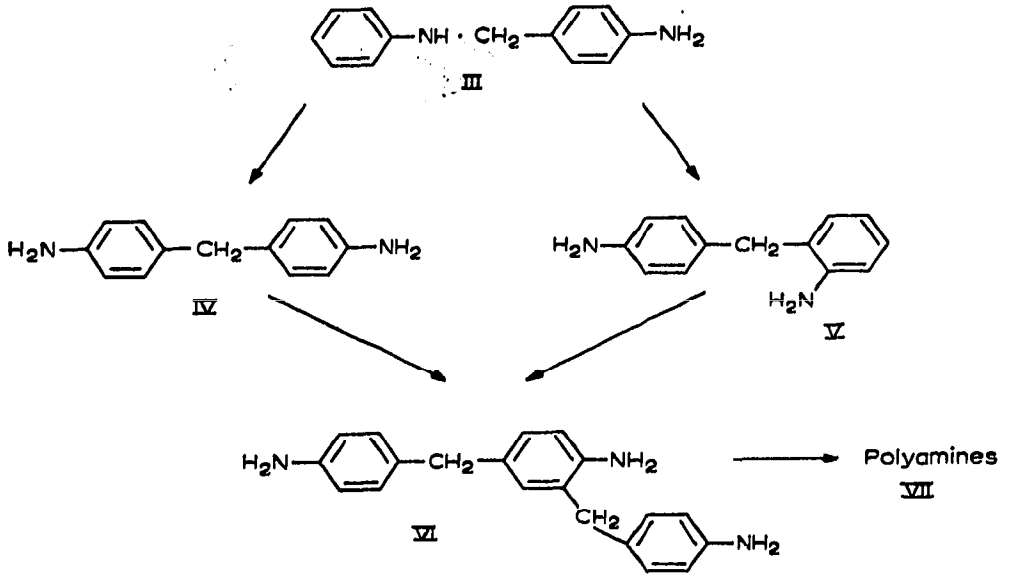


(b) Low formaldehyde–aniline ratio

When aniline is in excess, compound III is formed which, on heating, undergoes a rearrangement resulting in the formation of compounds IV–VII.



We are concerned with the development of a thin-layer chromatographic system which could be used for the rapid evaluation of the course of the reaction in formaldehyde–aniline condensations involving a low formaldehyde–aniline ratio, *i.e.* reaction (b). To this end we have chromatographed a series of diamines and one aminobenzyl derivative, as well as aniline, *o*-phenylenediamine (OPD) and *p*-phenylenediamine (PPD) as model compounds. From the results obtained we are able to assess the

chromatographic mechanism underlying the separations obtained in the systems studied.

EXPERIMENTAL

Solutions of the aromatic amines (1.0% in acetone) were prepared.

Silica Gel-D5 (25 g) was slurried with distilled water, and the slurry was used to coat 5 clean glass plates (20 cm × 20 cm) at an applied layer thickness of 0.25 mm using a Shandon applicator. The layers were allowed to air dry overnight.

Cellulose (15 g MN 300HR) was slurried with a solution of HDEHP (65 cm^3 of a 5% v/v solution in carbon tetrachloride), and the homogenate was used to coat clean glass plates at an applied layer thickness of 0.3 mm. They were then left for 1 h to allow the carbon tetrachloride to evaporate.

Samples of the amines (2 μl) were applied to the layers, the dispersing solvent was evaporated and the prepared chromatolayers were eluted in a double saturation chamber, *i.e.* the polythene bag technique[9], using the appropriate mobile phases discussed below.

For silica gel thin layers, the mobile phases were *n*-butanol–hydrochloric acid mixtures or *n*-butanol–acetic acid mixtures[10]. For the reversed-phase systems, the mobile phases were either aqueous hydrochloric acid 0.1–1.0 *M* or mixtures of aqueous hydrochloric acid (0.6–1.2 *M*) and aqueous sodium perchlorate (2*M*) in the ratio of 1:10. The development of the chromatograms was halted when the mobile phase had travelled a fixed distance (13.0 ± 0.5 cm) from the point of application of the samples. The time taken for this varied according to the system used. For the silica gel systems it was 2.5 ± 0.5 h whilst for the reversed-phase systems it was 1–1.25 h. After this the plates were dried in a forced draught oven at 85° for 20 min. They were then sprayed with *p*-dimethyl aminobenzaldehyde (0.5% w/v in ethanol) to reveal

TABLE I

R_F VALUES OF AMINO COMPOUNDS OBTAINED FROM THIN LAYERS OF CELLULOSE IMPREGNATED WITH BIS(2-ETHYLHEXYL)PHOSPHATE IN PERCHLORATE(2 *M*)–CHLORIDE (10:1) MEDIA

Amine	*Molarity of hydrochloric acid solution before dilution with sodium perchlorate solution (2.0 M)*					
	0.6	*0.7*	*0.8*	*0.9*	*1.0*	*1.2*
Aniline	0.57	0.61	0.60	0.60	0.61	0.65
o-Phenylenediamine	0.57	0.58	0.58	0.59	0.61	0.65
p-Phenylenediamine	0.85	0.89	0.89	0.88	0.85	0.88
2,2'-Diamino-diphenylmethane	0.22	0.25	0.27	0.31	0.33	0.44
2,4'-Diamino-diphenylmethane	0.37	0.43	0.44	0.51	0.54	0.62
4,4'-Diamino-diphenylmethane	0.37	0.44	0.45	0.51	0.54	0.62
4,4'-Diamino-3-methyl-diphenylmethane (a)	0.09	0.13	0.13	0.18	0.20	0.26
(b)	0.23	0.27	0.29	0.33	0.35	0.45
(c)	0.39	0.44	0.46	0.50	0.54	0.61
4,4'-Diamino-3,3'-dimethyl-diphenylmethane	0.14	0.19	0.18	0.22	0.24	0.28
2,4'-Diamino-4-(4''-aminobenzyl)-diphenylmethane (d)	0.20	0.29	0.31	0.41	0.46	0.55
(e)	0.34	0.43	0.44	0.52		

the amines as bright yellow spots on a white background. The R_F values, computed in the normal way, are recorded in Table I.

RESULTS AND DISCUSSION

The silica gel systems

These proved to be unsatisfactory for the resolution of the model compounds studied because, in general, all the solutes yielded extremely diffuse spots from which it was not possible to compute accurate R_F values; the approximate R_F values for all the compounds were identical. For these reasons the normal thin-layer chromatographic systems were abandoned in favour of a reversed-phase system.

Reversed-phase system

After considering the potential of the many liquid stationary phases used as thin-layer chromatographic impregnants, we decided to investigate the possibility of using the liquid cation exchanger, HDEHP. Our reason for this is the basic nature of the model compounds which under suitable conditions would give cationic species capable of exchanging with the labile proton on the layers. This should enable us to evaluate not only the ion-exchange potential of the stationary phase, which has been fully exploited for inorganic systems[1], but also the possibility of the enhancement of the ion-exchange mechanism by any molecular association between the non-polar part of the ion exchanger and the aromatic skeleton of the bases. We therefore initiated our experiments using aqueous hydrochloric acid as mobile phases.

In these, the amines were but partially resolved, the degree of separation was inadequate for the characterisation of the amines on the basis of their R_F values. In 0.1 M acid the amines essentially remained at the point of application to the layers whilst in 1.0 M acid they moved with the solvent front. Under the acid conditions investigated, the amines will undoubtedly be protonated and it is suggested that the amino-cation is solvated to a high degree and consequently their solubilities in the aqueous phase increase; hence they are carried with the solvent front in 1.0 M acid.

In an attempt to reduce the high degree of solvation of the amino-cation, and hence its tendency to migrate with the solvent front, we used a modified aqueous mobile phase containing perchlorate ions in addition to the chloride ions because SEKINE[11] has stated that the degree of solvation of inorganic cations is reduced by the presence of the perchlorate ion in the aqueous phase. The results using the mixed perchlorate–chloride mobile phases are shown in Table I. From these we make certain postulations concerning the chromatographic mechanism involved in the system.

Before a detailed consideration of the chromatographic mechanism, however, it is pertinent to point out that two of our model compounds gave multiple spots in the chromatographic system studied. 4,4′-Diamino-3-methyl-diphenylmethane gave three well defined spots. Of these the upper spot was considered to be the non-methylated 4,4′-diamino-diphenylmethane, *i.e.* spot (c) in Table I. Spot (b) for this mixture is thought to be the authentic 4,4′-diamino-3-methyl-diphenylmethane. The third spot for this mixture, *i.e.* spot (a), whilst having R_F values close to those for 4,4′-diamino-3,3′-dimethyl-diphenylmethane, could not be positively identified with this compound so that its identity must remain in doubt.

The compound 2,4′-diamino-4-(4″-aminobenzyl)-diphenylmethane gave two

spots, the upper one (spot(e)) which was small and barely discernable on the sprayed chromatograms, is probably either the 4,4'-or the 2,4'-diamino-diphenylmethane both of which are used in the preparation of the triamine. The lower spot, spot (d) is therefore considered to be the authentic tri-amine.

In a purely ion-exchange system the divalent cation, *i.e.* the diamines would be expected to be more firmly held than the monovalent monoamine. In this connection we would therefore expect the two phenylenediamines to have lower R_F values than aniline. The results, however, clearly show that *p*-phenylenediamine has much higher R_F values than aniline itself whilst the R_F value of the latter are comparable with those of the *o*-phenylenediamine. For these reasons, we suppose that ion exchange between the labile proton on the stationary phase and the organic cation plays but a minor part in the chromatographic mechanism investigated here. Rather, the system is best regarded as one in which molecular association occurs between the hydrocarbon residue of the stationary phase and the low-polarity aromatic skeleton of the amines. This retardation mechanism is opposed by the solvation of the amino group by the stationary phase. Thus the phenylenediamine has two amino groups to be solvated and hence it migrates further than aniline in which there is but a single amino group capable of solvation by the mobile phase. The results for the *o*-phenylenediamine are readily explained in terms of a steric effect in which the two adjacent amino groups mutually interfere with their own solvation by the aqueous mobile phases. Thus we are proposing a system in which the solutes are taken into the stationary phase by molecular association with the stationary phase by a predominately non-ionic partition mechanism whilst their removal from the stationary phase involves the solvation of the polar amino groups by the aqueous phase. Similar non-ionic partition mechanisms have been proposed by SOCZEWIŃSKI *et al.* for the paper chromatography[12] and for the solvent extraction[13] of amino acids in the system hexanone–HDEHP/aqueous buffer solutions.

Further credence is given to our view from the results obtained for other amines. Thus the phenylenediamines and the diamino-diphenylmethanes all have the same number of solvation points, *i.e.* amino groups in the molecules, but the latter group of compounds have significantly lower R_F values than the former. This we attribute to the increase in the size of the aromatic skeleton of the latter compounds compared with the former. The triamino compound, 2,4'-diamino-4-(4''-aminobenzyl)-diphenylmethane has lower R_F values than the diamino-diphenylmethanes thus indicating that the expected increase in R_F values consequent upon the presence of the third amino group is more than compensated for by the increased solvation of the aromatic skeleton by the stationary phase. This is caused by the presence of the extra phenyl nucleus within the molecule.

To return to the behavior of the diamino-diphenylmethanes we find a number of interesting features which support our hypothesis.

Firstly, the 2,2'-diamino-diphenylmethane has lower R_F values than either the 2,4'-, or the 4,4'-compounds. For the first of these compounds, two extreme configurations with respect to the amino groups are possible. In the first, the amino groups are in close proximity and clearly a steric hindrance to the solvation of both by the mobile phase will occur (*cf.* *o*-phenylenediamine). In the second configuration, the amino groups lie on opposite sides of the molecule so that the orientation of the hydrocarbon part of the molecule with respect to the stationary phase results in one

of the amino groups being forced into the stationary phase, thus reducing its availability for solvation by the mobile phase. Whilst accepting that the latter configuration represents the most relaxed form of the molecule, the overall result is the same whichever configuration is considered, for solvation by the mobile phase.

The comparability of R_F values for the pair 2,4'-, and 4,4'-diamino-diphenylmethane is to be expected on the basis of our hypothesis for the aromatic skeleton of both is identical and each possesses two amino groups to be solvated by the mobile phases. Effectively the retarding forces and the forces causing migration are equivalent in these two compounds and hence they would be expected to have identical R_F values. This has been found to be so.

The effect of substituting one or more methyl groups into the 4,4'-diaminodiphenylmethane molecule caused the R_F values to decrease. This reduction in R_F values probably stems from two sources, the methyl groups increasing the hydrocarbon part of the molecule and hence its ability to dissolve in the alkyl residue of the stationary phase, and because in each case the methyl group is substituted in a position ortho to an amino group, it will reduce the solvation of the amino group by the aqueous mobile phase. An effect comparable with this has been observed for phenols chromatographed by reversed-phase thin-layer chromatography[14,15].

CONCLUSION

A satisfactory separation of many of the low molecular weight compounds formed during the condensation of formaldehyde with aniline when the latter is in excess has been obtained.

In the reversed-phase system studied, it is unlikely that the retarding mechanism is one of ion exchange. Rather, it is a result of the molecular association between the aromatic skeleton of the solute and the hydrocarbon residue of the stationary phase. This is opposed by solvation of the amino groups by the aqueous mobile phases.

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