

Short Communication

Thin-layer chromatography on polyacrylonitrile

V. Consideration of separation mechanisms of some aliphatic and aromatic amines

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ABSTRACT

The chromatographic behaviour of ten aliphatic and aromatic amines on thin layers of polyacrylonitrile sorbent was investigated using seven aqueous solvent systems. It was established that an increase in the hydrophobic part of the amines results in their increased retention on this sorbent. A positive linear dependence between the number of carbon atoms in the *n*-alkyl groups of primary aliphatic amines and the corresponding R_M values was also established. The separation of the investigated amines was assumed to be based on non-specific hydrophobic interactions between their non-polar parts and the hydrocarbon chains of the sorbent.

INTRODUCTION

In previously published papers of this series [1–4] the application of polyacrylonitrile sorbent (PANS), as a bifunctional adsorbent consisting of polar cyano groups and non-polar hydrocarbon chains, to the separation of several classes of compounds was described and the corresponding separation mechanisms were considered. Thus, in the separation of isomeric *cis*–*trans* complexes of cobalt (III) [1] it was assumed that hydrogen bonds form between the cyano groups of this sorbent and N-hydrogens of the sorbate, and also that the sorbent

retains cationic complexes on the basis of ion-dipole interactions. It was further assumed that the separations of some food-stuff dyes [2], *tris*(β -diketonato) complexes of transition metals [3] as well as *tris*(alkylxanthato)cobalt(III) complexes [4] by means of aqueous solvent systems are based on non-specific interactions between the non-polar parts of the sorbent and the sorbates (reversed-phase chromatography). However, under conditions used for normal-phase chromatography, namely the application of non-aqueous solvent systems for the separation of *tris*(β -diketonato) complexes of cobalt(III), chromium(III) and ruthenium (III), which do not contain aromatic rings in their molecules [3], and *tris*(alkylxanthato)cobalt(III) complexes [4] it was assumed that these substances are sorbed on PANS by the mechanism of hydrogen bond formation between methyne hydrogen atoms

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of the sorbent and highly electronegative atoms of the sorbates. Finally, in investigations of the chromatographic behaviour of tris(β -diketonato) complexes of transition metals, containing aromatic rings in their molecules [3] using non-aqueous solvents, it was assumed that the sorption of these substances on PANS is based on donor–acceptor interactions of the π -electron systems of the sorbates and the cyano groups of the sorbent.

Continuing our investigations of the separation mechanisms of different sorbates on PANS, in this paper we wanted to examine the chromatographic behaviour of hydrochlorides of some aliphatic and aromatic amines by the application of aqueous solvent systems. Under these conditions amines occur in the form of positively charged cations containing various hydrophobic parts and may be expected to exhibit an interesting chromatographic behaviour. At the same time, these investigations may serve as a check and confirmation of the previously assumed possible interactions between PANS and different sorbates.

EXPERIMENTAL

The preparation of PANS, its application to microscope slides and development of chromatograms are described in our first paper [1]. The investigated *n*-butylamine, *n*-hexylamine, *n*-octylamine and *n*-decylamine (Merck, Darmstadt, Germany), *n*-dodecylamine, dihexylamine, N-isopropylcyclohexylamine (Fluka, Buchs, Switzerland) and N-alkylaryl amines (synthesized and analysed by Mr. Milovan Ivanović, IHTM, Belgrade, Yugoslavia, according to procedures described in the literature [5]) were

first, before being spotted on PANS layers, converted into the corresponding substituted ammonium chlorides by means of 6 mol dm⁻³ hydrochloric acid. To measured volumes of the latter solutions, whose concentration was about 2 mmol cm⁻³ and pH about 2, an equivalent volume of ethanol was added. In all the investigated cases the plates were spotted with 0.2 μ l of freshly prepared solutions.

All components of the chromatographic solvent systems used (Table I) were of analytical grade.

The detection of amines was performed by exposing developed plates to iodine vapour for 10 min.

RESULTS AND DISCUSSION

As can be seen from Table I, seven solvent systems were used for the separation of the investigated substances. These solvent systems, which mainly contain water, was selected above all because the investigated substances are water-soluble salts. In addition, the selected systems also contain Brønsted acids, which prevent protolysis of the sorbate cations.

The R_F values measured are listed in Table II. As may be seen from the table, the results obtained for primary aliphatic amines (substances 1–5) show that elongation of the alkyl group of the amines results in increased retention on PANS. This trend also holds for other cases where the hydrophobic part of a molecule is increased, illustrated by the following sequences:

- (a) $R_F(6) < R_F(2)$;
 (b) $R_F(10) < R_F(9) < R_F(8)$

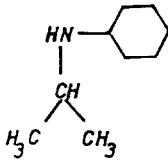
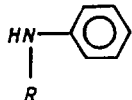
where the numbers in brackets correspond to the ordinal numbers of amines in Table II.

TABLE I

COMPOSITION OF THE CHROMATOGRAPHIC SOLVENT SYSTEMS USED AND THE CORRESPONDING DEVELOPMENT TIMES

No.	Solvent system	Volume ratio	Development time (min)
1	1 M hydrochloric acid	–	35
2	1.25 M hydrochloric acid–ethanol	80:20	45
3	0.125 M hydrochloric acid–ethanol	80:20	45
4	0.1 M perchloric acid	–	30
5	0.125 M perchloric acid–ethanol	80:20	40
6	1 M ammonium chloride	–	35
7	1.25 M ammonium chloride–ethanol	80:20	45

TABLE II
 R_F VALUES OF THE INVESTIGATED AMINES

No.	Amine	Solvent system ^a						
		1	2	3	4	5	6	7
1	$\text{CH}_3-(\text{CH}_2)_n-\text{NH}_2$ $n = 3$	79	86	84	79	87	81	85
2	$n = 5$	64	78	76	58	78	67	71
3	$n = 7$	36	71	58	23	54	50	56
4	$n = 9$	18	63	46	9	30	36	41
5	$n = 11$	10	46	25	0	17	24	27
6	$[\text{CH}_3-(\text{CH}_2)_5]_2\text{NH}$	47	53	31	11	28	39	47
7		88	90	86	79	86	83	91
8	 R = 2-propyl	81	87	81	71	79	78	88
9	R = 2-butyl	75	82	79	68	78	68	78
10	R = cycloheptyl	67	76	75	64	77	50	67

^a See Table I.

In addition, from Table II it may be seen that in all the investigated cases relatively smaller R_F values were established for the amine 8, which contains one aromatic ring, in comparison with the amine 7, in which this ring is completely hydrogenated.

Taking into account the chemical nature of PANS and that of the investigated substituted ammonium salts, the following most probable separation mechanisms can be assumed:

(1) The formation of hydrogen bonds between the cyano groups of the sorbent and N-hydrogens of a sorbate.

(2) Ion exchange of the investigated cations on carboxylic groups of the sorbent [1].

(3) Non-specific hydrophobic interactions between the hydrocarbon moieties of the investigated amines and the non-polar chains of PANS.

In the case of alkyl amines, however, the first interaction above is inconsistent with the obtained results, *i.e.*, if this interaction is predominant, a sequence of R_F values opposite to that observed should be expected. As is known, the positive inductive effect, which increases with elongation of an alkyl group, would decrease the effective positive charge on the hydrogen atoms of an alkyl-substituted ammonium group. This will weaken hydrogen bonds. The same effect would cause increased steric hindrance with chain elongation.

On the other hand, under conditions of ion-exchange chromatography of amines on different ion exchangers it has been established by other authors [6,7] that an increase in the non-polar part of amines results in their increased retention. Therefore, if this mechanism is relevant for the investigat-

ed process a sequence of aliphatic amine R_F values would be similar to that observed in this work. However, as is known [1], ion exchange on carboxylic groups is not possible when strongly acidic solvents are used (in our case solvents 1–5, Table I). Consequently, as the results obtained in this paper using these solvents are not significantly different from those established with the solvents containing salts, it seems that the ion-exchange mechanism in the latter case is not predominant.

From all the aforesaid it may be assumed that the separation of these substances takes place in a reversed-phase mode, *i.e.* by hydrophobic interactions [8], where, as it is known, an increase in the hydrophobicity of the sorbate results in increased retention. Such an assumption is supported by the fact that all the solvent systems used are similar to those applied in reversed-phase chromatography and by the observation that a decrease in the water content of a solvent system leads to an increase in the R_F value [9,10]. Similar behaviour has been observed on cyanopropyl-modified silica (which also contains cyano groups and hydrocarbon chains) by chromatography of some steroids using aqueous solvents [10] and was explained by the presence of non-polar hydrocarbon chains between the silica gel skeleton and the cyano groups.

Finally, a possible explanation for the observed sequence of amines 7 and 8 could be the fact that amine 8, which contains a benzene ring with planar configuration, exhibits a greater sorbate–sorbent contact surface than amine 7, which contains a non-planar cyclohexane ring [11]. A greater retention for benzene than cyclohexane was also established in adsorption gas chromatography on graphite, where the retention is exclusively based on dispersive sorbate–sorbent interactions.

In addition, a linear dependence between the number of carbon atoms in a *n*-alkyl group of primary aliphatic amines and the corresponding R_F values was established (Fig. 1).

On the basis of all the aforesaid it may be concluded that the results obtained in this work make more probable the hydrophobic interaction mechanism for the separation of other substances on PANS, proposed in our earlier papers [2–4], since it could be applied also to explain the chromatographic behaviour of amines investigated in this paper.

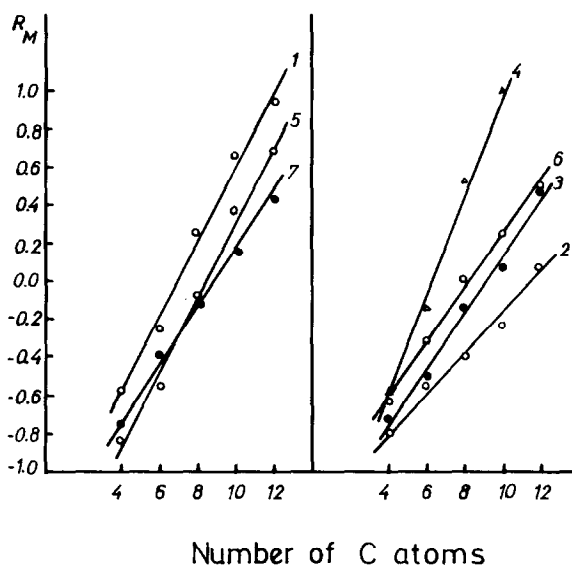


Fig. 1. Relation between the number of carbon atoms in a *n*-alkyl group of primary aliphatic amines and the corresponding R_M values. The numbers on the lines refer to the solvent system used given in Table I.

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