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THIN-LAYER CHROMATOGRAPHY OF ALIPHATIC AMINES

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SUMMARY

A large number of aliphatic amines have been studied by thin-layer chromatography. Some relationships between chemical structure, chromatographic behaviour and physical properties are discussed.

INTRODUCTION

Thin-layer chromatography (TLC) is one of the simplest techniques for examining and identifying the components in aliphatic amine mixtures. In most of the literature on this topic, specific analytical problems of separation[1], identification[2] and detection[3–7] are considered, particularly in biological studies. Studies on the general chromatographic behaviour of aliphatic amines have been especially focused on restricted groups[1,8–13] or on homogeneous classes such as alkanolamines[14,15], diamines[2,9,16–20], polyamines[2,16,18,21–23] and biogenic amines[2,16–18,24–27]. Further, in much of the literature reactions that give derivatives which are easily separated and in many instances are already coloured have been considered; some of these are dansyl derivatives[16–18,25–28], 2,4-dinitrophenyl derivatives[2,29], N,N-dimethyl-*p*-aminobenzene azobenzoylamides[30,31], 4-dimethylamino-3,5-dinitrobenzoylamides[32], 4-(phenylazo)benzenesulphonamides[33] and reaction products with 7-chloro-4-nitrobenzo-2-oxa-1,3-diazole[34].

The aim of the present study, which was started with an eluent referred to by Gnehm *et al.*[11], was a systematic collection of data on the direct chromatographic examination of a large number of aliphatic amines, with particular emphasis on eluents, adsorbents, R_F values and detection reagents. From these data, it is possible to find relationships between chemical structure, chromatographic behaviour and physical properties, which may be useful for identification purposes.

EXPERIMENTAL

Samples

The following groups of aliphatic amines were examined: linear mono-, di- and trialkylamines, mono- and diisoalkylamines, alkanolamines, N-alkylalkanolamines and polyamines. Volumes of 10 μl of a 0.5% water–alcohol solution of the

TABLE I

BEHAVIOUR OF ALIPHATIC AMINES IN FIVE ELUENTS AND WITH FIVE DETECTION SYSTEMS

Eluents and detection reagents are specified under Experimental; + = positive reaction; +− = faint reaction; − = negative reaction.

No.	*Compound*		*Eluent I*		*Eluent II*		*Eluent III*		*Eluent IV*		*Eluent V*		*Detection*				
	Empirical formula	*Name*	hR_F	R_M	hR_F	R_M	hR_F	R_M	hR_F	R_M	hR_F	R_M	*A*	*B*	*C*	*D*	*E*
1	CH_5N	Methylamine	3.5	1.44	6	1.195							+	+−	−	+−	+
2	$C_2H_5NO_2$	Glycine	0	∞	2	1.69	36	0.250	47	0.052	80	−0.602	+	+	+	+	+
3	C_2H_7N	Ethylamine	7	1.123	16	0.720							+	+−	−	+−	+
4	C_2H_7N	Dimethylamine	4	1.38	7	1.123	11	0.980	12	0.865			+−	+	+	+	−
5	C_2H_7NO	Ethanolamine	4	1.38	10	0.954	37	0.231	44	0.105	58	−0.140	+	+	+	+	+
6	$C_2H_8N_2$	Ethylenediamine	2	1.690	4	1.380	15	0.753	20	0.602	40	0.176	+	+	+	+	+
7	C_3H_9N	Propylamine	16	0.720	35	0.269							+	+−	+	+	+
8	C_3H_9N	Isopropylamine	17.5	0.673	36	0.250	73	−0.432					+−	+	+	+−	+
9	C_3H_9N	Trimethylamine			43	0.122							−	+−			−
10	C_3H_9NO	Propanolamine	4	1.380	8	1.061	28	0.410	31	0.288	50	±0.00	+	+	+	−	+
11	$C_3H_{10}N_2$	Propylenediamine	3	1.510	10	0.954	35	0.269	40	0.176	55	−0.087	+	+	+	+	+
12	C_4H_9NO	Morpholine	4.3	0.122	71	−0.389	86	−0.788					+−	+	+	+	−
13	$C_4H_{10}N_2$	Piperazine	3	1.510	5	1.279	23	0.525	25	0.477	40	0.176	+	+	+	+	−
14	$C_4H_{11}N$	Butylamine	22	0.550	48	0.035							+	+	+	+	+
15	$C_4H_{11}N$	Isobutylamine	31	0.347	58	−0.140	84	−0.720					+	+	+	+	+
16	$C_4H_{11}N$	Diethylamine	16	0.720	32	0.327	57	−0.122	41	0.158			+−	+−	+	−	−
17	$C_4H_{11}NO$	3-Methoxypropylamine	18	0.659	43	0.122	63	−0.231					+	+	+	+	+
18	$C_4H_{11}NO$	Ethylethanolamine	11	0.908	23	0.525	54	−0.070					+	+	+	+	−
19	$C_4H_{11}NO_2$	Diethanolamine	5	1.279	16	0.720	50	±0.00					+−	+	−	+	+−
20	$C_4H_{13}N_3$	Diethylenetriamine	0	∞	0	∞	7	1.123	8.5	1.032	30	0.368	+	+	+	−	+
21	$C_5H_{13}N$	Pentylamine	29	0.389	55	−0.087							+	+	+	+	+
22	$C_5H_{13}N$	Isoamylamine	30	0.368	56	−0.105	84	−0.720					+	+	+	+	+
23	$C_5H_{13}N$	2-Methylbutylamine	36	0.250	68	−0.327	85	−0.753					+	+	+	+	+
24	$C_6H_{13}N$	Cyclohexylamine	33	0.308	63	−0.231	85	−0.753					+−	+	+	+	+

25	$C_6H_{13}NO$	N-Ethylmorpholine	95	−1.279	100	∞							−	+	+	−	−
26	$C_6H_{15}N$	Hexylamine	34	0.288	65	−0.269							+	+	+	+	+
27	$C_6H_{15}N$	3-Amino-2,2′-dimethylbutane	51	−0.017	90	−0.954							−	+	+	+	+
28	$C_6H_{15}N$	2-Amino-3-methylpentane	47	0.052	78	−0.550	88	−0.865					−	+	+	+	+
29	$C_6H_{15}N$	2-Amino-4-methylpentane	42	0.140	73	−0.432	82	−0.659					−	+	+	+	+
30	$C_6H_{15}N$	Di-*n*-propylamine	51	−0.017	80	−0.602	91	−1.005					+−	+	+	+	−
31	$C_6H_{15}N$	Diisopropylamine	33	0.308	66	−0.288	90	−0.954					−	−	+	−	−
32	$C_6H_{15}N$	Triethylamine			75	−0.477							+−	+			−
33	$C_6H_{15}NO_2$	Ethyldiethanolamine	30	0.368	52	−0.035	84	0.720					+−	+	+	−	−
34	$C_6H_{15}NO_3$	Triethanolamine	18	0.659	36	0.250	75	−0.477					−	+	+	−	−
35	$C_7H_{17}N$	Heptylamine	36	0.250	70	−0.368							+	+	+	+	+
36	$C_7H_{17}NO_2$	Propyldiethanolamine	52	−0.035	69	−0.347	92	−1.061					+−	+	+	−	−
37	$C_8H_{19}N$	Octylamine	37.5	0.222	74	−0.454							+	+	+	+	+
38	$C_8H_{19}N$	2-Ethylhexylamine	54	−0.070	88	−0.865							+	+	+	+−	+
39	$C_8H_{19}N$	Di-*n*-butylamine	63	−0.231	95	−1.279							+	+	+	+	+
40	$C_8H_{19}N$	Diisobutylamine	85	−0.753	99	−1.996							+	+	+	+	+
41	$C_8H_{19}N$	*tert.*-Octylamine	52	−0.035	87	−0.826							−	+−	+	−	−
42	$C_8H_{23}N_5$	Tetraethylenepentamine					0	∞	3.0	1.510	20	0.602	+	+	+	−	+
43	$C_9H_{20}N_2$	N-(3-Aminopropyl)cyclohexylamine	5	1.279	18	0.659	61	−0.194					+	+	+	+	+
44	$C_9H_{21}N$	Nonylamine	39	0.194	77	−0.525							+	+	+	+	+
45	$C_9H_{21}NO_3$	Triisopropanolamine	52	−0.035	85	−0.753							−	+	+	−	−
46	$C_{10}H_{23}N$	Decylamine	40.5	0.167	78	−0.550							+	+	+	+	+
47	$C_{10}H_{23}NO$	2-Ethylhexylethanolamine	65	−0.269	93	−1.123							+	+	+	+	+
48	$C_{11}H_{25}N$	Undecylamine	42	0.140	79	−0.575							+	+	+	+	+
49	$C_{12}H_{27}N$	Dodecylamine	44	0.105	79	−0.575							+	+	+	+	+
50	$C_{13}H_{29}N$	Tridecylamine	47	0.052	80	−0.602							+	+	+	+	+
51	$C_{14}H_{31}N$	Tetradecylamine	50	±0.00	82	−0.659							+	+	+	+	+
52	$C_{15}H_{33}N$	Pentadecylamine	52	−0.035	83	−0.689							+	+	+	+	+
53	$C_{16}H_{35}N$	Hexadecylamine	55	−0.087	85	−0.753							+	+	+	+	+
54	$C_{16}H_{33}N$	Di-2-ethylhexylamine	100	∞									+	+	+	+	−
55	$C_{17}H_{37}N$	Heptadecylamine	58	−0.140	85	−0.753							+	+	+	+	+
56	$C_{18}H_{39}N$	Stearylamine	60	−0.176	85	−0.753							+	+	+	+	+

amine hydrochlorides were applied to the starting point on the chromatographic plates.

Adsorbents

The adsorbents used were silica gel G (Merck, Darmstadt, G.F.R.), Kieselguhr G (Merck), impregnated, after coating, by immersing the plates in a 5% solution of paraffin oil in acetone, and silanized silica gel H (Merck). Coating was effected by following the manufacturer's instructions.

Eluents

Adsorption chromatography on silica gel G was performed by using the following eluents of increasing polarity: chloroform–methanol–17% ammonia in the proportions (I) 82.5:15.5:2, (II) 70:26:4, (III) 40:40:20 and (IV) 25:50:25; and (V) methanol–17% ammonia (35:65).

Reversed-phase chromatography on impregnated Kieselguhr and silanized silica gel was performed with acetone–17% ammonia in the proportions (VI) 55:45 and (VII) 70:30.

Detection reagents

The detection reagents used were as follows:

(A) ninhydrin: 1% solution in ethanol–acetic acid (95:5);

(B) 1% potassium permanganate–1% potassium persulphate (1:1);

(C) iodine: 25% methanolic solution;

(D) 5% sodium nitroprussiate [sodium pentacyanonitrosylferrate(III), Na_2-$Fe(CN)_5NO \cdot 2H_2O$] solution in acetaldehyde mixed with an equal volume of 2% sodium carbonate solution;

(E) 1% 2,5-dimethoxytetrahydrofuran buffered solution of pH 6.6; after spraying, the plate must be heated in an oven at 110° for 5 min and then sprayed again with a 1% *p*-dimethylaminobenzaldehyde solution in 3% hydrochloric acid[5].

RESULTS AND DISCUSSION

Table I shows hR_F ($R_F \times 100$) and R_M [$\log (1/R_F - 1)$] values for 56 amines, obtained on silica gel G by the most suitable eluents and detection techniques.

Table II shows hR_F and R_M values of 13 straight-chain alkylamines obtained by chromatography on impregnated Kieselguhr and silanized silica gel; for these amines, no sharp separation could be obtained by working under the conditions given in Table I.

Adsorbents

Silica gel G in combination with eluents I–V is particularly useful for the adsorption chromatography of amines that have different polarities and different numbers and types of functional groups; however, this adsorbent does not resolve the fatty amine series.

Kieselguhr impregnated with paraffin oil and silanized silica gel, on the other hand, are useful for the reversed-phase partition chromatography of fatty amines.

TABLE II

BEHAVIOUR OF FATTY AMINES IN REVERSED-PHASE PARTITION CHROMATOGRAPHY

Eluents are specified under Experimental.

No.	*Compound*	*Paraffin oil-saturated Kieselguhr*				*Silanized silica gel, eluent VII*	
		Eluent VI		*Eluent VII*			
		hR_F	R_M	hR_F	R_M	hR_F	R_M
26	Hexylamine	70	−0.368	86	−0.788	44.5	0.096
35	Heptylamine	56	−0.105	82	−0.659	40	0.176
37	Octylamine	49	0.017	78	−0.550	37	0.231
44	Nonylamine	36	0.250	74	−0.454	33.3	0.302
46	Decylamine	27	0.432	70	−0.368	31	0.347
48	Undecylamine	19	0.630	65	−0.269	28	0.410
49	Dodecylamine	10	0.954	58	−0.140	26	0.454
50	Tridecylamine	6.5	1.158	50	±0.00	23	0.525
51	Tetradecylamine	4.5	1.327	43	0.122	21.5	0.562
52	Pentadecylamine	3.2	1.481	38	0.213	19.5	0.616
53	Hexadecylamine	2.5	1.591	30	0.368	17	0.689
55	Heptadecylamine	2.0	1.690	24	0.501	14.8	0.760
56	Stearylamine	1.5	1.817	18	0.659	13.3	0.814

Detection

From the results obtained with the five reagents tested, the following can be deduced:

(a) Ninhydrin (A) and dimethoxytetrahydrofuran (E) reagents are particularly useful only for primary amines.

(b) Iodine (C) and permanganate (B) reagents are almost generally suitable. Permanganate is to be preferred because of its ease of application and the better colour stability of the spots.

(c) Sodium nitroprussiate (D) in acetaldehyde is suitable, according to the literature[35], for secondary aliphatic amines; however, fairly good detection of primary and tertiary amines was also achieved.

(d) Only ninhydrin can be used with all three adsorbents; the other reagents are suitable only with silica gel G.

Relationship between chemical structure and chromatographic behaviour

The aliphatic amines examined were subdivided into groups according to their structural characteristics and, for each homogeneous group, the chromatographic behaviour was studied.

Influence of the aliphatic chain length. For adsorption chromatography on silica gel (see Table I), and for the same number and type of functional groups in the molecule, the R_M values decrease as the aliphatic chain length increases; with straight-chain alkylamines, this decrease is large for the first terms members and becomes smaller as the chain length increases.

It was further noticed that, for straight-chain monoalkylamines, the R_M values bear a linear relationship to the weight percentage of the amino group relative to the molecular weight rather than to the number of carbon atoms in the alkyl radicals.

The relationship between the weight percentage of amino groups and the number (n) of carbon atoms is given by

$$NH_2\,(\%) = \frac{1.600}{17 + 14n}$$

Fig. 1 shows R_M values as a function of the percentage of amino groups in the molecule for fatty amines.

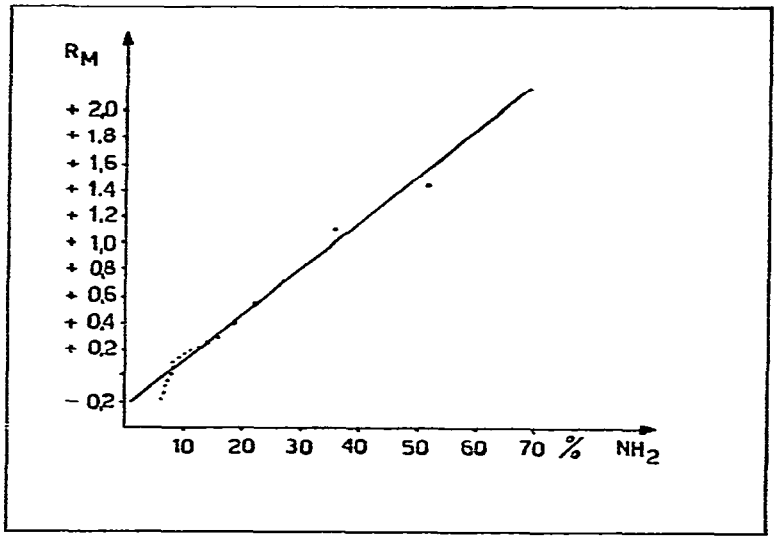

Fig. 1. Relationship between R_M and percentage of NH_2 in the molecule for fatty amines.

In reversed-phase partition chromatography, the R_M values increase as the length of the aliphatic chain increases (see Table II); in this instance, for the three eluents tested, there is a linear relationship between R_M and the number of carbon atoms in the molecule (see Fig. 2).

The change in R_M (ΔR_M) due to one $-CH_2-$ group is different in the three chromatographic systems, as follows: +0.21 on impregnated Kieselguhr with eluent VI, +0.12 on impregnated Kieselguhr with eluent VII and +0.06 on silanized silica gel with eluent VII. These values show that Kieselguhr impregnated with paraffin oil has a greater resolving power for the CH_2 group than silanized silica gel.

Other relationships between chemical structure and chromatographic behaviour. For compounds with the same functional groups and the same number of carbon atoms, those containing a branched alkyl chain have lower R_M values than the corresponding compounds with a straight alkyl chain, except for diisopropylamine, which has a higher R_M value than di-*n*-propylamine.

On increasing the number of functional groups ($-NH_2$, $-OH$), the R_M values increase. On replacing amino hydrogen atoms with either alkyl or hydroxyalkyl groups, a decrease in R_M values occurs, the decrease with the latter groups being lower than that with the former for a constant number of carbon atoms.

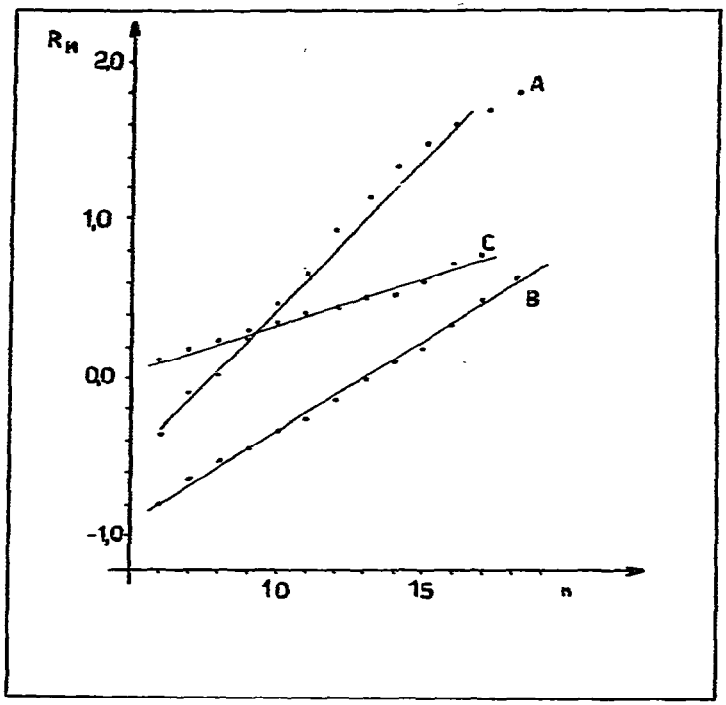

Fig. 2. Relationship between R_M and number of carbon atoms (n) for fatty amines. A, Saturated Kieselguhr, eluent VI; B, saturated Kieselguhr, eluent VII; C, silanized silica gel, eluent VII.

Relationship between chromatographic behaviour and physical properties of the amines

An attempt was made to correlate the chromatographic behaviour with physical properties such as dielectric constant, dipole moment, boiling point and melting point.

In adsorption chromatography, the behaviour seems to be correlated with the dielectric constant and the dipole moment (R_M values increase as these parameters increase), but the data available in the literature are insufficient for this type of relationship to be confirmed.

In reversed-phase partition chromatography, however, it has been found that with all three chromatographic systems a linear relationship exists between the R_M values and the boiling points (R_M values increase as the boiling points increase) (see Fig. 3).

CONCLUSION

The systematic study of the chromatographic behaviour of the 56 amines has enabled us to evaluate a series of eluents, adsorbents and detection systems that could be useful for the analysis of very different types of amines such as fatty amines, high-boiling alkylamines, alkanolamines and polyamines.

The critical evaluation of the results has enabled us to establish correlations between the chromatographic behaviour and chemical structure and physical proper-

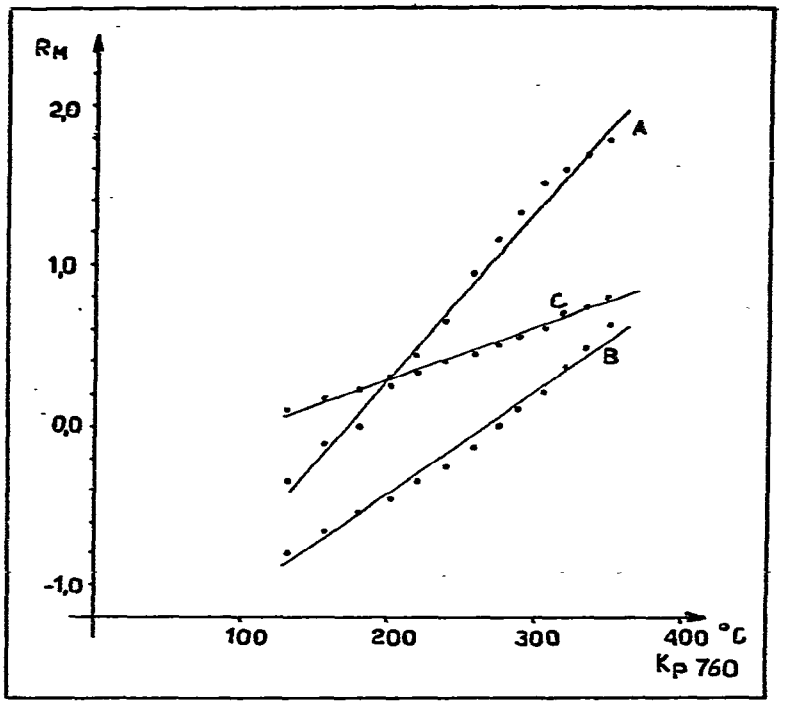

Fig. 3. Relationship between R_M and $K_{P\ 760}$ (boiling points at 760 mmHg) for fatty amines. A, Saturated Kieselguhr, eluent VI; B, saturated Kieselguhr, eluent VII; C, silanized silica gel, eluent VII.

ties; these correlations could facilitate the detection and determination of unknown products.

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