CHROM. 4084

GAS CHROMATOGRAPHIC ANALYSIS OF ALIPHATIC AMINES

THE USE OF ETHYLENE GLYCOLS AS STATIONARY PHASES

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(First received February 21st, 1969; revised manuscript received March 24th, 1969)

SUMMARY

The separation of amines on polyethylene glycol stationary phases is principally due to three types of solute–solvent attractive forces including donor and acceptor hydrogen-bonding. It is suggested that differences in retention time are principally due to differences in the entropy of formation of the acceptor hydrogen bond.

The retention times of amines on a series of ethylene glycols are compared with each other and with those obtained using Apiezon L. Non-polar columns are most satisfactory for the separation of amines within a homologous series, but for amines with similar boiling points, as polar a column as possible should be used, although peak tailing becomes more apparent and may impair an efficient separation. For the most polar stationary phases, the support material must be coated with polyethyleneimine. If potassium hydroxide is used, the primary and secondary amines may not be eluted.

INTRODUCTION

Liquid phases used for the gas chromatographic separation of basic nitrogen compounds differ greatly in polarity ranging from paraffins and silicone oils to highly polar compounds such as diglycerol[1–3]. However, there has been no systematic work into the effect of the change in polarity of the liquid phase on the retention time of the amine, although two recent studies have been made on the separation of hydrocarbons and both oxygen- and halogen-containing organic compounds using polyethylene glycols of different molecular weights[4,5].

This paper is concerned with two aspects of the separation of amines by gas–liquid chromatography. The effect of changing the polarity of the stationary phase on the retention properties of aliphatic amines is examined with particular attention being paid to the class of amine and to the structure of the alkyl group within the class. The results should enable a more effective selection of the appropriate stationary phase for the separation of mixtures of amines.

The paper is also concerned with peak-tailing, which is often observed during the separation of amines. The tailing has generally been ascribed to adsorption of the bases on sites on the solid support, and is reduced by using an inert support[6] or by treating the support with a silane[7] or with a base[8]. The nature of the interactions between the amine and both the stationary phase and the support is investigated by comparing the separation of amines on differently treated solids.

EXPERIMENTAL

The apparatus and methods have been described previously[9,10].

Materials

Amines. The majority of the amines were obtained commercially and purified by distillation. The following tertiary amines were prepared by the reaction of formic acid and formaldehyde on the corresponding primary amine[11]: N,N-dimethylethylamine, N,N-dimethyl-*n*-propylamine, N,N-dimethylisopropylamine, N,N-dimethyl-*n*-butylamine, N,N-dimethyl-*sec.*-butylamine and N,N-dimethyl-*tert.*-butylamine. N-Methyldiethylamine was prepared by the same method from diethylamine. The secondary amines, N-methylisopropylamine and N-methyl-*sec.*-butylamine were obtained by oxidative demethylation of the corresponding N,N-dimethylamine[12]. Neopentylamine was prepared by reduction of pivalamide using lithium aluminium hydride[13].

Packing materials. The solid used was Celite (acid washed, 100–120 mesh) (W. G. Pye and Co., Ltd.). The coating materials were ethylene glycol (B.D.H. Ltd.), the polyethylene glycols Carbowax 200, 400, 600 and 1000 (J.J.'s (Chromatography) Ltd.), Carbowax 20M (Union Carbide Ltd.) and Polyox WSR 35 (mol. wt. 2×10^5) and WSR 205 (mol. wt. 6×10^5) (supplied by Union Carbide Ltd.), Apiezon L (Apiezon Products Ltd.), and polyethyleneimine (PEI) (supplied by Kodak Ltd. as Montrek 18).

Columns used in this investigation

(I) Celite + PEI 5% + ethylene glycol 20% w/w.

(II) Celite + PEI 5% + Carbowax (a) 200, (b) 400, (c) 600, (d) 1000, and (e) 20M 20% w/w.

(III) Celite + KOH 5% + (a) Carbowax 1000, (b) Carbowax 20M, (c) Polyox WSR 35, and (d) Polyox WSR 205 20% w/w.

(IV) Celite + KOH 5% + Apiezon L 20% w/w.

RESULTS

Comparison of potassium hydroxide and PEI as modificants, using Carbowax 1000 and Carbowax 20M as stationary phases (columns II(d) and (e) and III(a) and (b))

Adjusted retention times, t_r, for aliphatic amines on these columns are given in Tables I and II. Using Carbowax 1000, the retention times on the columns in which the solid has been treated with PEI are longer than those treated with potassium hydroxide, by a factor of about 1.5. With Carbowax 20M, the retention times are more similar.

TABLE I

ADJUSTED RETENTION TIMES (min) FOR ALIPHATIC AMINES ON CELITE–POLYETHYLENEIMINE COLUMNS AT 60°

Carrier gas: nitrogen 25 ml/min. Glass column: 1.6 m × 4 mm I.D.

Stationary phase (20% w/w)	*Ethylene glycol*	*Carbowax 200*	*Carbowax 400*	*Carbowax 600*	*Carbowax 1000*	*Carbowax 20 M*
Methylamine	17.0	17.3	10.8	4.5	2.3	0.7
Ethylamine	17.9	11.5	8.9	4.9	2.8	0.9
Isopropylamine	13.7	9.6	6.5	3.9	2.7	0.8
tert.-Butylamine	15.8	7.5	5.2	3.6	2.6	0.8
n-Propylamine	22.1	14.7	14.0	7.5	5.2	1.5
sec.-Butylamine	19.7	14.6	10.3	5.8	5.3	1.6
Isobutylamine	21.7	16.5	11.4	8.0	6.5	—
tert.-Pentylamine	19.9	15.2	9.5	7.2	6.2	1.8
n-Butylamine	39.0	24.9	25.1	14.9	11.1	3.1
Neopentylamine	12.5	12.4	10.2	7.2	6.9	1.8
1-Methyl-*n*-butylamine	30.2	34.4	17.1	13.1	10.8	3.2
3-Aminopentane	22.5	21.0	12.8	11.0	9.9	3.1
Isopentylamine	49.9	69.5	35.1	24.6	17.8	4.8
n-Pentylamine	62.5	80.2	51.0	32.7	24.9	6.5
n-Hexylamine	107.0	—	—	65.5	46.2	13.3
Dimethylamine	11.6	6.2	3.6	2.2	1.5	0.6
N-Methylisopropylamine	11.8	7.5	4.8	2.8	3.1	1.0
Diethylamine	14.4	9.6	5.6	3.5	2.8	1.0
N-Ethylisopropylamine	10.7	7.2	4.9	3.7	3.1	1.1
N-Methyl-*sec.*-butylamine	17.5	10.4	7.1	5.7	4.9	1.4
N-Ethyl-*n*-propylamine	15.0	11.4	7.6	5.9	5.0	1.8
Diisopropylamine	5.9	5.0	3.7	3.0	2.9	1.1
N-Methyl-*n*-butylamine	25.9	19.1	12.6	9.5	7.5	2.6
Di-*n*-propylamine	15.4	15.2	10.6	8.5	8.6	3.1
Di-*sec.*-butylamine	6.1	8.5	7.4	8.0	8.4	3.6
Diisobutylamine	4.6	8.0	7.7	8.5	9.4	4.3
Di-*n*-butylamine	35.0	52.8	39.4	36.0	35.2	12.5
Trimethylamine	1.5	0.8	0.6	0.6	0.6	0.4
N,N-Dimethylethylamine	—	1.5	1.0	0.7	0.9	0.4
N,N-Dimethyl-*n*-propylamine	1.9	1.9	1.5	1.5	1.5	0.7
N-Methyldiethylamine	2.5	2.1	1.7	1.5	1.7	0.8
N,N-Dimethylisopropylamine	4.0	2.7	2.0	1.8	1.9	0.8
Triethylamine	2.7	2.8	2.3	2.2	2.5	1.1
N,N-Dimethyl-*tert.*-butylamine	5.9	4.4	3.5	3.3	3.7	1.4
N,N-Dimethyl-*sec.*-butylamine	3.3	3.2	2.7	2.8	3.1	1.4
N,N-Dimethyl-*n*-butylamine	3.3	2.7	2.8	2.9	3.4	1.4
Tri-*n*-propylamine	2.0	5.6	5.3	8.0	9.0	4.4
Tri-*n*-butylamine	—	29.7	31.0	39.5	51.8	28.9

The role played by PEI in the separation of amines on the Carbowax 1000 columns is emphasised by the shape of the peaks. The symmetry is much improved if Celite is treated with PEI rather than with potassium hydroxide. Indeed, when using a potassium hydroxide–Carbowax 1000 column, primary amines such as *n*-butylamine, isopentylamine and *n*-pentylamine are eluted as a smudge, whereas they are readily separated on PEI–Carbowax 1000.

Variation of molecular weight of ethylene glycols on PEI-treated columns (columns I and II(a–e))

The retention times of primary amines increase with decreasing molecular weight of the ethylene glycol stationary phase (Table I). This trend is also observed for secondary and tertiary amines of low molecular weight. However, for secondary and tertiary amines with a higher molecular weight, this effect no longer holds. Thus, for some amines, there is little change in retention time with molecular weight of ethylene glycol (*e.g.*, N,N-dimethyl-*n*-propylamine for ethylene glycol to Carbowax 1000). For other amines, the retention time increases with increasing molecular weight of the glycol (*e.g.*, tri-*n*-butylamine for Carbowax 200 to Carbowax 1000), while for still other amines the retention time reaches a maximum (di-*n*-butylamine on ethylene glycol to Carbowax 20M).

Peak asymmetry increases on decreasing the molecular weight of the stationary phase, being particularly apparent with primary amines. Within a class, amines with normal alkyl groups generally give worse peak tailing than those with branched alkyl groups.

Variation of molecular weight of polyethylene glycols on potassium hydroxide-treated columns (columns III(a–d))

Retention times for all amines decrease on passing from Carbowax 1000 to polyethylene glycols of higher molecular weight (Table II). Peak symmetry also improves as the molecular weight of the stationary phase increases.

Comparison of polyethylene glycols and Apiezon L as stationary phases for the separation of amines (columns III(a–d) and IV)

When retention times of primary amines on Apiezon L are compared with the corresponding values using the Carbowax 1000 column, the lower primary amines are eluted more slowly on the polar column, but on increasing the chain length of the primary amines, they are eluted more quickly (Table II). This effect is not seen on columns treated with a polyethylene glycol of higher molecular weight, all primary amines being eluted faster on the polar column. Secondary and tertiary amines are eluted more rapidly on all the polar columns studied than on Apiezon L, the ratio of retention time of the amine on the polar to that on the non-polar column decreasing on passing from primary to tertiary amines.

DISCUSSION

The separation of complex organic mixtures by gas–liquid chromatography often involves the selection of stationary phases by trial and error or the use of either more than one column or mixed stationary phases.

The elution of amines on Apiezon L, as the liquid phase, resembles strongly that obtained using porous aromatic polymers[9] and silicone oils[14]. This is well illustrated by comparing the log t_r–boiling point plots for Apiezon L (Fig. 1) with those obtained with these other columns[9,14]. First, the lines drawn through points for *n*-alkyl primary, secondary and tertiary amines are linear, and, although many branched-chain amines do not fit on these lines, the deviations are small. The lines for tertiary amines are above those for secondary and primary amines and converge with these lines to give

TABLE II

ADJUSTED RETENTION TIMES (min) FOR ALIPHATIC AMINES ON CELITE–POTASSIUM HYDROXIDE COLUMNS AT 60°

Carrier gas: nitrogen 25 ml/min. Glass column: 1.6 m × 4 mm I.D.

Stationary phase (20% w/w)	*Carbowax 1000*	*Carbowax 20 M*	*Polyox WSR 35*	*Polyox WSR 205*	*Apiezon L*
Methylamine	1.2	0.5	0.8	0.3	—
Ethylamine	1.6	0.6	0.4	0.3	—
Isopropylamine	1.7	0.7	0.4	0.4	1.0
tert.-Butylamine	1.7	0.8	0.6	0.3	1.5
n-Propylamine	3.2	1.4	0.8	0.6	1.7
sec.-Butylamine	3.5	1.7	1.0	0.6	3.0
Isobutylamine	4.3	2.1	1.2	0.9	3.5
tert.-Pentylamine	3.9	1.9	1.2	0.9	4.7
n-Butylamine	—	3.2	1.7	1.3	4.7
Neopentylamine	4.6	2.6	1.6	1.1	—
1-Methyl-*n*-butylamine	6.9	3.4	1.8	2.0	6.9
3-Aminopentane	6.4	3.5	1.8	1.4	—
Isopentylamine	—	4.9	2.8	2.1	8.5
n-Pentylamine	—	6.8	3.7	3.0	12.5
n-Hexylamine	—	14.5	7.9	6.3	32.0
Dimethylamine	1.0	0.4	0.4	0.2	—
N-Methylisopropylamine	1.9	—	0.6	—	—
Diethylamine	1.9	0.9	0.6	0.4	2.8
N-Ethylisopropylamine	2.1	1.1	0.7	0.5	4.4
N-Methyl-*sec.*-butylamine	3.3	—	—	—	6.3
N-Ethyl-*n*-propylamine	3.4	1.7	1.1	0.8	6.8
Diisopropylamine	1.9	1.2	0.8	0.5	6.2
N-Methyl-*n*-butylamine	6.3	2.9	1.6	1.2	7.7
Di-*n*-propylamine	5.8	3.5	2.0	1.5	15.8
Di-*sec.*-butylamine	6.2	4.4	2.6	2.0	36.4
Diisobutylamine	6.9	5.2	3.1	2.5	43.0
Di-*n*-butylamine	23.6	14.4	8.3	6.6	—
Trimethylamine	0.3	0.2	0.2	0.2	—
N,N-Dimethylethylamine	—	0.5	0.3	0.3	1.9
N,N-Dimethyl-*n*-propylamine	1.1	0.7	0.5	—	4.1
N-Methyldiethylamine	1.2	0.8	0.6	0.4	4.2
N,N-Dimethylisopropylamine	1.4	0.9	0.5	0.4	4.5
Triethylamine	1.8	1.2	0.8	0.7	8.3
N,N-Dimethyl-*tert.*-butylamine	2.3	1.5	0.7	0.6	—
N,N-Dimethyl-*sec.*-butylamine	2.1	1.5	1.0	0.7	10.3
N,N-Dimethyl-*n*-butylamine	2.2	1.6	0.9	0.7	—
Tri-*n*-propylamine	6.5	5.4	3.6	2.7	—
Tri-*n*-butylamine	41.5	32.7	24.1	22.2	—

isodromos points at around 140°. Thus the process is similar to that encountered when separating aliphatic amines on aromatic polymers[9], separation being due to intermolecular association (presumably principally dispersion forces between solute and solvent).

However, these results contrast strongly with those obtained for the elution of amines on columns coated with polyethylene glycols. The gas chromatography process on polar phases is more complex, for a number of new interactions is possible between the solute and solvent which are not present using Apiezon L.

The elution of amines on polyethylene glycols can be discussed in terms of three

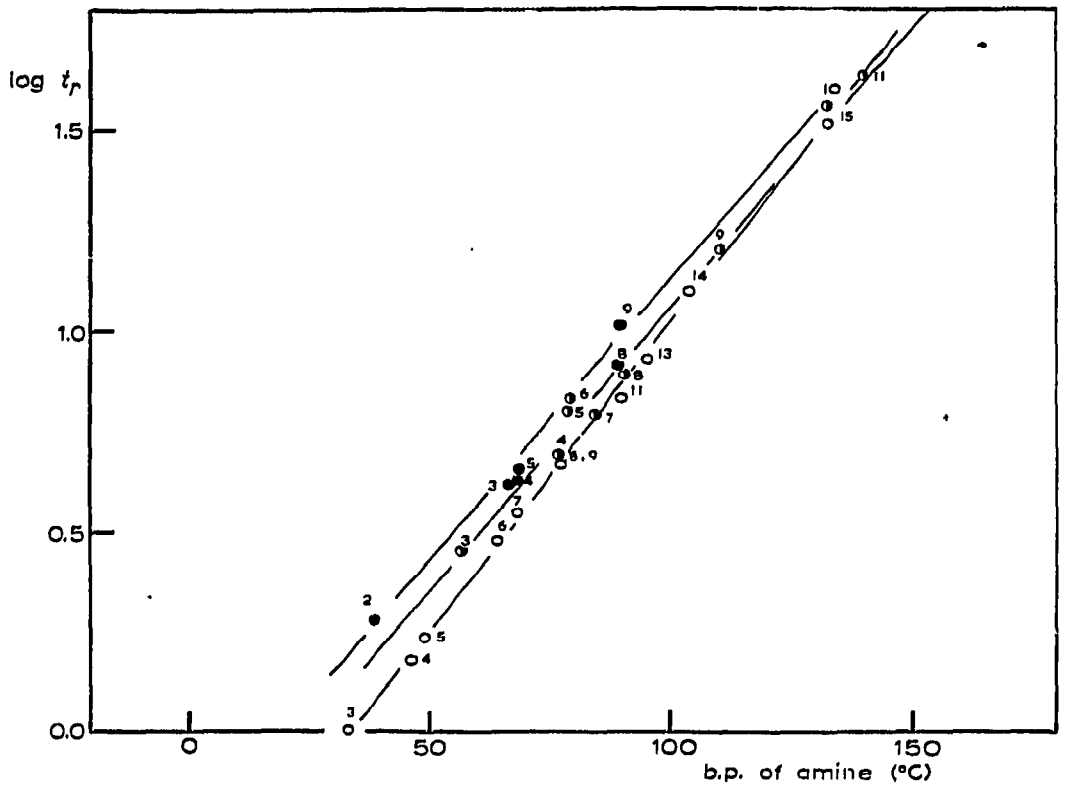

Fig. 1. Plot of log t_r against boiling point of amine. Column: Celite–KOH 5%–Apiezon L 20% w/w, 60°. ○ *Primary amines:* 1 = methylamine; 2 = ethylamine; 3 = isopropylamine; 4 = *tert.*-butylamine; 5 = *n*-propylamine; 6 = *sec.*-butylamine; 7 = isobutylamine; 8 = *tert.*-pentylamine; 9 = *n*-butylamine; 10 = neopentylamine; 11 = 1-methyl-*n*-butylamine; 12 = 3-aminopentane; 13 = isopentylamine; 14 = *n*-pentylamine; 15 = *n*-hexylamine. ◑ *Secondary amines:* 1 = dimethylamine; 2 = N-methylisopropylamine[15]; 3 = diethylamine; 4 = N-ethylisopropylamine; 5 = N-methyl-*sec.*-butylamine; 6 = N-ethyl-*n*-propylamine; 7 = diisopropylamine; 8 = N-methyl-*n*-butylamine; 9 = di-*n*-propylamine; 10 = di-*sec.*-butylamine; 11 = diisobutylamine; 12 = di-*n*-butylamine. ● *Tertiary amines:* 1 = trimethylamine; 2 = N,N-dimethylethylamine; 3 = N,N-dimethyl-*n*-propylamine[16]; 4 = N-methyldiethylamine; 5 = N,N-dimethylisopropylamine[17]; 6 = N,N-dimethyl-*tert.*-butylamine[18]; 7 = triethylamine; 8 = N,N-dimethyl-*sec.*-butylamine[19]; 9 = N,N-dimethyl-*n*-butylamine; 10 = tri-*n*-propylamine; 11 = tri-*n*-butylamine. For boiling points, see refs. 20 and 21, except where indicated above.

types of interaction between the amines and the polyethylene glycol liquid phase. These are:

(1) donor hydrogen-bonding[5] of the >N–H bond of the primary or secondary amine with the oxygen of the polyethylene glycols;

(2) acceptor hydrogen-bonding[5] of the lone pair on the nitrogen atom of the primary, secondary or tertiary amine with the terminal hydroxyl groups of the liquid phase;

(3) other intermolecular attractive forces.

The total interaction energy of an amine with the polyethylene glycol arises from a combination of these effects, the predominant interaction depending on the structure of the amine and molecular weight of the liquid phase.

Donor hydrogen-bonding

On plotting log t_r of each amine against its boiling point, separate lines may be

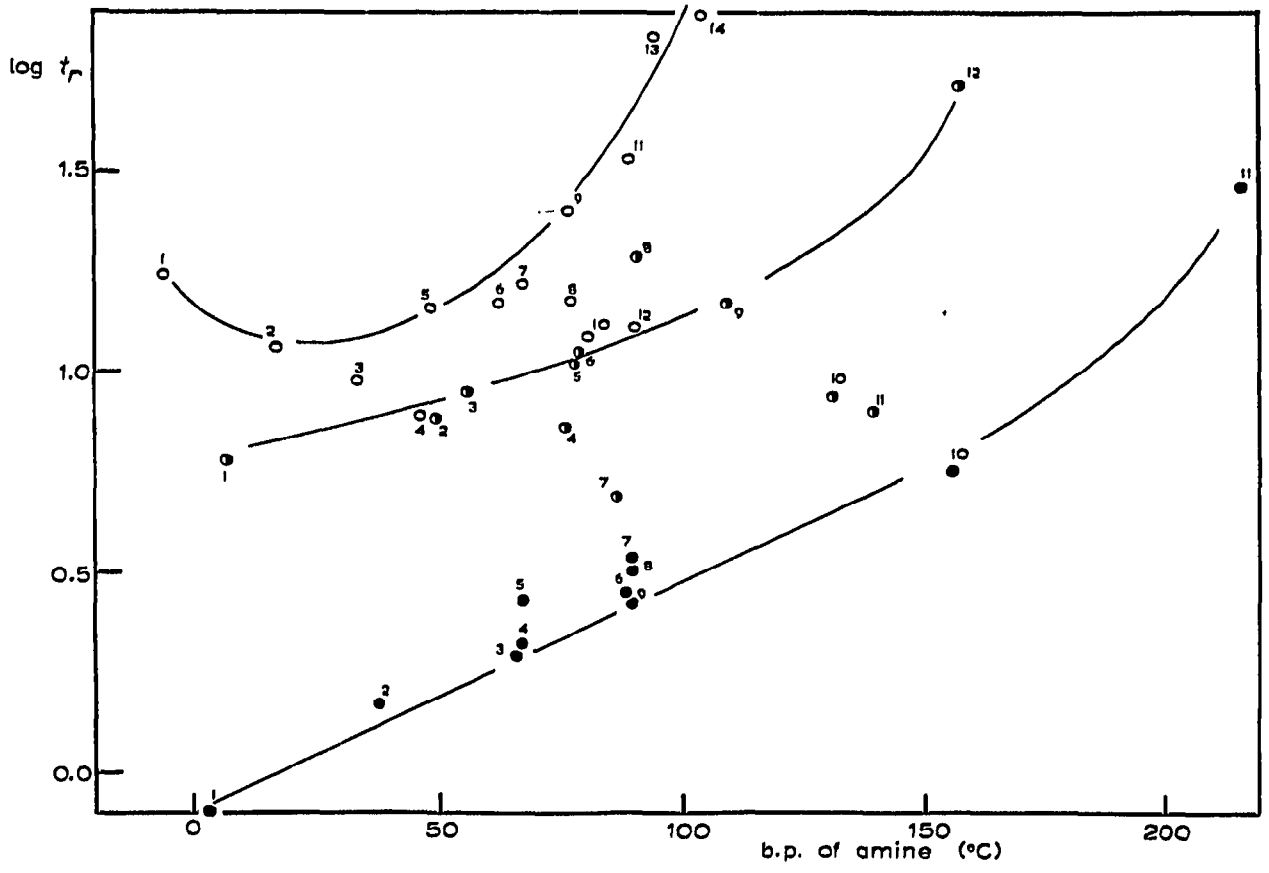

Fig. 2. Plot of log t_r against boiling point of the amine. Column: Celite–PEI 5%–Carbowax 200 20% w/w, 60°. ○ primary amines; ◑ secondary amines; ● tertiary amines.

drawn through primary, $CH_3(CH_2)_nNH_2$, secondary, $[CH_3(CH_2)_n]_2NH$ and tertiary, $[CH_3(CH_2)_n]_3N$, amines (Figs. 2 and 3). Further, these plots show that the retention times of primary amines are considerably greater than those of isomeric secondary amines, which in turn are greater than those of the tertiary compounds. This difference in retention times suggests that one important mode of separation of amines involves donor hydrogen-bonding by the amine >N–H to the polyethylene glycol. Thus, a primary amine which can most readily form these donor hydrogen bonds is most strongly retained while the isomeric tertiary amine for which such an interaction is impossible has the shortest retention time.

Acceptor hydrogen-bonding

Although donor hydrogen-bonding is the predominant interaction leading to the different retentive properties of primary, secondary and tertiary amines, differences arise through acceptor hydrogen-bonding. These differences are maximal for liquid phases of low molecular weight which have the highest proportion of terminal hydroxyl groups. Thus, it is clear from a log t_r–boiling point plot (Figs. 2 and 3) that all primary amines do not fit on the line for *n*-alkylamines, nor do all the points for secondary and tertiary amines lie on their respective lines. The points for primary amines deviate below the line and the extent of the deviation depends on the degree of branching in the alkyl side chain; the greater the branching and the nearer it is to the nitrogen atom the further the point for the amine lies from the line.

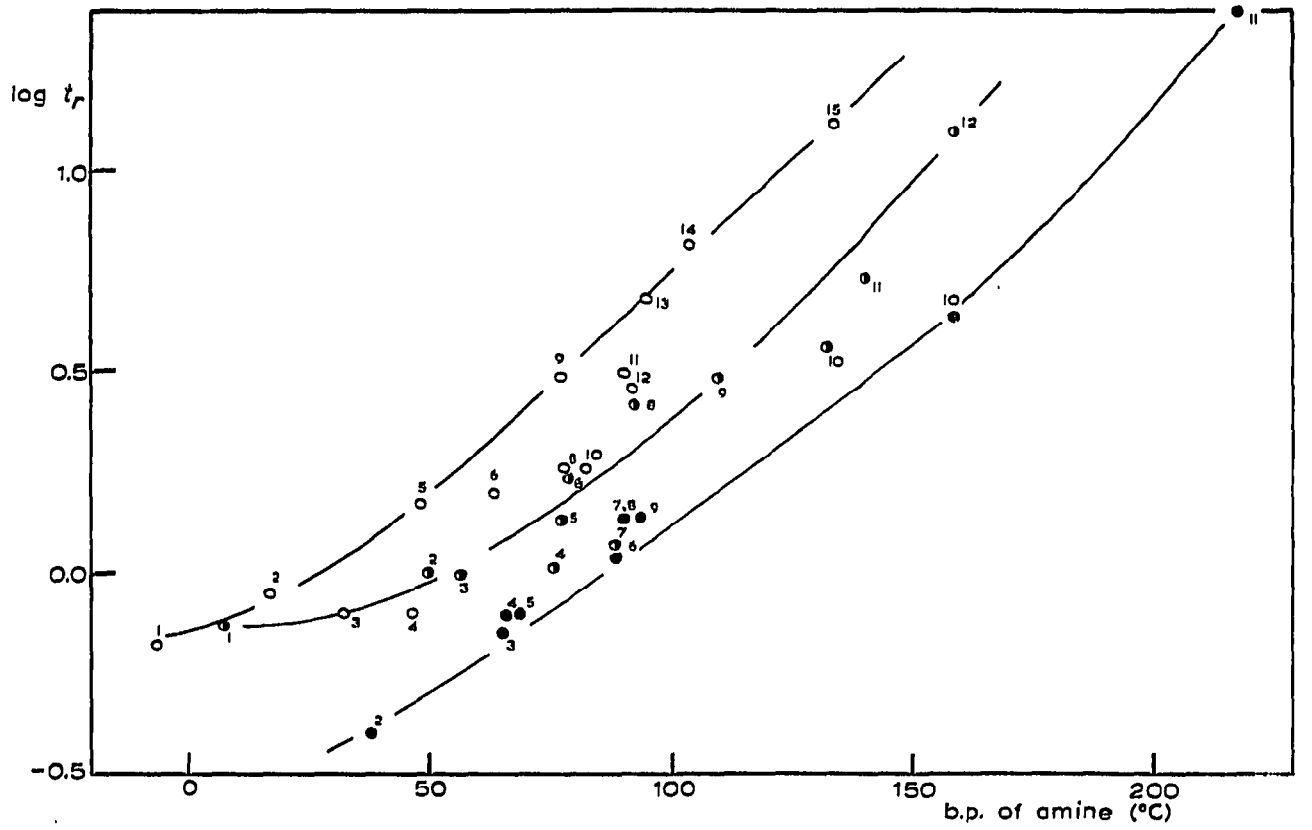

Fig. 3. Plot of log t_r against boiling point of the amine. Column: Celite–PEI 5%–Carbowax 20 M 20% w/w, 60°. ○ primary amines; ◑ secondary amines; ● tertiary amines.

With tertiary amines, although a similar effect is observed, most of the points lie above the line, while with secondary amines the points for branched-chain amines deviate above and below the line.

Further, a comparison of the log t_r–boiling point plots for different stationary phases shows that these deviations are maximal with ethylene glycol and decrease as the molecular weight of the stationary phase increases (for example, Figs. 2 and 3). This observation can be rationalised in terms of an acceptor hydrogen-bonding between the terminal hydroxyls of the polyglycol and the amine. Thus, for primary amines acceptor hydrogen-bonding is maximal with the *n*-alkyl compounds and branching, particularly on the α-carbon, hinders this hydrogen-bonding, thereby reducing the interaction between amine and liquid phase, resulting in a reduced retention time. With tertiary amines a similar effect might be expected. However, N,N-dimethyl-*tert.*-butylamine and other branched-chain amines have longer retention times than would be predicted by comparison with their straight-chain isomers. Examination of molecular models (Courtauld) of N,N-dimethyl-*tert.*-butylamine and N,N-dimethyl-*n*-butylamine shows that the nitrogen atom in the former compound is more available for acceptor hydrogen-bonding than in the latter, for in the *n*-butyl compound the alkyl side-chain can effectively fold round the nitrogen atom, whereas that is not possible in the *tert.*-butyl compound. Thus branching of the side-chain of tertiary amines allows the amines to be retained more strongly by the liquid phase.

Although the behaviour of secondary amines lies between that of the primary and tertiary compounds, they resemble more closely the former.

The log t_r–boiling point plots show further evidence for acceptor hydrogen-bonding. The plots for the elution of amines on non-polar columns are straight lines (*cf.* Fig. 1). However, the lines are curved with the polar polyethylene glycols as liquid phases (for example, Figs. 2 and 3), the curvature of the lines being maximal for the low molecular weight primary amines on low molecular weight liquid phases. As a result, in the extreme case of ethylene glycol or Carbowax 200, the retention times of primary *n*-alkylamines reach a minimum with ethylamine and *n*-propylamine (Table I and Fig. 2). Thus, by changing the molecular weight of the polyethylene glycol it is possible to elute methylamine before or after *n*-propylamine.

Considering the series of primary *n*-alkylamines, it is the retention times of the low molecular weight amines on the lowest molecular weight liquid phases which are longer than might be expected, suggesting that the curvature is due principally to acceptor hydrogen-bonding between the amines and the terminal hydroxyl groups. This type of hydrogen bonding will be maximal with methylamine on ethylene glycol and will decrease as the molecular weight of the amine or liquid phase increases. In agreement with this conclusion the log t_r–boiling point plots become more linear as the molecular weights of the amine and polyglycol increase.

The order of elution of secondary and tertiary amines in particular is markedly altered by changing the stationary phase. For example, dimethyl-, diisopropyl-, di-*sec.*-butyl- and diisobutylamine on polyethylene glycols above 1000 are eluted in the order of increasing boiling point, but the order changes below Carbowax 1000 and on ethylene glycol, it is diisobutyl-, diisopropyl-, di-*sec.*-butyl- and dimethylamine. Clearly this change in the relative retention times of the amines must be explicable in terms of the nature of the interaction of the amine with the liquid phase. Obviously with the secondary amines steric hindrance to hydrogen bonding arising from branching plays a significant role. The effect of steric hindrance can also be seen with tertiary amines. For example, on highly polar columns, tri-*n*-propylamine is eluted before triethylamine (Table I).

A major problem in the elution of primary and secondary amines on columns prepared from polyethylene glycols is peak tailing. As treatment of the support material with alkali does not remove tailing (although peak symmetry is improved), the cause of the tailing cannot be entirely attributed to acid sites on the solid. The tailing must be, in part, due to an interaction between the amine and the liquid phase. Peak tailing is most pronounced under those conditions which show maximal acceptor hydrogen-bonding. Thus, tertiary amines show the least tailing and primary amines the most. Further in a series of isomeric primary amines peak distortion is greatest with the *n*-alkyl and at a minimum with the *tert.*-alkylamine. Indeed, with the polyethylene glycols of lower molecular weight, some amines are not eluted. It is clear that a highly hindered nitrogen atom will be less able to hydrogen bond with the terminal hydroxyl groups of the liquid phase and as a result the peaks are symmetrical.

Further, if columns with the same polyethylene glycol are compared, it is found that the extent of peak tailing depends on whether the support material has been treated with potassium hydroxide or with PEI. The inorganic base is less effective as a modificant with Carbowax 200 to 1000. Indeed, the amine may be totally adsorbed. For example, *n*-butyl-, *n*-pentyl- and isopentylamine are not eluted from potassium

hydroxide–Carbowax 1000 columns while the more branched amines are eluted although the peaks are grossly distorted. With polyethylene glycols of lower molecular weight on a potassium hydroxide-treated support, even many of the branched-chain amines are totally retained, while on columns using PEI, the amines are eluted satisfactorily. It appears that PEI is able, in part, to form acceptor hydrogen bonds with the terminal hydroxyl groups of the polyethylene glycol, competing effectively with the eluting amine for the active sites, thereby reducing peak asymmetry. The inorganic base is unable to fulfil this role and merely neutralises acid sites on the solid support.

In a recent study on the relative retention volumes of alcohols on three stationary phases[22], *n*-heptadecane, di-*n*-octyl ether and di-*n*-octyl ketone, it has been shown that although the heat of formation of hydrogen bonds is not affected by change in structure of the solute, it is apparent that the structure of the solute does affect the entropy of formation, presumably due to greater steric hindrance provided by the alkyl groups of the tertiary and secondary alcohols. It is not possible in our study to evaluate quantitatively the contribution that the change of the structure of the alkyl group has to any change in the heat of formation of the hydrogen bond, as the hydroxyl groups on the solvent molecules associate both intra- and intermolecularly with other solvent molecules, as well as with the solute (amine) molecules, and there will be simultaneous equilibria between the two types of solvent–solvent hydrogen-bonding and the two types of solute–solvent hydrogen-bonding explained above. However, we agree with MARTIRE AND RIEDL that the principal effect of change of structure will be in the entropy contribution to the free energy of formation of the bond, and thus we have explained the changes in acceptor hydrogen-bonding in terms of changes in steric hindrance of bonding between the hydroxyl groups of the solvent and the lone pair on the nitrogen atom of the solute.

Other intermolecular attractive forces

Although the retention times for primary amines decrease as the molecular weight of the polyethylene glycol increases, the ratio of retention time to the relative amount of hydroxyl groups in the stationary phase is more or less constant beyond Carbowax 200 (Fig. 4). However, this ratio continues to increase for secondary and tertiary amines, particularly for those with large alkyl groups, such as di-*n*-butyl- and tri-*n*-butylamine. This suggests that these amines dissolve more readily in the less polar phase. This can be explained by considering either that the percentage of the nitrogen in the molecule is now so small that the amine is behaving as a non-polar solute. This is shown by comparing the increase in retention time of higher tertiary amines on passing from Carbowax 1000 and Carbowax 20M to Apiezon L. Indeed, a similar effect has already been noted for hydrocarbons[4]. Or one can consider that the nitrogen atom in a secondary and tertiary amine is more readily hindered from acceptor hydrogen-bonding than are primary amines. The relative importance of the attractive forces outlined above for the retention properties of the amine solute depends upon the polarity of the column. Obviously, the more polar the solvent, the more important are the forces due to hydrogen bonding. However, the stereochemistry of the solute is most important, and this can be illustrated by comparing the relative retention times of triethylamine and tri-*n*-propylamine (Table II). On a highly polar column, where the most important interaction is acceptor hydrogen-bonding, tri-*n*-propylamine is eluted first, presumably, as the molecular models show, because there is steric hindrance

to hydrogen-bonding between the solvent and the nitrogen atom of the amine. However, on less polar columns, other attractive forces become more important, the solubility of the hydrocarbon part of the molecule becoming the predominant factor in determining the order of elution and triethylamine is eluted well before tri-*n*-propylamine.

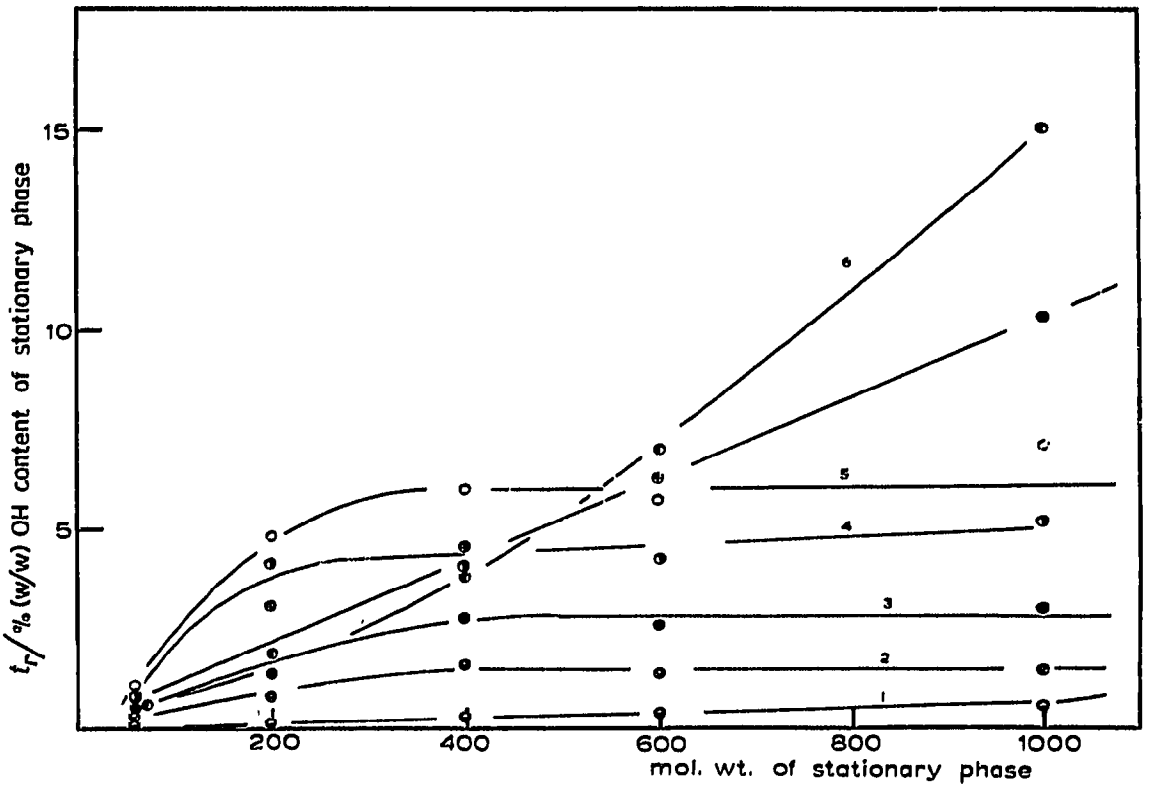

Fig. 4. Relation of retention time of amines with change of molecular weight of the stationary phase. Celite–PEI 5%–ethylene glycol 20% w/w, 60°. 1 = triethylamine; 2 = *n*-propylamine; 3 = *n*-butylamine; 4 = isopentylamine; 5 = *n*-pentylamine; 6 = di-*n*-butylamine; 7 = tri-*n*-butylamine.

Results from this paper indicate that Apiezon L proves to be the most satisfactory solute for the separation of amines within a homologous series for the gradient of the log t_r–boiling point plots decreases as the polarity of the liquid phase increases. Thus other useful solutes for such a separation include Polyox WSR 35 and WSR 205. In order to separate amines with similar boiling points, a polar column is more satisfactory, although on the most polar columns, the column support must be coated with an organic base such as PEI for elution to occur, and even then peak tailing may interfere with the separation of primary and secondary amines. However, the utility of polar columns to separate amines with similar boiling points can be illustrated by the separation of di-*sec*.-butylamine into its diastereoisomers on a Carbowax 400 column[23]. This observation agrees with the work of KARGER *et al.*, who have shown that the separation of diastereoisomeric esters by gas chromatography is very dependent on the polarity of the column material[24].

ACKNOWLEDGEMENTS

We thank Miss M. A. WARRISS and K. M. KITSON for most helpful technical assistance and Shell Research Ltd. for an equipment grant.

REFERENCES

1 J. S. FITZGERALD, *Australian J. Appl. Sci.*, 12 (1961) 51.
2 M. A. HUGHES, *J. Appl. Chem.*, 12 (1962) 450.
3 R. V. GOLOVNYA, G. A. MIRONOV AND I. P. ZHURAVLEVA, *Dokl. Akad. Nauk. SSSR*, 163 (1965) 369.
4 Y. WATANABE, K. ISOMURA AND Y. TOMARI, *Kogyo Kagaku Zasshi*, 70 (1967) 1311.
5 M. B. EVANS AND J. F. SMITH, *J. Chromatog.*, 36 (1968) 489.
6 C. LANDAULT AND G. GUIOCHON, *J. Chromatog.*, 13 (1964) 327.
7 W. J. A. VANDENHEUVEL, W. L. GARDINER AND E. C. HORNING, *Anal. Chem.*, 36 (1964) 1550.
8 D. M. OTTENSTEIN, *J. Gas Chromatog.*, 1 (1963) 11.
9 J. R. LINDSAY SMITH AND D. J. WADDINGTON, *Anal. Chem.*, 40 (1968) 522.
10 J. R. LINDSAY SMITH AND D. J. WADDINGTON, *J. Chromatog.*, 36 (1968) 145.
11 H. T. CLARKE, H. B. GILLESPIE AND S. Z. WEISSHAUS, *J. Am. Chem. Soc.*, 55 (1933) 4571.
12 T. D. PERRINE, *J. Org. Chem.*, 16 (1951) 1303.
13 S. L. SHAPIRO, V. A. PARRINO AND L. FREEDMAN, *J. Am. Chem. Soc.*, 81 (1959) 3728.
14 A. H. AL-TAIAR, J. R. LINDSAY SMITH AND D. J. WADDINGTON, to be published.
15 J. V. BRAUN, F. JOSTES AND H. WAGNER, *Ber.*, 61B (1928) 1423.
16 W. HANHART AND C. K. INGOLD, *J. Chem. Soc.*, (1927) 997.
17 J. V. BRAUN, *Ann.*, 382 (1911) 1.
18 A. SKITA AND F. KEIL, *Monatsh.*, 53–54 (1929) 753.
19 E. GROVENSTEIN, E. P. BLANCHARD, D. A. GORDON AND R. W. STEVENSON, *J. Am. Chem. Soc.*, 81 (1959) 4842.
20 *Handbook of Chemistry and Physics*, 46th Ed., The Chemical Rubber Co., Cleveland, 1965.
21 *Dictionary of Organic Compounds*, Eyre and Spottiswoode, and E. and F. N. Spon, London, 1965.
22 D. E. MARTIRE AND P. RIEDL, *J. Phys. Chem.*, 72 (1968) 3478.
23 M. A. WARRISS, private communication, 1968.
24 B. L. KARGER, B. L. STERN, H. C. ROSE AND W. KEANE, in A. B. LITTLEWOOD (Editor), *Proc. Sixth Intern. Symp. Gas Chromatog., Rome, 1966*, Elsevier, Amsterdam, 1967, p. 240.