Journal of Chromatography, 95 (1974) 91–101

CHROM. 7449

CHARACTERISTICS OF DONOR–ACCEPTOR PROPERTIES OF AMINES AND CYCLIC NITROGEN-CONTAINING SUBSTANCES DETERMINED BY THEIR RETENTION ON STATIONARY PHASES OF DIFFERENT TYPES

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(Received March 12th, 1974)

SUMMARY

The gas chromatographic behaviours of mono-, di- and trialkylamines, ethyleneamines, amino alcohols, aromatic amines and nitrogen heterocycles of the ethylenimine, pyrrolidine, pyrrole, piperidine, pyridine and 1,4-diazine series were studied on stationary phases with different electronic characteristics, including non-polar (Apiezon M, polymethylsiloxane PMS-100), electron donor (1,2,3-tris-(2-cyanoethoxy)propane, polydiethylene glycol phthalate) and electron acceptor (diglycerol, polyethylene glycol 2000) phases. The positions of the points corresponding to amine retentions on the Brown triangular diagram serve as characteristics of the donor–acceptor properties of nitrogen-containing substances. The enthalpy of the donor–acceptor interaction between sorbents and sorbates has been calculated by analyzing the heats of solution of amines in stationary phases.

INTRODUCTION

The method of characterizing donor–acceptor properties of sorbates or stationary phases by studying the gas chromatographic behaviour of substances on three types of stationary phases with different electronic properties, namely on non-polar, electron donor and electron acceptor stationary phases, was introduced by Brown[1] in 1960. Although not widely used as yet, it has already shown its advantages in the identification of steroids[2], alcohols and esters[3], as well as in the choice of optimal compositions for binary stationary phases[4] and in the identification of hydrocarbons and their chloro-derivatives[5].

Amines are also of great interest in such studies. Active hydrogen atoms and an unshared electron pair on the nitrogen atom being present in their molecules, the formation of hydrogen bonds is favoured through both hydrogen and nitrogen atoms. This paper reports a study of the relative donor–acceptor properties of amines and their affinity towards the formation of hydrogen bonds with electron donor and electron acceptor stationary phases.

EXPERIMENTAL

Apparatus and columns

Experiments were carried out on Griffin 2B and AGK-3 gas chromatographs with a thermal conductivity detector in the temperature range 100–200° under the conditions shown in Table I.

TABLE I

EXPERIMENTAL CONDITIONS USED

Parameter	*Gas chromatograph*	
	Griffin 2B	*AGK-3*
Column length (m)	3.3	3.0
Column inside diameter (mm)	4.0	4.0
Column material	Glass	Stainless steel
Carrier gas (helium) flow-rate (ml/min)	25	50
Inlet pressure (mm Hg)	560–670	1320–1500
Outlet pressure (mm Hg)	170–260	Atmospheric
Sample volume (μl)	0.5–2	0.3–1

Non-polar (Apiezon M and polymethylsiloxane PMS-100), electron donor (polydiethylene glycol phthalate and 1,2,3-tris-(2-cyanoethoxy)propane) and electron acceptor (diglycerol, polyethylene glycol 2000) phases were used as stationary phases (25%, w/w, on Celite 545, 44–60 mesh, modified with 0.5% of potassium hydroxide).

Substances studied and accuracy of measurements

Mono-, di- and trialkylamines (*n*- and *iso*-C_2–C_{12}), aliphatic diamines and amino alcohols, aromatic amines and nitrogen heterocycles of the ethylenimine, pyrrolidine, pyrrole, piperidine, pyridine and 1,4-diazine series were studied.

Retention indices and specific retention volumes were determined according to Kaiser[6]. The maximum error in measuring the retention indices calculated according to Takács and Králik[7] did not exceed ±4 units[5]. The accuracy of determination of the heats of solution was ±0.1 kcal/mole.

RESULTS AND DISCUSSION

The retention indices obtained for the amino compounds[5] were used for calculating fractions of retention indices for a combination of the three (non-polar, electron donor and electron acceptor) columns. The calculation is based on an equation suggested by Zarazir *et al.*[3]. The retention index fractions obtained were plotted on a Brown diagram[1,2].

Such a diagram for a system of phases (Apiezon M–polyethylene glycol 2000–polydiethylene glycol phthalate) is shown in Fig. 1. On this triangular diagram, each amine is characterized by a definite point, the location of which is determined by the total electronic properties of the substance and its degree of interaction with each of the stationary phases. As all of the substances studied possess considerable polarity, all the points are grouped in the lower part of the triangle. Therefore, in Fig. 1 and

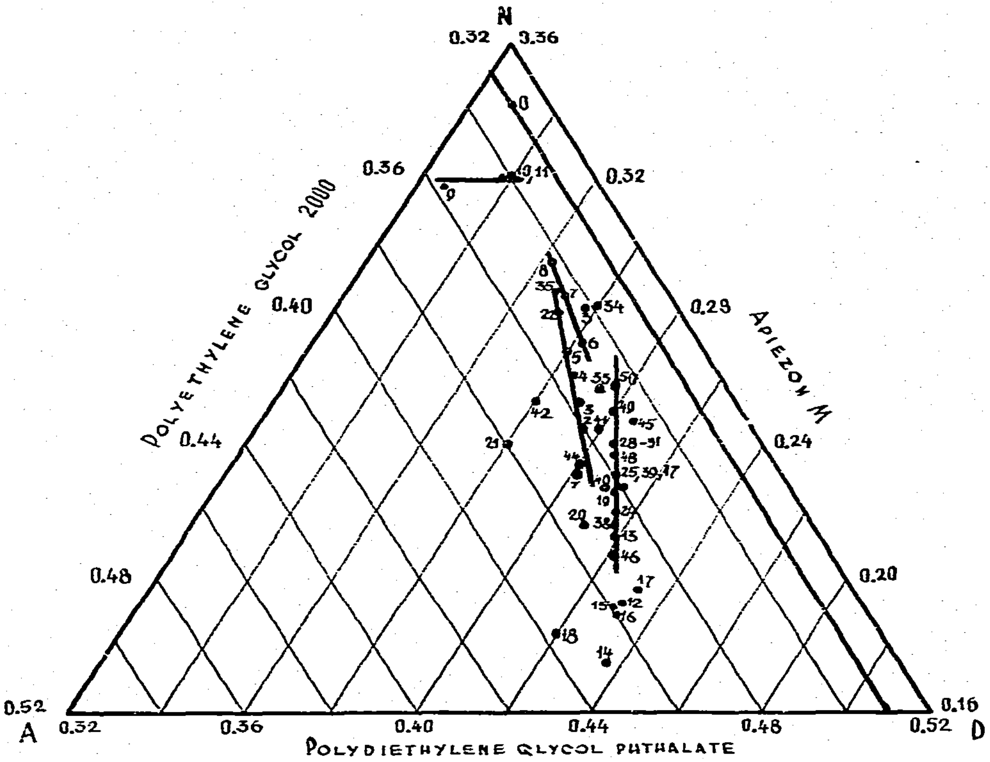

Fig. 1. Comparative retentions of nitrogen-containing compounds on Apiezon M, polyethylene glycol 2000 and polydiethylene glycol phthalate at 150 . 1 = Propylamine; 2 = butylamine; 3 = amylamine; 4 = hexylamine; 5 = heptylamine; 6 = diethylamine; 7 = dipropylamine; 8 = dibutylamine; 9 = triethylamine; 10 = tripropylamine; 11 = tributylamine; 12 = ethylenediamine; 13 = diethylenetriamine; 14 = ethanolamine; 15 = 1-aminopropanol-2; 16 = 1-aminopropanol-3; 17 = ethylenimine; 18 = pyrrole; 19 = 1-methylpyrrole; 20 = 2,5-dimethylpyrrole; 21 = pyrrolidine; 22 = 1-methylpyrrolidine; 24 = pyridine; 25 = 2-methylpyridine; 26 = 3-methylpyridine; 27 = 4-methylpyridine; 28 = 2,3-dimethylpyridine; 29 = 2,4-dimethylpyridine; 30 = 2,5-dimethylpyridine; 31 = 2,6-dimethylpyridine; 32 = 2,4,6-trimethylpyridine; 33 = piperidine; 34 = 1-methylpiperidine; 35 = 1-ethylpiperidine; 37 = morpholine; 38 = pyrazine; 39 = methylpyrazine; 40 = piperazine; 41 = 1-methylpiperazine; 42 = 1-ethylpiperazine; 43 = 1,4-diethylpiperazine; 44 = 1-(2-aminoethyl)piperazine; 45 = triethylenediamine; 46 = aniline; 47 = methylaniline; 48 = ethylaniline; 49 = dimethylaniline; 50 = diethylaniline.

subsequently, only the part of the triangle that contains points corresponding to the amines is shown.

Primary and secondary amines can act as both electron donors and electron acceptors, depending on the media. Therefore, their position with respect to the symmetry axis passing through the N-apex (Apiezon M) is determined by the comparative strengths of the donor and acceptor phases used. In the case presented in Fig. 1, polyethylene glycol, which has weak acceptor properties, acts as an electron acceptor phase. Hence, in these circumstances, amines show mainly electron acceptor activity, and their retention points tend towards the electron donor phase vertex D (polydiethylene glycol phthalate). As the donor--acceptor property ratio within the homologous series of the compounds studied remains constant, and the polarity decreases with molecular size, the points lie on the straight lines directed toward the N-apex. Homologues of higher molecular weight are situated higher, corresponding to the increase in the content of the hydrocarbon moiety.

The highest proton donor activity was observed in the case of polyfunctional aliphatic amines (ethylenediamine, diethylenetriamine and amino alcohols). They also possess the highest polarity of the substances studied.

Within the system studied, electron donor properties were found to be most pronounced in tertiary alkylamines. These are the only compounds that have corresponding points shifted towards the acceptor side of the Brown diagram. As a large proportion of their molecular weight is due to the alkyl radical, the tertiary amine points are situated closer to the N-apex of the diagram than are those of other molecules and they are in the vicinity of the centre of gravity of the triangle.

The points corresponding to mono- and dialkylamines are distributed along straight lines that pass through the centre of gravity of the triangle towards the N-apex. Weak electron acceptor properties and the presence of electron donor oxygen atoms in the molecules of polyethylene glycol 2000 account for the relative locations of the straight lines of the mono- and dialkylamines. A greater affinity towards this stationary phase is observed in the case of primary amines, owing to their structural specificity, which favours interaction through the unshared electron pair (with the hydrogen atom of hydroxylic groups in polyethylene glycol), as well as through two hydrogen atoms (with the ether oxygen atom of the phase).

The donor–acceptor properties of saturated six-membered nitrogen heterocycles basically correspond to those of dialkylamines. The heterocycle points lie in the vicinity of the straight line corresponding to dialkylamines, but are shifted downwards owing to their higher polarity. The proton donor capacity slightly decreases in the order piperidine $\gg$ piperazine $\gg$ morpholine. The proton donor properties are strongest in the three-membered heterocycle ethylenimine, whereas pyrrolidine (five-membered) tends more towards the electron donor side.

In a similar manner to trialkylamines, N-substituted heterocycles form a group of points situated closer to the centre of gravity of the triangle in comparison with other amines, owing to their low polarity. All cyclic amines of an aromatic nature (homologues of aniline, pyrazine and pyridine) are distributed along a common straight line. The points of unsubstituted aniline, pyrazine and pyridine lie lowest, followed by those of methyl and dimethyl derivatives, with the points corresponding to N,N-disubstituted anilines at the top of the line. The vertical position of the line indicates approximately equal donor–acceptor property ratios of all of the substances studied. As molecules of cyclic amines contain nitrogen atoms with different degrees of substitution and electronic configurations, it may be assumed that the donor–acceptor interaction in the system is determined not by the nitrogen atom, but is probably due largely to the aromatic ring. Similar behaviour has been observed with phthalic anhydride, which tends towards the formation of donor–acceptor complexes with aromatic hydrocarbons.

If, instead of polyethylene glycol 2000, a stronger electron acceptor such as diglycerol is used, the distribution of the points that characterize amine retention changes (Fig. 2). As before, the points are situated in the lower part of the diagram, but their even distribution with respect to the vertical symmetry axis indicates both proton

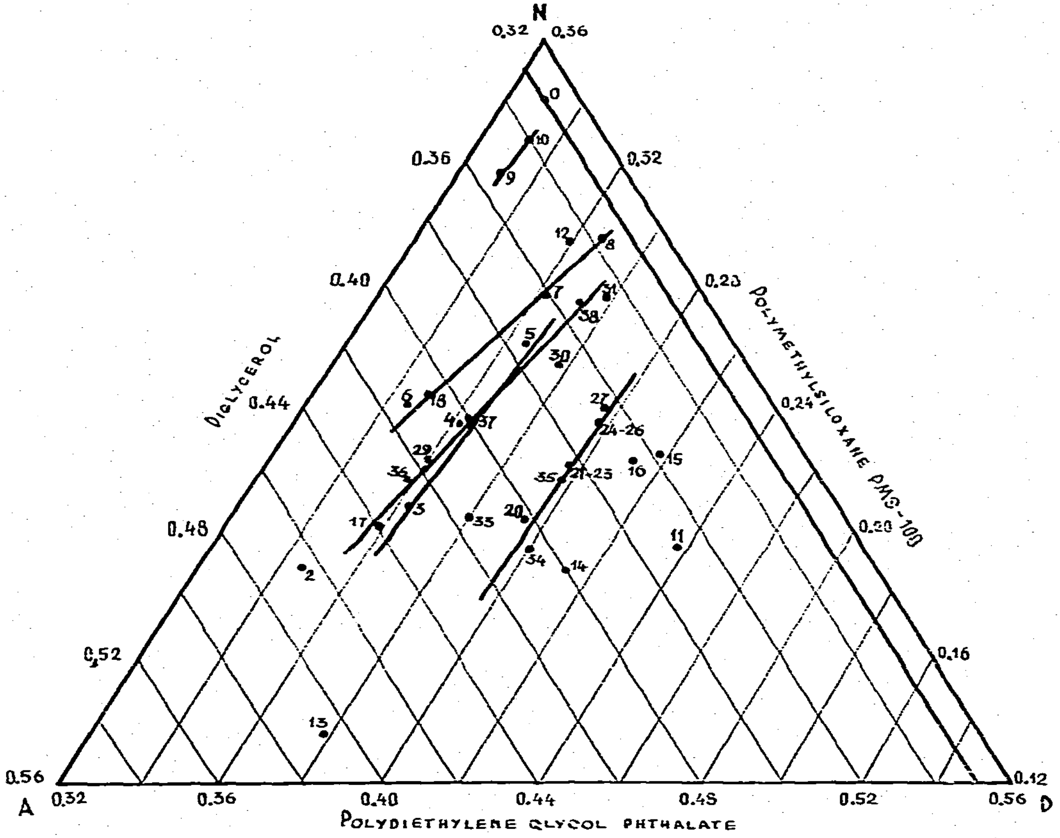

Fig. 2. Comparative retentions of nitrogen-containing compounds on polymethylsiloxane PMS-100, diglycerol and polydiethylene glycol phthalate at 130°. 1 = Ethylamine; 2 = propylamine; 3 = butylamine; 4 = amylamine; 5 = heptylamine; 6 = diethylamine; 7 = dipropylamine; 8 = dibutylamine; 9 = tripropylamine; 10 = tributylamine; 11 = ethylenediamine; 12 = N,N,N',N'-tetraethylethylenediamine; 13 = ethylenimine; 14 = pyrrole; 15 = 1-methylpyrrole; 16 = 2,5-dimethylpyrrole; 17 = pyrrolidine; 18 = 1-methylpyrrolidine; 20 = pyridine; 21 = 2-methylpyridine; 22 = 3-methylpyridine; 23 = 4-methylpyridine; 24 = 2,3-dimethylpyridine; 25 = 2,4-dimethylpyridine; 26 = 2,5-dimethylpyridine; 27 = 2,6-dimethylpyridine; 28 = 2,4,6-trimethylpyridine; 29 = piperidine; 30 = 1-methylpiperidine; 31 = 1-ethylpiperidine; 33 = morpholine; 34 = pyrazine; 35 = methylpyrazine; 36 = 1-methylpiperazine; 37 1-ethylpiperazine; 38 = 1,4-diethylpiperazine.

donor and proton acceptor properties in amines. It should be noted that the distribution of the points corresponding to trialkylamines has not changed essentially, whereas the proton acceptor properties of dialkylamines are more pronounced with respect to diglycerol than those of monoalkylamines, in accordance with the basicity of the substances of these series. The prevalence of proton acceptor properties can also be observed with saturated nitrogen-containing heterocycles. On the other hand, aromatic heterocycles behave as electron acceptors when involved in donor-acceptor interactions with polydiethylene glycol phthalate.

The electron donor properties of amines are even more pronounced in a system containing polymethylsiloxane PMS-100 as non-polar, diglycerol as electron acceptor and 1,2,3-tris-(2-cyanoethoxy)propane as electron donor stationary phases (Fig. 3). The points that characterize the retention of all substances are positioned closer to the A-apex (diglycerol) and the interaction is strongest between diglycerol and primary amines. Compounds that contain a secondary amino group (dialkylamines and saturated nitrogen-containing heterocycles) produce points that lie along the straight line directed towards the N-apex, electron donor properties being more pronounced in nitrogen heterocycles. Only a slight change was observed in the donor–acceptor properties of trialkylamines and N-substituted heterocycles as compared with other systems of stationary phases. Pyridine and pyrazine homologues ran along parallel straight lines, the pyrazine base line (with a more pronounced electron donor function) lying closer to the A-apex (diglycerol). The proton donor function was more pronounced in ethylenediamine and pyrrole compared with other amines.

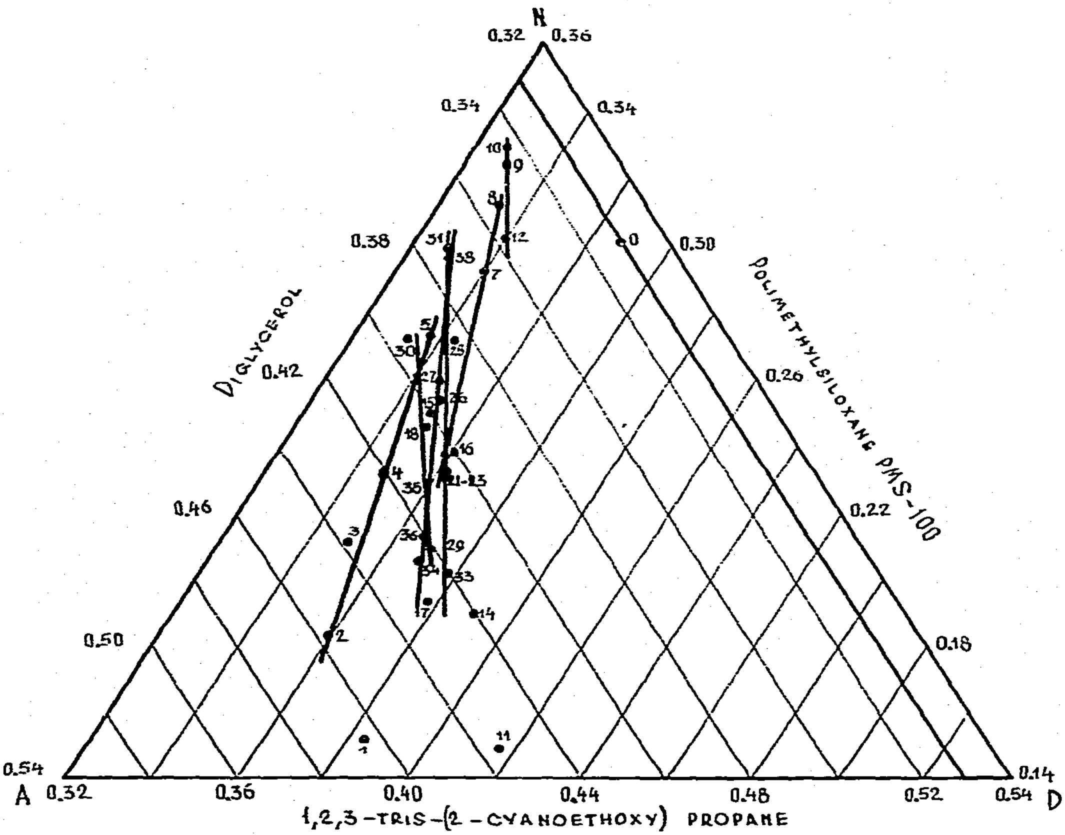

Fig. 3. Comparative retentions of nitrogen-containing compounds on polymethylsiloxane PMS-100, diglycerol and 1,2,3-tris-(2-cyanoethoxy)propane at 130°. Compounds are numbered as in Fig. 2.

The results obtained show that amine donor–acceptor properties vary, depending on the nature of the stationary phase. The positions of the points corresponding to amino compounds on the Brown triangular diagram are characteristic and can be used successfully for identification purposes. For group identification, it seems to be more expedient to plot homomorphy factors of amines on the triangular diagram, thus excluding the effects of the hydrocarbon moiety[2,3]. As can be seen from Fig. 4, each homologous series is characterized by a single point on the diagram.

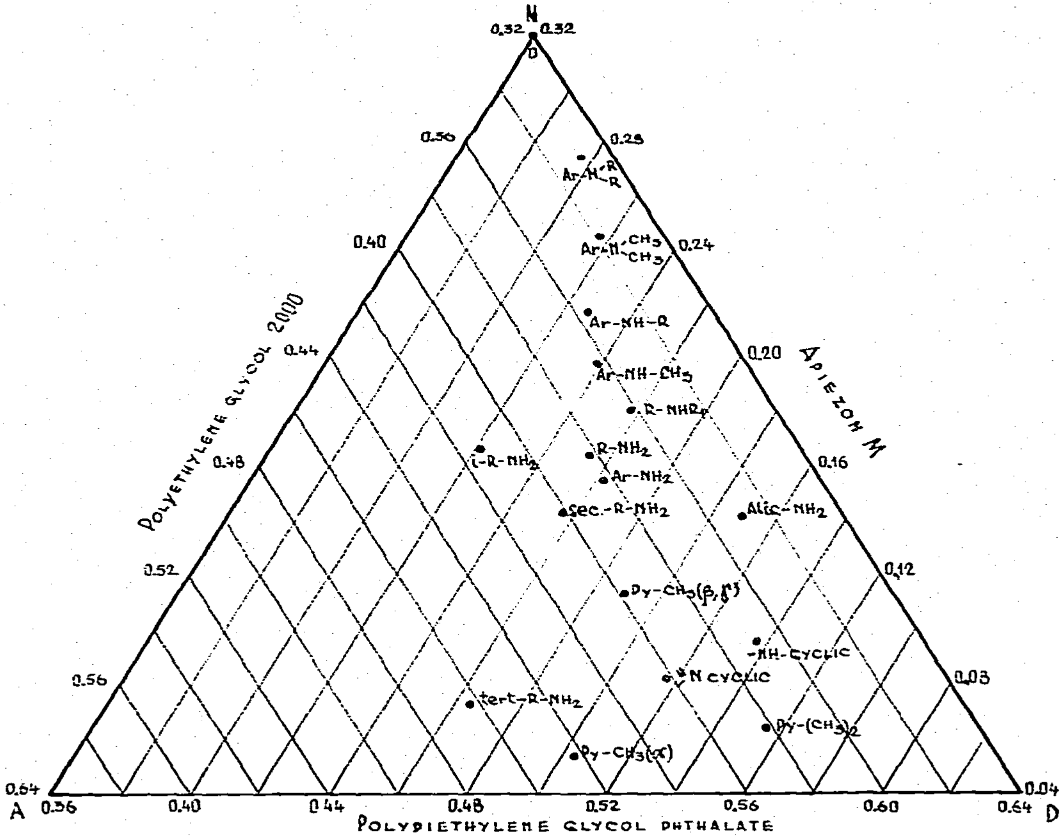

Fig. 4. Comparative retentions of functional groups of nitrogen-containing compounds at 150°.

An attempt was made to establish quantitative characteristics for the degree of donor–acceptor interaction between nitrogen-containing compounds and the stationary phases.

Heats of solution were calculated on the basis of the temperature dependence of the specific retention volumes of amines, which is linear for Apiezon M, polymethylsiloxane PMS-100 and polyethylene glycol 2000 in the range 120–200°, for polydiethylene glycol phthalate in the range 120–180° and for diglycerol and 1,2,3-tris-(2-cyanoethoxy)propane in the range 100–130°. The enthalpy of donor–acceptor interaction was determined as the difference between the enthalpies of an amine solution in the non-polar stationary phase on the one hand and in the electron donor or electron acceptor phase on the other. This so-called "method of two liquid phases"[9], used for the evaluation of donor–acceptor interactions, is not absolutely strict. Firstly, it assumes equality of the dispersion forces of the interactions with non-polar and polar phases, which is by no means always the case, owing to the different sizes of the molecules of those phases. Secondly, this method gives only an estimate of the total enthalpy of all specific interactions. However, when applied to substances that belong to the same class (amines), the method produces results that can serve to a certain extent as a comparative characteristic of donor–acceptor interactions. Owing to the moderate polarity of the stationary phases used in our experiments, it is reasonable to expect hydrogen bonding to predominate in the interactions and its contribution towards the total enthalpy of solution to be of decisive importance.

The differences in the heats of solution of aliphatic amines characterizing the heat of hydrogen bonding are given in Table II.

TABLE II

DIFFERENCES IN HEATS OF SOLUTION OF ALIPHATIC AMINO COMPOUNDS IN POLAR AND NON-POLAR STATIONARY PHASES (kcal/mole)

Abbrevations: A = Apiezon; S = polymethylsiloxane PMS-100; P = polyethylene glycol 2000; Ph = polydiethylene glycol phthalate; D = diglycerol; C = 1,2,3-tris-(2-cyanoethoxy)propane.

Substance	*P–A*	*P–S*	*D–A*	*D–S*	*Ph–S*	*C–A*	*C–S*
Ethylamine	−0.7		10.3			−9.3	
n-Propylamine	−0.6	−2.4	−7.7	9.5	−2.0	−12.5	−14.3
n-Butylamine	−0.4	−2.9	−7.5	10.0	−1.4	−11.4	13.9
Amylamine	−0.7	−3.0	−7.0	−9.3	1.6	−11.9	−14.2
Heptylamine	−0.3	−3.1	−6.6	−8.8		−10.7	−13.5
Isopropylamine	0.4	−2.4	9.1	−11.1	2.9	12.5	14.5
Isobutylamine	−0.7	3.7	−9.0	10.2	3.0	11.0	−14.0
sec.-Butylamine	−0.3	−3.2	−7.3	10.2	−3.1	−14.4	−17.3
tert.-Butylamine	−0.9	−3.2	−10.2	−12.5	−3.8	−18.6	−20.9
Diethylamine	−0.9		−8.1	−8.5	−0.1	−9.2	−9.6
Dipropylamine	−0.7		8.3	−8.9	0.4	−8.2	−8.8
Dibutylamine	−0.8		−8.9	−9.6		−7.9	−8.6
Triethylamine	−0.6				−2.0	−4.3	−6.0
Tripropylamine	−0.4		−0.1	−1.7	−1.4	−4.0	−5.6
Tributylamine	−0.5		−1.4	−0.7	−0.5	−3.2	−5.3
Ethylenediamine	−2.9	3.9			−3.3		
1,2-Propylenediamine	−2.1	−1.9			3.2		
N,N,N′,N′-Tetramethylethylenediamine	−0.6	−0.5			−0.1		
N,N,N′,N′-Tetraethylethylenediamine	−0.4	−0.2			−0.9		
Diethylenetriamine	−3.3	−4.1			−3.8		
Ethanolamine	−3.7	−6.4			−4.1		
1-Aminopropanol-3	−2.8	−4.9			−4.6		
1-Aminopropanol-2	−2.2	−2.0					
2-Aminopropanol-1	−4.8				−2.5		
3-Aminobutanol-1	−2.4						

In interactions with electron donor stationary phases, amines act as proton donors, and hydrogen bonds thus formed with 1,2,3-tris-(2-cyanoethoxy)propane are stronger than those with polydiethylene glycol phthalate. Thus, we obtain 6–7 kcal/mole per hydrogen bond between amines and 1,2,3-tris-(2-cyanoethoxy)propane, whereas the same bond with polydiethylene glycol phthalate gives a value of only 0.8–

1.0 kcal/mole. The strength of the hydrogen bond increases in amines in which the amino group is positioned at the secondary carbon atom, and reaches a maximum value at NH_2-substitution at the tertiary carbon atom. It should be noted that with dialkylamines that are capable of forming only one hydrogen bond of the N–H······O(N) type, the enthalpies of the latter amount to 8–9 kcal/mole. Increased interaction forces between 1,2,3-tris-(2-cyanoethoxy)propane and dialkylamines, compared with those of monoalkylamines, are represented by the mutual positions of the straight lines on the Brown triangle corresponding to the respective series of substances (Fig. 3). Tertiary amines, which are not capable of N–H······O(N) type of hydrogen bonding, are characterized by the differences in the heats of solution between 1,2,3-tris-(2-cyanoethoxy)propane and the non-polar phases, amounting to 4–6 kcal/mole. This value is probably caused by strong dipole–dipole interactions between the sorbent and sorbate molecules. Such a phenomenon is not observed with the less polar polydiethylene glycol phthalate. On the other hand, tertiary amines have a slightly greater heat of solution in the non-polar stationary phase. This example shows the drawbacks of the method of using two liquid phases for evaluating the enthalpy of donor–acceptor interactions, as one obtains only the total value of the latter. The true enthalpy of the hydrogen bond is lower, about 1–3 kcal/mole, considering the high polarity of the cyanoethyl ester and a significant contribution of orientation forces.

Amines act as electron donors with respect to the electron acceptor stationary phase (diglycerol) and form a hydrogen bond of the N·····H–O type. The enthalpy of this bond in both primary and secondary amines is considerable (9–10 kcal/mole), exceeding that of the hydrogen bond with polydiethylene glycol phthalate and with 1,2,3-tris-(2-cyanoethoxy)propane. If the electron donor nature of the stationary phase is less pronounced (polyethylene glycol 2000), the enthalpy of the hydrogen bond is also lower.

Table III shows the enthalpies of the donor–acceptor interactions between cyclic nitrogen-containing compounds and the stationary phases. The maximum difference in the interaction with electron donor stationary phases was observed with aromatic heterocycles, probably owing to the formation of a donor–acceptor complex.

The enthalpy of the N–H·····O hydrogen bond between 1,2,3-tris-(2-cyanoethoxy)propane and polydiethylene glycol phthalate on the one hand and saturated nitrogen heterocycles on the other amounts to 9–10 and 0.8–1 kcal/mole, respectively, just as with alkylamines, whereas the enthalpy of the donor–acceptor bond between 1,2,3-(2-cyanoethoxy)propane and N-substituted heterocycles is only 2–3 kcal/mole, and with polydiethylene glycol phthalate, as with tertiary amines, there is no hydrogen bonding at all. The enthalpy of the N·····H–O hydrogen bond type with diglycerol is approximately the same as in aliphatic amines: aromatic heterocycles (homologues of pyridine, pyrazine and especially pyrrole and its derivatives) are characterized by lower enthalpies of the hydrogen bond owing to the presence of an unshared electron pair on the nitrogen atom in the aromatic sextet of π-electrons. A similar change in hydrogen bond strength is observed with polyethylene glycol 2000, except that the effects are less pronounced. These results show that the differences in the heats of solution of amines in the non-polar stationary phase; on the one hand, and in diglycerol and polydiethylene glycol phthalate on the other, are approximately the same for corresponding types of hydrogen bonds and depend only slightly on the geometry and

TABLE III

DIFFERENCES IN HEATS OF SOLUTION OF CYCLIC AMINO COMPOUNDS IN POLAR AND NON-POLAR STATIONARY PHASES (kcal/mole)

Abbreviations as in Table II.

Substance	*P–A*	*P–S*	*D–A*	*D–S*	*Ph–A*	*Ph–S*	*C–A*	*C–S*
Ethylenimine				−6.5				−7.2
Pyrrolidine	−4.3	−3.7	9.2	−8.6	1.6	−1.0	−13.0	−12.4
1-Methylpyrrolidine	−2.1	−1.3	−7.9	−7.6	1.2	−0.5	−3.4	−3.1
Pyrrole	−6.3	−7.1	−4.4	−5.2	−2.2	−3.0	−10.2	−11.0
1-Methylpyrrole	−3.4	−4.3	−2.5	−3.4	−0.9	−1.8	−9.8	−10.7
2,5-Dimethylpyrrole	−4.6	−6.1	−2.6	−4.1	−0.7	−2.2	−9.1	−10.6
Piperidine	−3.8	−4.1	−7.6	−7.9	0.0	−0.8	−8.7	−9.0
1-Methylpiperidine	−2.5	−2.5	−6.9	−6.9	−1.0	−1.0	−3.9	−2.9
1-Ethylpiperidine	−2.2	−2.2	−6.9	−6.9	−1.4	−1.4	−2.5	−2.5
Pyridine	−3.4	−3.9	−5.9	−6.4	1.0	−1.5	−12.4	−12.9
2-Methylpyridine	−3.1	2.6	−6.1	−5.6	−1.2	0.9	−12.9	−12.4
3-Methylpyridine	−3.0	−2.4	−6.3	−5.7	−1.4	0.8	−11.7	−11.1
4-Methylpyridine	−3.1	−2.6	6.4	−5.9	−1.5	−1.0	−12.6	−12.1
2,3-Dimethylpyridine	−2.8	−1.9	−4.3	−3.8	0.9	−0.5	−11.7	−11.4
2,4-Dimethylpyridine	−2.6	−1.7	−4.8	−3.9	−1.2	−0.4	−11.1	−10.2
2,5-Dimethylpyridine	−2.4	−1.4	−4.6	−3.6	1.3	−0.3	−11.2	−10.2
2,6-Dimethylpyridine	−2.4	−1.7	4.9	4.2	0.9	0.2	−10.2	−9.5
2,4,6-Trimethylpyridine	1.3	0.4	4.2	3.3	0.9	0.0	10.1	−9.2
Piperazine	−3.6	−2.4	18.2	18.0	2.3	−2.1		
1-Methylpiperazine	−2.4	−1.7	15.3	−14.6	−1.4	−0.7	−10.0	−9.3
1-Ethylpiperazine	−2.4	−1.7	−15.2	−14.5	1.3	1.1	−10.6	−9.9
1,4-Diethylpiperazine	−0.9	−0.4	15.0	−12.5	0.5	0.0	−2.6	−2.1
1-(2-Aminoethyl)piperazine	−3.8	4.3	13.0		−3.4	3.9		
Pyrazine	−3.5	−3.1	−6.9	6.5	2.4	−2.0	−12.8	−12.4
Methylpyrazine	−2.5	−2.3	−5.2	−5.0	−1.9	1.7	12.7	12.5
Triethylenediamine	−1.1	−2.3			−1.6	−0.8		
Morpholine	−2.6	−1.6			2.4	1.4		

polarity of the molecules. This supports the view that donor–acceptor interactions actually play a decisive role in intermolecular attraction. Hence measurements of the differences in heats of solution adequately characterize the hydrogen bond enthalpy of sorbates with the given stationary phases.

In the case of 1,2,3-tris-(2-cyanoethoxy)propane, an important part is also played by other specific interactions, and the differences in heats of solution characterize only the total enthalpy of interaction.

CONCLUSIONS

Points corresponding to the retentions of amino compounds have been found to form separate groups on the Brown triangular diagram in accordance with the donor–acceptor properties of the compounds and the degree of their interactions with the stationary phases. Electron donor properties are most pronounced in polyfunctional amines (ethyleneamines and amine alcohols), and electron acceptor properties are strongest in trialkylamines. The degree of electron donor and electron acceptor activity of amines is strongly dependent on the donor–acceptor properties of the stationary phase.

The characteristic location of the points corresponding to the retentions of amines can be used for identification purposes. A diagram can be used in which are plotted fractions of homomorphy factors of amines for group identification.

Analysis of the enthalpy of donor–acceptor interaction shows that hydrogen bonding with electron acceptor stationary phases is most typical for amines. Other types of donor–acceptor interactions, apart from hydrogen bonding, have been observed with electron donor stationary phases, especially in the case of aromatic amino compounds.

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