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SORPTION OF AMINO COMPOUNDS ON A NON-POLAR STATIONARY PHASE AND AT THE PHASE BOUNDARIES

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SUMMARY

The sorption of mono-, di- and trialkylamines, aniline and its homologues, cyclohexylamine and 5- and 6-membered nitrogen-containing heterocyclic compounds has been studied by gas chromatography using helium as the carrier gas, Apiezon M as the stationary phase and Celite 545 as the solid support. Dissolution in the liquid stationary phase is the main process responsible for the retention of amino compounds in the system studied. The contributions of interfacial adsorption account for 3-25% (or almost 30% in the case of polyfunctional alkylamines) of the total retention volume. For C₃-C₈ *n*- and isomonoalkylamines, polyfunctional alkylamines, C₄-C₆ dialkylamines, cyclohexylamine and nitrogeneous heterocycles, adsorption at the interfaces is related predominantly to adsorption on the surface of the solid support, whereas with higher monoalkylamines, C₈-C₁₄ dialkylamines, trialkylamines and arylamines adsorption at the gas-liquid interface prevails.

INTRODUCTION

Adsorption of compounds in gas-liquid chromatography is a complex process involving (with complete coating of the support surface with the stationary phase) adsorption of sorbate molecules at the gas-liquid interface, dissolution in the bulk of the liquid stationary phase and adsorption at the liquid-solid interface.

The relative contributions of the above processes to retention volumes depend on the nature of the sorbate, the stationary phase and the support. The influence of interfacial adsorption on the separation of non-polar substances on non-polar stationary phases is negligible, whereas the retention of polar compounds on non-polar stationary phases is considerably affected by adsorption on the solid support¹⁻⁶. However, there is much controversy concerning the role of the adsorption of polar compounds at the gas-non-polar liquid interface. It has been established^{7,8} that alcohols adsorb insignificantly on the surface of hydrocarbon liquid phases whereas in other studies^{9,10} a considerable contribution of this type of adsorption to the retention volumes was reported. According to Conder¹¹, this discrepancy may be due to variation in the adsorption conditions, *i.e.*, the contribution of adsorption of small

polar molecules at the gas-liquid interface is insignificant at certain final sorbate concentrations, but it tends to increase considerably upon infinite dilution.

The influence of interfacial sorption on the retention of amines has not been studied so far, except for the work of Crowne *et al.*¹², who measured adsorption coefficients for aniline and dimethylaniline at the interface between the gas and tritoyl phosphate containing 2,4,7-trinitrofluorenone. He took no account of adsorption of arylamine on the solid support. The present investigation was performed in order to evaluate the contributions of solution and adsorption at the gas (helium)-liquid (Apiezon M) and liquid-solid support (Celite 545) interfaces to the retention volumes of mono-, di- and trialkylamines, arylamines, cyclohexylamine and 5- and 6-membered nitrogen-containing heterocycles.

For the description of the total process we used the three-term equation proposed by Berezkin *et al.*³:

$$V_N^S = K_L V_L^S + K_{GL} S_L^S + K_L K_S S_S$$

where V_N is the total specific retention volume per amount of column packing that corresponds to gram of solid support, K_L , K_{GL} and K_S are coefficients of the partition of the sorbate in the bulk liquid phase and of adsorption at the gas-liquid and liquid-solid interfaces, respectively, V_L and S_L are the volume and surface area of the liquid phase per gram of support, respectively, and S_S is the specific surface area of the solid support.

EXPERIMENTAL

Apparatus and columns

The experiments were carried out at 150, 180 and 200°C on a Griffin 2B gas chromatograph equipped with a thermal conductivity detector (the accuracy of temperature regulation in thermostat oven was $\pm 0.1^\circ\text{C}$). Glass columns (3.3 m \times 0.4 cm I.D.) with 7.5, 15 and 20% of Apiezon M on Celite 545 (44-60 mesh) were used. The flow-rate of the carrier gas was 25 cm³/min, the inlet pressure was 75,000-90,000 N/m² the outlet pressure was 22,500-35,000 N/m² and the sample volume 0.2-0.5 μl . The retention times were measured with a two-hand chronometer providing ± 0.1 sec accuracy. The specific area of sorbents was determined by the low-temperature nitrogen desorption method¹³.

Chemicals and calculation methods

The gas chromatographic properties of the following classes of nitrogen-containing compounds were evaluated: C₂-C₁₆ *n*- and iso-mono-, di- and trialkylamines, aniline and its N-alkyl and N,N-dialkyl derivatives, *o*-, *m*- and *p*-toluidines, cyclohexylamine and heterocyclics of the pyrrolidine, pyrrole, piperidine, pyridine, morpholine and 1,4-diazine series.

Specific retention volumes of amines per gram of solid support, V_N^S , were measured. Sorption coefficients and the relative contributions of solution and interfacial adsorption to V_N^S were calculated using the "reference point" method developed by Berezkin and co-workers^{4,14}.

RESULTS AND DISCUSSION

Partition coefficients of aliphatic amines in Apiezon M (K_L) and the appropriate adsorption coefficients at the gas-liquid (K_{GL}) and liquid-solid interfaces (K_S), as well as the relative contributions of individual types of adsorption to V_N^S determined at 180°C, are summarized in Table I. The corresponding values for cyclic amino compounds are given in Table II. The values of K_L , K_{GL} and K_S for alkyl- and arylamines and nitrogen-containing heterocycles measured at 150 and 200°C can be found in refs. 15-17. The same studies report the absolute values of the contributions to V_N^S of the individual sorption processes. All of the sorption coefficients tend to decrease with increasing column temperature.

Solution of amino compounds in the stationary phase is the predominant type of sorption. The relative contributions of this process to V_N^S is 70-97%, the lowest

TABLE I

SORPTION COEFFICIENTS OF ALIPHATIC AMINES IN APIEZON M AND AT THE PHASE BOUNDARIES AND CONTRIBUTIONS OF THE PROCESS OF SOLUTION AND INTERFACIAL SORPTION TO THE RETENTION VOLUMES AT 180°C

Amine	K_L	K_{GL}	K_S	$\frac{K_L V_L^S}{V_N^S} \cdot 100$	$\frac{K_{GL} S_L^S}{V_N^S} \cdot 100$	$\frac{K_L K_S S_S}{V_N^S} \cdot 100$
Propylamine	2.97	$2.27 \cdot 10^{-7}$	$4.48 \cdot 10^{-6}$	81.13	0.12	18.75
Butylamine	5.38	$2.36 \cdot 10^{-6}$	$3.60 \cdot 10^{-6}$	83.72	0.70	15.58
Amylamine	9.97	$7.87 \cdot 10^{-6}$	$3.17 \cdot 10^{-6}$	84.84	1.27	13.89
Heptylamine	28.28	$4.06 \cdot 10^{-5}$	$1.94 \cdot 10^{-6}$	88.72	2.41	8.87
Octylamine	48.06	$6.40 \cdot 10^{-5}$	$1.84 \cdot 10^{-6}$	89.25	2.25	8.50
Isopropylamine	1.72	$1.84 \cdot 10^{-6}$	$4.30 \cdot 10^{-6}$	80.50	1.62	17.88
Isobutylamine	4.15	$1.92 \cdot 10^{-6}$	$3.45 \cdot 10^{-6}$	84.28	0.64	14.98
Isoamylamine	8.60	$1.92 \cdot 10^{-6}$	$1.51 \cdot 10^{-6}$	92.41	0.39	7.20
sec.-Butylamine	3.70	$4.46 \cdot 10^{-5}$	$2.63 \cdot 10^{-7}$	80.50	18.40	1.10
tert.-Butylamine	2.35	$1.81 \cdot 10^{-5}$	$6.67 \cdot 10^{-8}$	86.97	12.72	0.31
Diethylamine	4.01	$3.18 \cdot 10^{-7}$	$2.59 \cdot 10^{-6}$	88.10	0.13	11.77
Dipropylamine	11.34	$2.94 \cdot 10^{-5}$	$1.52 \cdot 10^{-6}$	88.68	4.36	6.98
Dibutylamine	32.07	$1.63 \cdot 10^{-4}$	$4.69 \cdot 10^{-7}$	89.25	8.59	2.16
Diamylamine	87.77	$4.56 \cdot 10^{-4}$	$7.14 \cdot 10^{-8}$	90.73	8.93	0.34
Dihexylamine	190.89	$2.20 \cdot 10^{-3}$	$4.60 \cdot 10^{-8}$	81.89	17.92	0.19
Diheptylamine	551.43	$6.62 \cdot 10^{-3}$	$7.27 \cdot 10^{-9}$	81.45	18.52	0.03
Diisopropylamine	6.06	$4.05 \cdot 10^{-5}$	$1.01 \cdot 10^{-7}$	88.36	11.18	0.46
Diisoamylamine	57.44	$3.43 \cdot 10^{-4}$	$2.66 \cdot 10^{-8}$	89.72	10.16	0.12
Triethylamine	7.41	$6.20 \cdot 10^{-5}$	$2.86 \cdot 10^{-8}$	86.20	13.67	0.13
Tripropylamine	27.19	$1.75 \cdot 10^{-4}$	$2.05 \cdot 10^{-8}$	89.02	10.88	0.10
Tributylamine	99.50	$4.70 \cdot 10^{-4}$	$1.69 \cdot 10^{-8}$	91.71	8.21	0.08
Triamylamine	365.79	$1.45 \cdot 10^{-3}$	$4.44 \cdot 10^{-9}$	93.00	7.00	0.01
Ethylenediamine	5.17	$4.79 \cdot 10^{-6}$	$7.85 \cdot 10^{-6}$	70.28	1.24	28.48
1,1,4,4-Tetramethylethylene diamine	13.06	$8.00 \cdot 10^{-5}$	$4.46 \cdot 10^{-7}$	87.79	10.19	2.02
1,1,4,4-Tetraethylethylene diamine	54.29	$3.56 \cdot 10^{-4}$	$4.93 \cdot 10^{-8}$	88.75	11.03	0.22
1,2-Propylenediamine	6.29	$3.06 \cdot 10^{-5}$	$6.51 \cdot 10^{-6}$	70.04	6.45	23.51
Diethylenetriamine	36.50	$1.80 \cdot 10^{-4}$	$3.46 \cdot 10^{-6}$	78.59	7.36	14.05

TABLE II

SORPTION COEFFICIENTS OF CYCLIC AMINES IN APIEZON M AND AT THE PHASE BOUNDARIES AND CONTRIBUTIONS OF THE PROCESS OF SOLUTION AND INTERFACIAL SORPTION TO THE RETENTION VOLUMES AT 180°C

<i>Amine</i>	K_L	K_{GL}	K_S	$\frac{K_L V_L^S}{V_N^S} \cdot 100$	$\frac{K_{GL} S_L^S}{V_N^S} \cdot 100$	$\frac{K_L K_S S_S}{V_N^S} \cdot 100$
Aniline	35.01	$2.69 \cdot 10^{-4}$	$6.45 \cdot 10^{-7}$	86.18	12.55	1.27
<i>o</i> -Toluidine	58.24	$5.26 \cdot 10^{-4}$	$3.10 \cdot 10^{-8}$	85.26	14.60	0.14
<i>m</i> -Toluidine	57.97	$5.35 \cdot 10^{-4}$	$3.02 \cdot 10^{-8}$	85.01	14.86	0.13
<i>p</i> -Toluidine	55.33	$4.93 \cdot 10^{-4}$	$3.60 \cdot 10^{-7}$	84.21	14.23	1.56
N-Methylaniline	57.95	$4.88 \cdot 10^{-4}$	$6.71 \cdot 10^{-7}$	85.36	13.62	1.02
N-Ethylaniline	78.10	$6.38 \cdot 10^{-4}$	$6.48 \cdot 10^{-7}$	85.80	13.28	0.92
N,N-Dimethylaniline	70.31	$6.11 \cdot 10^{-4}$	$5.93 \cdot 10^{-8}$	85.78	14.13	0.09
N,N-Diethylaniline	120.70	$1.06 \cdot 10^{-3}$	$1.06 \cdot 10^{-9}$	85.67	14.32	0.01
Cyclohexylamine	19.72	$1.00 \cdot 10^{-7}$	$4.75 \cdot 10^{-6}$	80.32	0.01	19.67
Pyrrolidine	8.49	$1.67 \cdot 10^{-6}$	$2.86 \cdot 10^{-6}$	86.88	0.32	12.80
Pyrrrole	8.71	$2.66 \cdot 10^{-6}$	$2.71 \cdot 10^{-6}$	87.30	0.49	12.21
1-Methylpyrrole	9.98	$2.13 \cdot 10^{-6}$	$2.55 \cdot 10^{-6}$	88.04	0.35	11.60
2,5-Dimethylpyrrole	23.84	$4.99 \cdot 10^{-6}$	$2.57 \cdot 10^{-6}$	87.98	0.35	11.67
Piperidine	13.95	$2.64 \cdot 10^{-6}$	$2.26 \cdot 10^{-6}$	89.27	0.32	10.41
1-Methylpiperidine	14.99	$3.51 \cdot 10^{-6}$	$1.60 \cdot 10^{-6}$	92.02	0.41	7.57
1-Ethylpiperidine	23.05	$4.96 \cdot 10^{-6}$	$1.42 \cdot 10^{-6}$	92.83	0.38	6.79
Pyridine	11.66	$2.71 \cdot 10^{-6}$	$2.47 \cdot 10^{-6}$	88.34	0.38	11.27
2-Methylpyridine	17.72	$4.13 \cdot 10^{-6}$	$1.63 \cdot 10^{-6}$	91.86	0.41	7.73
3-Methylpyridine	22.84	$4.93 \cdot 10^{-6}$	$2.02 \cdot 10^{-6}$	90.20	0.37	9.41
4-Methylpyridine	23.07	$4.13 \cdot 10^{-6}$	$1.91 \cdot 10^{-6}$	90.77	0.31	8.92
2,3-Dimethylpyridine	26.10	$7.60 \cdot 10^{-6}$	$1.54 \cdot 10^{-6}$	92.28	0.37	7.35
2,4-Dimethylpyridine	33.37	$7.71 \cdot 10^{-6}$	$1.53 \cdot 10^{-6}$	92.33	0.40	7.27
2,5-Dimethylpyridine	33.31	$7.28 \cdot 10^{-6}$	$1.44 \cdot 10^{-6}$	92.74	0.39	6.87
2,6-Dimethylpyridine	24.93	$4.84 \cdot 10^{-6}$	$1.39 \cdot 10^{-6}$	92.99	0.34	6.67
2,4,6-Trimethylpyridine	47.20	$2.99 \cdot 10^{-5}$	$4.98 \cdot 10^{-7}$	96.37	1.16	2.47
Piperazine	19.54	$1.15 \cdot 10^{-7}$	$4.30 \cdot 10^{-6}$	81.85	0.01	18.14
1-Methylpiperazine	19.93	$2.68 \cdot 10^{-7}$	$3.64 \cdot 10^{-6}$	84.19	0.02	15.79
1-Ethylpiperazine	31.36	$5.90 \cdot 10^{-7}$	$3.51 \cdot 10^{-6}$	84.63	0.03	15.34
1,4-Diethylpiperazine	53.27	$2.49 \cdot 10^{-7}$	$1.99 \cdot 10^{-6}$	90.70	0.01	9.30
1-(2-Aminoethyl)-piperazine	79.59	$1.61 \cdot 10^{-5}$	$5.61 \cdot 10^{-6}$	77.65	0.30	22.05
Pyrazine	9.46	$3.80 \cdot 10^{-7}$	$3.37 \cdot 10^{-6}$	85.15	0.07	14.78
Methylpyrazine	16.39	$1.44 \cdot 10^{-6}$	$2.56 \cdot 10^{-6}$	88.37	0.15	11.48
Pyrimidine	9.96	$2.96 \cdot 10^{-6}$	$3.94 \cdot 10^{-6}$	82.96	0.38	16.58
Triethylenediamine	50.54	$6.31 \cdot 10^{-7}$	$2.78 \cdot 10^{-6}$	87.46	0.02	12.52
Morpholine	13.88	$3.01 \cdot 10^{-7}$	$2.81 \cdot 10^{-6}$	87.30	0.04	12.66

values (70–80% V_N^S) being found for polyfunctional aliphatic amines, cyclohexylamine and 1-(2-aminoethyl)piperazine (at 150°C also for piperazine¹⁷); the highest values (90–97%) are characteristic of C₉–C₁₅ trialkylamines, alkylpyridines and alkylpiperidines. With increase in column temperature the relative contributions of dissolution to V_N^S increase^{15–17}. Comparing the values of the relative contributions of dissolution of aliphatic amines to V_N^S over a wide range of molecular masses and

plotting the values of these contributions *versus* the number of carbon atoms in amine molecules, a curve is obtained with a maximum that corresponds to amines containing hydrocarbon chains with 11–12 carbon atoms (Fig. 1). This phenomenon is related to better solubility as a result of increased dispersion forces of intermolecular attraction with increasing number of carbon atoms and to enhanced sorption at the gas-liquid interface due to the surface activity of higher alkylamines.

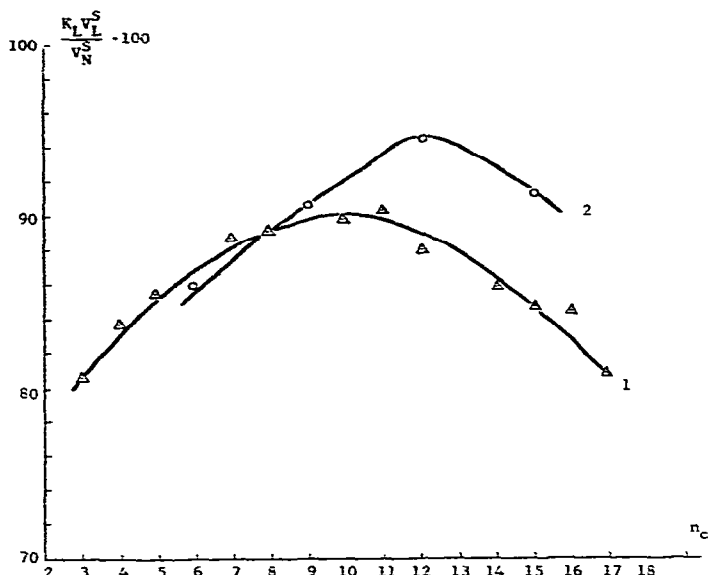


Fig. 1. Dependence of the relative contributions to V_N^S on the number of carbon atoms in the molecule for monoalkylamines (1) and trialkylamines (2).

To evaluate the effects of the physico-chemical properties and structures of amino compounds on the dissolution process the correlation analysis of K_L values was performed. The parameters used included the number of carbon atoms in the molecule, n_C , the number of tertiary carbons in the molecule, $n_{C(t)}$, the number of radicals at nitrogen atoms n_R , dipole moments, μ , and the sum of Palm's steric constants, $\sum E_S^0$. The following regression equations were obtained:

$$K_L = b_0 + b_1 n_C \quad (1)$$

$$K_L = b_0 + b_1 n_C + b_4 \mu + b_5 \sum E_S^0 \quad (2)$$

$$K_L = b_0 + b_1 n_C + b_2 n_{C(t)} \quad (3)$$

$$K_L = b_0 + b_1 n_C + b_2 n_{C(t)} + b_3 n_R \quad (4)$$

$$K_L = b_0 + b_1 n_C + b_5 \sum E_S^0 \quad (5)$$

$$K_L = b_0 + b_1 n_C + b_3 n_R + b_5 \sum E_S^0 \quad (6)$$

TABLE III

COEFFICIENTS OF REGRESSION EQUATIONS DESCRIBING THE PROCESSES OF AMINO COMPOUNDS ADSORPTION

Correlated values	Classes of amines	Equation type	b_0	b_1	b_2
K_L	Alkylamines	1	-105.49	1.44	-
	Alkylamines	2	-107.88	1.53	-
	Alkylamines	3	-115.01	1.51	9.81
	Alkylamines	4	-108.72	1.91	3.37
	Arylamines	6	-271.69	47.77	-
	Pyridine bases	5	-105.48	20.67	-
	Other N-heterocycles	5	-15.49	9.37	-
K_{GL}	Alkylamines	3	$-6.56 \cdot 10^{-4}$	$1.50 \cdot 10^{-4}$	$8.24 \cdot 10^{-5}$
	Alkylamines	4	$-5.15 \cdot 10^{-4}$	$1.90 \cdot 10^{-4}$	$2.56 \cdot 10^{-4}$
	Arylamines	6	$-2.63 \cdot 10^{-3}$	$5.69 \cdot 10^{-4}$	-
	Pyridine bases	5	$-6.02 \cdot 10^{-4}$	$1.20 \cdot 10^{-4}$	-
	Other N-heterocycles	5	$-3.53 \cdot 10^{-6}$	$2.04 \cdot 10^{-6}$	-
K_S	Alkylamines	7	$8.88 \cdot 10^{-6}$	-	-
	Alkylamines	8	$-3.48 \cdot 10^{-5}$	-	-
	Alkylamines	9	$2.63 \cdot 10^{-5}$	-	-
	Alkylamines	10	$-1.40 \cdot 10^{-5}$	-	-
	Arylamines	10*	$-4.43 \cdot 10^{-6}$	-	-
	Pyridine bases	7	$2.24 \cdot 10^{-6}$	-	-

* The pK_b values were used instead of ionization potential to obtain factor b_6 .

The coefficients found by the method of least squares and correlation coefficients, r , are given in Table III. As shown, alkylamines (only monoamines were tested) exhibit a satisfactory correlation between K_L and n_C values (eqn. 1). Introduction into the regression equation of terms including μ and $\sum E_S^0$ values fails to improve the correlation, and consequently these factors do not affect K_L values. On the other hand, introduction into eqn. 1 of terms characterizing the branching of hydrocarbon chains, *i.e.*, $n_{C(1)}$ and n_R (eqns. 3 and 4), significantly increases the r values. Thus, the results of correlation analysis indicate the predominance of dispersion interaction between the stationary phase and alkylamine molecules. The $\ln K_L$ values appear to be linearly correlated with n_C (Fig. 2). An increase in K_L values is also observed in the series of cyclic compounds in which the size of the molecule (number of alkyl substituents and chain length) is increased (see Table II). Unlike alkylamines, the K_L values of cyclic amino compounds are influenced by the environment of the nitrogen atoms. The K_L values found for heterocyclic bases are satisfactorily described by eqn. 5 containing steric constants in addition to n_C , whereas the K_L values of arylamines fit eqn. 6, containing n_R in addition to the above factors (Table III). The relationship between K_L and steric factors (the presence of alkyl groups in α -positions to the N atom in alkylpyridines) and the effects of replacement of hydrogen atoms at the nitrogen atoms with hydrocarbon radicals (in arylamines) suggest a specific intermolecular interaction upon solution.

b_3	b_4	b_5	b_6	b_7	b_8	r
—	—	—	—	—	—	0.880
—	2.92	8.26	—	—	—	0.881
—	—	—	—	—	—	0.885
-24.18	—	—	—	—	—	0.904
53.91	—	-76.40	—	—	—	0.995
—	—	33.53	—	—	—	0.978
—	—	-9.96	—	—	—	0.936
—	—	—	—	—	—	0.806
$-2.05 \cdot 10^{-4}$	—	—	—	—	—	0.858
$-2.00 \cdot 10^{-4}$	—	$6.72 \cdot 10^{-5}$	—	—	—	0.984
—	—	$8.35 \cdot 10^{-5}$	—	—	—	0.914
—	—	$-2.09 \cdot 10^{-6}$	—	—	—	0.660
—	$-1.48 \cdot 10^{-6}$	$4.69 \cdot 10^{-6}$	—	—	—	0.720
—	$-4.88 \cdot 10^{-7}$	$-1.87 \cdot 10^{-6}$	$4.57 \cdot 10^{-6}$	—	—	0.877
—	$-7.88 \cdot 10^{-6}$	$3.58 \cdot 10^{-6}$	$-1.95 \cdot 10^{-6}$	$4.17 \cdot 10^{-6}$	—	0.921
—	$3.61 \cdot 10^{-7}$	$-3.54 \cdot 10^{-6}$	$7.49 \cdot 10^{-7}$	$1.34 \cdot 10^{-6}$	$2.66 \cdot 10^{-5}$	0.977
—	$1.94 \cdot 10^{-6}$	$-2.06 \cdot 10^{-8}$	$-2.16 \cdot 10^{-8}$	$6.41 \cdot 10^{-8}$	$1.11 \cdot 10^{-5}$	0.852
—	$-3.47 \cdot 10^{-7}$	$2.80 \cdot 10^{-6}$	—	—	—	0.943

Adsorption at the gas–non-polar liquid interface relies largely on the nature of amino compounds. The K_{GL} values of alkylamines show a wide variation over the range 10^{-3} – 10^{-7} (Table I). A sharp increase in K_{GL} values is observed in homologous series with increasing molecular size (*e.g.*, elongation of the hydrocarbon chain in monoalkylamines from C_{10} to C_{18} leads to a 1000-fold increase in K_{GL}^{18} , whereas in dialkylamines the increase in K_{GL} at elongation of the hydrocarbon chain from C_4 to C_{14} is 10,000-fold). The K_{GL} values show a linear correlation with n_C^{18} (Table III). Increased K_{GL} values are also obtained for branched aliphatic radicals (Table III). The contribution of this type of sorption to V_N^S ranges from 0.1% (for propyl- and diethylamine) and 2.25% (octylamine) to 18–26% (for octadecylamine¹⁸ and dihexylamine). The observed dependence of alkylamine adsorption on n_C can be explained by increased surface activity, as the combination of polar amino groups with long hydrocarbon chains in the molecules of higher alkylamines stimulates the accumulation of these molecules on the surface of the non-polar liquid.

According to adsorption at the gas–liquid interface, cyclic amino compounds can be arranged into two groups. The K_{GL} values for aromatic amines are of the order of 10^{-3} – 10^{-4} (Table II), the relative contributions of the process to V_N^S amounting to 14–16%. The high surface activity of arylamines is due to the aromatic nature of the ring. Cyclohexylamine is characterized by very low K_{GL} values and a negligible contribution of the process to V_N^S (Table II). The effect of the phenyl ring is equivalent to

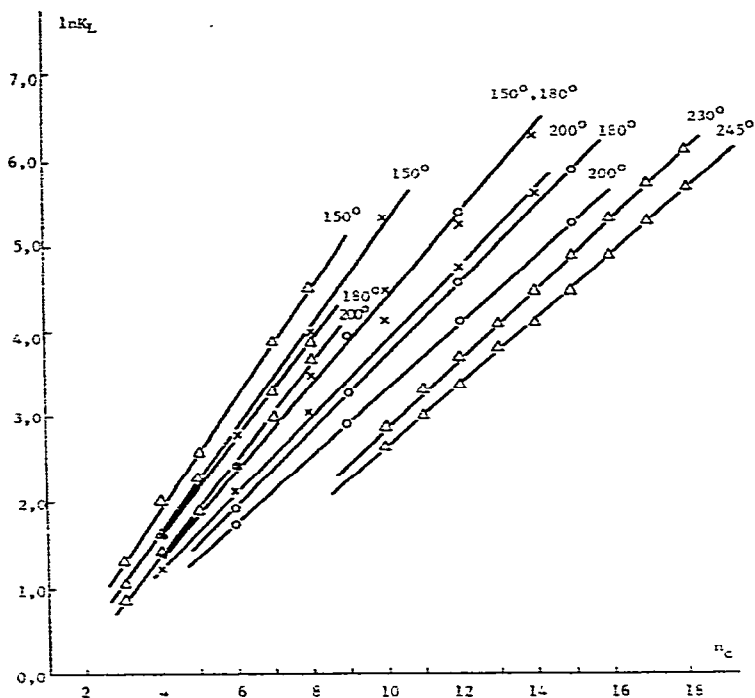


Fig. 2. Dependence of the logarithm of the partition coefficient on the number of carbon atoms in the molecule for *n*-alkylamines in Apiezon M. Δ , Monoalkylamines; X, dialkylamines; O, trialkylamines.

elongation of the alkyl chain by 9–10 carbon atoms. This effect is less pronounced in the pyridine series, the contributions of their sorption on the Apiezon M surface being considerable only at 150°C^{17} . For other nitrogen-containing heterocyclic bases adsorption at the gas–non-polar liquid interface is not very typical. Small and compact heterocyclic molecule possess a very low surface activity. Their K_{GL} values are comparable to those of lower alkylamines, the minimum values being found with symmetrical 1,4-diazines. The K_{GL} values of heterocyclic bases show the same correlations with n_C , n_R and $\sum E_S^{\text{N}}$ as the K_L values (Table III).

Adsorption on the solid support is mainly characteristic of comparatively small molecules of alkylamines (10–20% of V_N^{S} for C_3 – C_{12} monoalkylamines and diethylamine), heterocyclic bases and cyclohexylamine (also 10–20% of V_N^{S}). This process is manifested to the greatest extent with aliphatic diamines and 1,4-diazines (15–30% of V_N^{S}). The K_S values are comparable to K_{GL} except for 1,4-diazines, which have K_S values 1–2 orders of magnitude higher than K_{GL} (Table II). Adsorption on the solid support is weakened under the influence of factors that reduce the base properties of amines or shield the unshared electron pair on the nitrogen atom (delocalization of the unshared electron pair, steric hindrance preventing the interactions via the nitrogen atom, *e.g.*, in the case of replacement of hydrogen atoms with alkyl radicals at the nitrogen or α -carbon atom). This indicates that at adsorption on the liquid–solid interface dominates the specific interaction between amines and the active sites of the surface, involving the unshared electron pair on the nitrogen atom (the mobile hydrogen atoms at the nitrogen are also implicated to some extent). This suggestion is

confirmed by the results of correlation analysis demonstrating a relationship between K_S values and dipole moments, the number of hydrogen atoms on the nitrogen atom, n_H , ionization potentials, IP (for arylamines pK_b values were used instead of ionization potentials), and a steric constants (Table III, eqns. 7-10):

$$K_S = b_0 + b_4\mu + b_5 \sum E_S^o \quad (7)$$

$$K_S = b_0 + b_4\mu + b_5 \sum E_S^o + b_6IP \quad (8)$$

$$K_S = b_0 + b_4\mu + b_5 \sum E_S^o + b_6IP + b_7n_H \quad (9)$$

$$K_S = b_0 + b_4\mu + b_5 \sum E_S^o + b_6IP + b_7n_H + b_81/n_C \quad (10)$$

The increase in molecular size in most instances leads to a decrease in K_S values (Tables I and II), the latter being correlated with the reciprocal of the number of carbon atoms. Introduction of this factor into eqn. 9 leads to an increase in the correlation coefficients from 0.921 to 0.977 for alkylamines (Table III) and from 0.581 to 0.852 for arylamines.

Consequently, interfacial adsorption appears to be an important feature in the course of gas chromatographic analysis of amines using a non-polar sorbent. For small alkylamine molecules, cyclohexylamine and nitrogen-containing heterocycles, adsorption occurs mainly on the solid support, whereas for arylamines and higher alkylamines it occurs at the gas-liquid interface. The high values of the correlation coefficients relating K_S and K_{GL} with physico-chemical parameters of the molecules allow the degree of interfacial adsorption to be predicted.

CONCLUSION

Retention of mono-, di- and trialkylamines with normal and branched carbon chains, aromatic amines and nitrogen-containing saturated and aromatic heterocyclic compounds by a non-polar stationary phase is predominantly determined by their dissolution, the contributions amounting to 80-97% of V_N^s . A certain decrease in the contribution of solution to the retention process (70% V_N^s) is observed with diamines containing a primary amino group at the α -carbon. These substances are characterized by a significantly higher contribution of adsorption on solid supports.

The contribution of adsorption on the support to amine retention tends to decrease with increase in molecular mass (as much as by two orders of magnitude). The contribution of adsorption at the gas-liquid interface shows a wide variation (0.12-18%) in the alkylamine series and depends to a much greater extent on the structural properties of amines (normal or branched chain, amino group located on a primary, secondary or tertiary carbon atom, etc.) than the contribution of dissolution. On the other hand, this contribution for aromatic amines is much greater (13-15%) than the contribution of adsorption on the solid support (0.01-1.6%) and shows little variation with respect to the structural peculiarities of the molecule. The contribution of adsorption at the gas-liquid interface appears to be insignificant for all of the nitrogen heterocycles studied, varying from 0.01 to 0.49% (except for 2,4,6-trimethylpyridine).

With increase in temperature the relative contribution of solution to retention increases, together with a simultaneous decrease in the contribution of adsorption on the solid support. Correlation analysis on the relationship between adsorption coefficients on the one hand and structural properties and physico-chemical parameters on the other suggest that in the course of solution of amines in the stationary phase the prevailing type of interaction between the stationary phase and amines is the dispersion interaction. However, when the hydrogen atom in the N-H group is replaced with an alkyl radical or when alkyl groups are situated close to the amino groups, a considerable influence of the specific intermolecular attraction forces on the retention occurs. A similar situation is found for the process of amino compound adsorption at the gas-liquid interface. For the adsorption of amines on the solid support, the specific interaction of the unshared electron pair on the nitrogen atom in amines with the active sites on the surface predominates.

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