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THERMODYNAMICS OF MOLECULAR ASSOCIATION

TRI-*n*-ALKYLAMINE-CHLOROALKANE SYSTEMS

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SUMMARY

Gas-liquid chromatography has been used to study complexation between four tri-*n*-alkylamines (tri-*n*-butyl-, tri-*n*-pentyl-, tri-*n*-hexyl- and tri-*n*-octyl-amine) and five haloalkanes at infinite-dilution conditions. The reference solvent for all the systems studied was *n*-tetradecane. The proton affinity of the amines increases from tri-*n*-butylamine to tri-*n*-hexylamine, and then decreases for tri-*n*-octylamine. Such behaviour is attributed to enhanced basicity of the amine molecule with increasing alkyl-chain length. With tri-*n*-octylamine, the shielding effect of the alkyl chain becomes more pronounced (steric-hindrance effect) and results in decreased ability of the nitrogen atom to form complexes. The thermodynamic parameters of complexation reactions and reactions of solution have been determined at temperatures of 25, 30, 40, 45 and 50° for all the systems.

INTRODUCTION

In the past 10 years, gas-liquid chromatography (GLC) has been extensively employed for the examination of weak molecular associations¹⁻³. Two different approaches have been used to establish equilibrium constants of molecular associations of such types as hydrogen bonding and charge-transfer complex formation. The method of Cadogan and Purnell⁴, further developed by Eon *et al.*⁵, is more general, but is also more laborious, as it involves the use of at least five chromatographic columns [each containing a different concentration of proton-acceptor (or proton-donor) solvent in an inert reference solvent]. The second method, originally proposed by Martire and Riedl⁶, involves use of two columns only, each containing pure solvent, reference and proton acceptor (or donor). However, this method requires some additional assumption: the choice of the liquid phases must be such that they have approximately the same molecular size, shape and polarizability. When this assumption is valid, the two methods give results in excellent agreement and of comparable precision⁷.

Martire and Riedl⁶ have shown that the apparent stability constant, K' , of a

weak organic molecular complex formed between a non-volatile solvent and a volatile solute can be determined by using the rather simple equation:

$$K' + 1 = \frac{(\bar{V}_g^0)_R (V_g^0)_A}{(V_g^0)_R (\bar{V}_g^0)_A} \quad (1)$$

in which $(\bar{V}_g^0)_R$ and $(\bar{V}_g^0)_A$ are the specific retention volumes of the alkane solute, and $(V_g^0)_R$ and $(V_g^0)_A$ the specific retention volumes of the donor solute, on the reference and proton-acceptor solvents, respectively.

Eqn. 1 is valid if:

- (1) The reaction between accepting solvent (A) and donating solute (D) is of the well-defined (1:1) type given by the relationship $A + D \rightleftharpoons AD$.
- (2) There is no self-association of molecules of A.
- (3) Molecules of the acceptor and reference solvent (R) are of the same shape, size and polarizability (or, at least, the absolute values of these properties are very close).

If requirements (1) and (2) are not fulfilled, mixed equilibria exist in the system, so that additional assumptions and analytical procedures are necessary. Self-association of solute molecules is avoided, as the solute is infinitely diluted in the solvent (as assumed by the definition of the chromatographic process). If we take infinite dilution as the standard state of the system, the apparent and the thermodynamic stability constants (K' and K) are related by the expression:

$$K' = \frac{C_{AD}^{\circ}}{C_D} = K C_A \gamma_A \quad (2)$$

The activity coefficients, γ_{AD} and γ_D in eqn. 2 are assumed to be unity, since, according to the above definition, $\gamma \rightarrow 1$ as $C \rightarrow 0$; further, the activity coefficient of the solvent (γ_A) is not unity, since C_A is far from 0. Concentrations of the acceptor-liquid phases could be determined from the densities of the stationary phases at the experimental temperatures, and, from the assumptions already made, the value for γ_A can be calculated from the equation derived by Martire and Riedl⁶, *viz.*

$$\gamma_A = \frac{(\bar{V}_g^0)_A M_A}{(\bar{V}_g^0)_R M_R} \quad (3)$$

where M_A and M_R are the molecular weights of the acceptor and reference stationary phases. Substitution of the value for C_A in eqns. 2 and 3 gives the value for K .

By determining K at several temperatures, the thermodynamic parameters ΔH_r and ΔS_r , *i.e.*, the enthalpy and entropy of the reaction, can be derived.

EXPERIMENTAL

Apparatus and procedure

The GLC apparatus used was a Perkin-Elmer Model 881, with a modified column thermostat. The flame ionisation detector was operated at 135°, and the injector block was maintained at *ca.* 120°. Columns were placed in the water bath, and the

temperature was thermostatically controlled and measured to within 0.05° . Nitrogen was used as carrier gas (flow-rate *ca.* 30 ml/min), the exact flow being measured with a soap-bubble flowmeter and the inlet pressure with precision manometer (Matheson, Chicago, Ill., U.S.A.); the outlet pressure was assumed to be atmospheric.

Retention times were measured, by means of a stop-watch, at the peak maximum. The dead-time of the system was determined by measuring the retention time of a small sample of methane, assuming dissolution of methane in the solvents studied to be negligible.

Stainless-steel columns (2 m \times 2.2 mm I.D.) were used in all experiments, the samples being introduced into the injection port as a vapour in volumes from 0.5 to 3 μ l by means of a 10- μ l Hamilton syringe. There was no noticeable adsorption at interfaces, since there was no dependence of retention volume on sample size, and all chromatographic peaks were symmetrical.

The densities of the stationary phases were measured with a Digitale Dichtemessrichtung densitometer (Anton Paar, Graz, Austria) equipped with a Lauda Ultrathermostat and Lauda R52 electronic temperature-regulation system.

Stationary phases

Tri-*n*-butylamine (TBA) (BDH, Poole, Great Britain) was subjected to molecular distillation in a Zeiss apparatus at 30° and 0.01 torr. Tri-*n*-hexylamine (THA) (Eastman, Rochester, N.Y., U.S.A.) was purified by molecular distillation at 75° and 0.05 torr. Tri-*n*-pentylamine (TPA) (Eastman) and tri-*n*-octylamine (TOA) (Fluka, Buchs, Switzerland) were used without further treatment, as was the reference solvent, *n*-tetradecane (TD) (BDH). The purities of all the solvents used were checked by GLC on a 5% SE-30 column at 180° ; all were better than 98%.

Preparation of columns

The solid support used was Johns-Manville Chromosorb P (80–100 mesh); it was coated with the solvents by the slurry method, each in amount approx. 10% (w/w); the ashing method⁶ was used to determine the exact amounts of the liquid phases. Only for TBA were small corrections necessary for liquid-phase loss from the column. In order to obtain accurate results, two columns with TBA were used, and retention volumes were calculated as average values from successive measurements on both. It should be noted that the values obtained with the different columns showed good agreement within the range of experimental error.

Solutes

n-Pentane and 1,2-dichloroethane (BDH), *n*-hexane, cyclohexane, chloroform and carbon tetrachloride (Carlo Erba, Milan, Italy), dichloromethane and 1,1,1-trichloroethane (Fluka) were used without further purification (solute purity is not an important consideration in GLC measurements).

RESULTS

Table I contains some important physical properties of the solvents used in this paper. Specific retention volumes (V_g^0) were determined in the usual manner⁸ for

TABLE I
SOME IMPORTANT PHYSICAL PROPERTIES OF THE SOLVENTS

Solvent	Mol. wt.	$\alpha \cdot 10^{-23}$	Density (g/ml) at				
			25°	30°	40°	45°	50°
TBA	185.36	2.45	0.7744	0.7684	0.7631	0.7579	0.7545
TPA	227.44	3.07	0.7893	0.7856	0.7781	0.7738	0.7689
THA	269.50	3.55	0.796*	0.792*	0.786*	0.782*	0.779*
TOA	353.25	4.63	0.8098	0.8064	0.7994	0.7961	0.7917
TD	198.40	2.66	0.7594	0.7558	0.7484	0.7442	0.7403

* Data taken from ref. 14; values for 25° and 45° graphically interpolated.

each solute with each solvent at five temperatures (25, 30, 40, 45 and 50°), and the average retention time from 4 to 10 successive measurements was used in the calculations. The experimental (V_R^0) data (for which the standard deviation never exceeded 1%) are shown in Table II.

TABLE II
SPECIFIC RETENTION VOLUMES, (V_R^0), OF SOLUTES ON FIVE STATIONARY PHASES A VARIOUS TEMPERATURES

Solute	TBA					TPA					THA
	25°	30°	40°	45°	50°	25°	30°	40°	45°	50°	25°
<i>n</i> -Pentane	158.5	130.7	90.40	75.89	63.83	179.3	149.0	104.6	88.08	74.93	149.1
<i>n</i> -Hexane	515.4	412.4	269.4	219.1	180.3	579.2	465.1	307.6	251.4	207.9	478.3
Cyclohexane	890.3	709.2	459.3	372.0	305.0	102.3	819.4	535.4	435.8	358.8	870.6
CH ₂ Cl ₂	149.4	123.4	85.61	71.69	60.67	181.8	150.1	104.2	87.31	73.90	184.8
CHCl ₃	605.3	474.2	298.9	238.5	193.0	738.7	580.0	365.4	292.0	236.4	782.4
CCl ₄	770.0	615.7	401.3	326.0	268.1	924.4	739.8	483.4	393.2	323.7	822.3
CH ₃ CCl ₃	598.9	480.1	314.8	265.5	211.5	701.2	565.3	374.6	306.8	254.2	637.5
CH ₂ ClCH ₂ Cl	536.8	432.1	285.5	233.5	193.2	638.0	514.0	340.3	278.5	230.6	620.5

TABLE III
ACTIVITY COEFFICIENTS (γ_2^∞) OF SOLUTES AT INFINITE DILUTION IN THE STUDIED SOLVENTS AT VARIOUS TEMPERATURES

Solute	TBA					TPA					THA
	25°	30°	40°	45°	50°	25°	30°	40°	45°	50°	25°
<i>n</i> -Pentane	1.132	1.144	1.172	1.192	1.206	0.815	0.818	0.826	0.834	0.838	0.827
<i>n</i> -Hexane	1.179	1.192	1.221	1.243	1.258	0.855	0.859	0.872	0.883	0.889	0.874
Cyclohexane	1.058	1.065	1.084	1.099	1.109	0.750	0.751	0.757	0.765	0.768	0.744
CH ₂ Cl ₂	1.412	1.406	1.400	1.404	1.402	0.946	0.942	0.937	0.940	0.938	0.785
CHCl ₃	0.782	0.812	0.872	0.909	0.940	0.522	0.541	0.581	0.605	0.625	0.416
CCl ₄	1.036	1.044	1.066	1.082	1.093	0.703	0.708	0.721	0.731	0.738	0.667
CH ₃ CCl ₃	1.244	1.249	1.265	1.279	1.287	0.866	0.865	0.866	0.872	0.873	0.804
CH ₂ ClCH ₂ Cl	2.055	2.031	1.996	1.990	1.976	1.409	1.391	1.365	1.360	1.349	1.223

The activity coefficient for each solute at infinite dilution (γ_2^∞) was calculated from the expression⁹

$$\gamma_2^\infty = \frac{1.704 \cdot 10^7}{M_1 p_2^0 V_g^0} \quad (4)$$

where M_1 is the solvent molecular weight and p_2^0 is the vapour pressure of the pure solute at the column temperature. The vapour pressures were calculated by means of the Antoine equation, using literature values^{10,11} for the Antoine constants. This empirical equation was chosen because it has been shown¹² to give the best results for γ_2^∞ measured by GLC in this low-temperature region. The calculated activity coefficients are listed in Table III.

The values for γ_2^∞ have not been corrected for non-ideality of the gas phase,^c as this was not the predominant aim of our work, and absolute activity coefficients are not necessary for the computations and discussion that follow.

In Fig. 1 are shown plots of the logarithms of the activity coefficients against

				TOA				TD					
30°	40°	45°	50°	25°	30°	40°	45°	50°	25°	30°	40°	45°	50°
125.7	89.33	75.87	65.07	130.0	109.1	78.05	66.34	56.93	160.8	133.4	93.29	78.42	66.60
389.0	262.3	216.6	180.8	414.9	337.8	228.0	188.4	157.4	525.6	423.1	279.6	228.6	189.2
704.5	470.2	386.4	321.2	766.9	621.6	416.2	342.5	285.4	839.1	717.0	471.4	384.5	317.4
153.2	107.5	90.00	76.42	133.5	111.9	79.88	67.82	58.13	109.6	92.30	66.54	56.76	48.87
614.2	387.0	309.3	250.4	483.2	396.9	272.6	227.3	191.3	344.5	281.8	192.0	159.3	133.7
664.7	442.9	363.6	302.0	675.6	560.6	392.6	330.3	280.7	727.7	587.6	390.6	320.3	265.8
518.2	349.0	288.0	240.4	521.9	421.7	280.8	230.5	191.4	539.1	438.4	295.3	243.7	203.5
502.9	336.6	227.0	230.6	469.4	391.2	276.2	233.3	199.0	420.2	342.9	232.6	192.6	161.3

				TOA				TD					
30°	40°	45°	50°	25°	30°	40°	45°	50°	25°	30°	40°	45°	50°
0.818	0.816	0.816	0.814	0.724	0.719	0.713	0.712	0.710	1.042	1.047	1.362	1.073	1.080
0.869	0.863	0.864	0.863	0.769	0.763	0.757	0.758	0.756	1.080	1.085	1.099	1.113	1.120
0.737	0.728	0.727	0.724	0.644	0.638	0.628	0.623	0.622	0.986	0.984	0.987	0.993	0.996
0.779	0.767	0.769	0.766	0.829	0.813	0.787	0.779	0.768	1.798	1.756	1.683	1.683	1.626
0.431	0.463	0.482	0.498	0.514	0.509	0.502	0.501	0.498	1.284	1.277	1.268	1.271	1.268
0.665	0.664	0.667	0.667	0.620	0.602	0.572	0.560	0.548	1.024	1.022	1.023	1.029	1.030
0.796	0.784	0.783	0.779	0.749	0.746	0.744	0.747	0.746	1.291	1.278	1.260	1.257	1.250
1.200	1.163	1.153	1.139	1.233	1.177	1.082	1.045	1.007	2.453	2.391	2.289	2.254	2.212

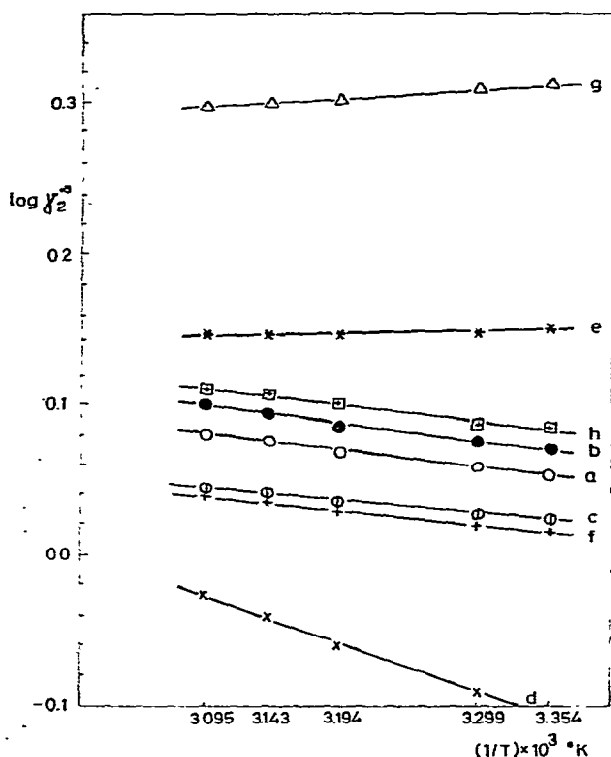


Fig. 1. Dependence of $\log \gamma_2^\infty$ on $1/T$ for TBA as solvent. (a) = *n*-Pentane; (b) = *n*-hexane; (c) = cyclohexane; (d) = chloroform; (e) = dichloromethane; (f) = carbon tetrachloride; (g) = 1,2-dichloromethane; (h) = 1,1,1-trichloroethane.

the inverse of the absolute temperature for all the solutes studied and with TBA as solvent; similar plots were obtained for the other four solvents used. From the temperature dependence of γ_2^∞ , the excess of the partial molar enthalpy of solution can

TABLE IV

EXCESS OF THE PARTIAL MOLAR ENTHALPY ($\Delta\bar{H}_E$, kcal/mole) AND ENTROPY ($\Delta\bar{S}_E$, cal/mole·°K) OF SOLUTION

Solute	TBA		TPA		THA
	$\Delta\bar{H}_E$	$\Delta\bar{S}_E$	$\Delta\bar{H}_E$	$\Delta\bar{S}_E$	$\Delta\bar{H}_E$
<i>n</i> -Pentane	-0.49 ± 0.06	-1.92 ± 0.04	-0.21 ± 0.06	-0.34 ± 0.09	0.10 ± 0.10
<i>n</i> -Hexane	-0.50 ± 0.08	-2.02 ± 0.04	-0.30 ± 0.08	-0.72 ± 0.04	0.09 ± 0.07
Cyclohexane	-0.37 ± 0.08	-1.34 ± 0.05	-0.19 ± 0.35	-0.12 ± 0.22	0.22 ± 0.19
CH ₂ Cl ₂	0.05 ± 0.06	-0.52 ± 0.04	0.06 ± 0.06	0.32 ± 0.04	0.19 ± 0.11
CHCl ₃	-1.41 ± 0.08	-4.26 ± 0.13	-1.39 ± 0.06	-3.40 ± 0.04	-1.39 ± 0.07
CCl ₄	-0.42 ± 0.08	-1.52 ± 0.04	-0.37 ± 0.07	-0.54 ± 0.09	0.0 ± 0.07
CH ₃ CCl ₃	-0.27 ± 0.07	-1.32 ± 0.04	0.0 ± 0.15	-0.34 ± 0.04	0.24 ± 0.08
CH ₂ ClCH ₂ Cl	0.29 ± 0.08	-0.42 ± 0.08	0.33 ± 0.08	-0.40 ± 0.00	0.54 ± 0.09

be deduced, and the excess of the partial molar free energy of solution can be calculated by using the expression:

$$\Delta\bar{G}_E = RT \ln \gamma_2^\infty \quad (5)$$

By combining this value with the values for $\Delta\bar{H}_E$, we can derive the excess of the partial molar entropy of solution, $\Delta\bar{S}_E$. Values of $\Delta\bar{H}_E$ and $\Delta\bar{S}_E$ are shown in Table IV, together with the propagated error.

The ratio $(\bar{V}_E^0)_R/(\bar{V}_E^0)_A$ is important in calculating the value of the apparent stability constant. This ratio has been determined and used in further calculations as the average value of the individual ratios for all the alkane solutes studied. There is only a slight difference between the values of this ratio for each individual alkane studied for the same acceptor-reference solvent pair. In general, the values for *n*-pentane and *n*-hexane are much closer to each other, whereas the value for cyclohexane is somewhat lower. This is probably attributable to differences in the solution-entropy factor. The errors in the ratio of specific retention volumes, shown in Table V, are calculated as a standard deviation from the individual values. This error becomes more pronounced as the similarity between the physical properties (discussed above) of the acceptor and reference solvents diminishes.

The pure-solvent concentrations and the estimated (from eqn. 3) corresponding activity coefficients are shown in Table VI.

From the values in Tables II, V and VI, the equilibrium constants were computed by using eqns. 1 and 2; these values are listed in Table VII, the errors being propagated by means of the usual formula. There is a tendency for an increase in the standard deviation of values for *K* as we go from TBA to TOA; this can also be explained by increasing dissimilarities between the reference and proton-acceptor phases, which also follow the above order (see Table I).

Finally, the enthalpy and entropy of complex formation have been determined, from the least-squares best fit for plots of $\log K$ against the reciprocal of temperature, for each system studied. Fig. 2 shows a typical plot obtained with TBA as proton-acceptor solvent; the values of ΔH_r and ΔS_r , with the corresponding standard deviations, are shown in Table VIII.

$\Delta\bar{S}_E$	TOA		TD	
	$\Delta\bar{H}_E$	$\Delta\bar{S}_E$	$\Delta\bar{H}_E$	$\Delta\bar{S}_E$
0.68 ± 0.05	0.15 ± 0.06	1.14 ± 0.05	-0.28 ± 0.18	-0.98 ± 0.04
0.62 ± 0.04	0.12 ± 0.10	0.90 ± 0.00	-0.28 ± 0.06	-1.08 ± 0.04
1.32 ± 0.04	0.26 ± 0.08	1.74 ± 0.05	-0.08 ± 0.08	-0.22 ± 0.04
1.12 ± 0.05	0.58 ± 0.06	2.32 ± 0.04	0.72 ± 0.01	1.22 ± 0.04
-2.92 ± 0.04	0.24 ± 0.07	2.12 ± 0.04	0.09 ± 0.05	0.20 ± 0.00
0.80 ± 0.00	0.94 ± 0.07	4.12 ± 0.04	-0.05 ± 0.07	-0.20 ± 0.00
1.22 ± 0.04	0.02 ± 0.08	0.60 ± 0.00	0.24 ± 0.24	0.30 ± 0.00
1.40 ± 0.00	1.55 ± 0.08	4.86 ± 0.09	0.79 ± 0.08	0.90 ± 0.00

TABLE V

AVERAGE VALUES OF RATIO $(\bar{V}_g^0)_R/(\bar{V}_g^0)_A$ AT VARIOUS TEMPERATURES

Reference/Acceptor	25°	30°	40°	45°	50°
TD/TBA	1.012 ± 0.008	1.019 ± 0.008	1.032 ± 0.006	1.038 ± 0.006	1.044 ± 0.004
TD/TPA	0.892 ± 0.018	0.894 ± 0.014	0.892 ± 0.015	0.894 ± 0.014	0.894 ± 0.014
TD/THA	1.068 ± 0.038	1.056 ± 0.035	1.038 ± 0.032	1.028 ± 0.031	1.019 ± 0.029
TD/TOA	1.223 ± 0.053	1.212 ± 0.051	1.184 ± 0.042	1.173 ± 0.046	1.161 ± 0.045

TABLE VI

CONCENTRATIONS (C_A) AND ACTIVITY COEFFICIENTS (γ_A) OF PURE ACCEPTOR SOLVENTS AT VARIOUS TEMPERATURES

Solvent	25°		30°		40°		45°		50°	
	C_A	γ_A	C_A	γ_A	C_A	γ_A	C_A	γ_A	C_A	γ_A
TBA	4.1756	0.945	4.1379	0.952	4.1109	0.964	4.0866	0.970	4.0625	0.975
TPA	3.3811	1.284	3.4558	1.281	3.4206	1.284	3.4030	1.282	3.3855	1.281
THA	2.9536	1.272	2.9388	1.286	2.9165	1.309	2.9035	1.321	2.8905	1.332
TOA	2.2929	1.455	2.2816	1.469	2.2618	1.503	2.2533	1.518	2.2420	1.533

TABLE VII

EQUILIBRIUM CONSTANTS, K (l/mole), OF CHLOROALKANES WITH THE AMINES STUDIED AT VARIOUS TEMPERATURES

Solute	Temperature				
	25°	30°	40°	45°	50°
<i>With TBA as solvent</i>					
CH ₂ Cl ₂	0.096 ± 0.003	0.092 ± 0.003	0.083 ± 0.002	0.078 ± 0.002	0.075 ± 0.001
CHCl ₃	0.197 ± 0.004	0.182 ± 0.003	0.153 ± 0.002	0.140 ± 0.002	0.128 ± 0.002
CCl ₄	0.018 ± 0.002	0.017 ± 0.002	0.015 ± 0.002	0.014 ± 0.001	0.013 ± 0.001
CH ₃ CCl ₃	0.032 ± 0.002	0.030 ± 0.002	0.025 ± 0.002	0.023 ± 0.001	0.021 ± 0.001
CH ₂ ClCH ₂ Cl	0.074 ± 0.001	0.072 ± 0.002	0.067 ± 0.002	0.065 ± 0.002	0.063 ± 0.001
<i>With TPA as solvent</i>					
CH ₂ Cl ₂	0.111 ± 0.006	0.103 ± 0.005	0.091 ± 0.005	0.086 ± 0.005	0.081 ± 0.005
CHCl ₃	0.210 ± 0.009	0.190 ± 0.006	0.159 ± 0.006	0.153 ± 0.001	0.134 ± 0.006
CCl ₄	0.031 ± 0.005	0.028 ± 0.004	0.024 ± 0.004	0.022 ± 0.004	0.021 ± 0.004
CH ₃ CCl ₃	0.037 ± 0.005	0.035 ± 0.004	0.030 ± 0.004	0.028 ± 0.004	0.027 ± 0.004
CH ₂ ClCH ₂ Cl	0.082 ± 0.006	0.074 ± 0.005	0.069 ± 0.005	0.067 ± 0.004	0.064 ± 0.005
<i>With THA as solvent</i>					
CH ₂ Cl ₂	0.213 ± 0.017	0.199 ± 0.015	0.165 ± 0.013	0.164 ± 0.013	0.154 ± 0.012
CHCl ₃	0.379 ± 0.023	0.344 ± 0.020	0.286 ± 0.017	0.259 ± 0.016	0.227 ± 0.020
CCl ₄	0.055 ± 0.011	0.051 ± 0.010	0.046 ± 0.010	0.043 ± 0.009	0.041 ± 0.008
CH ₃ CCl ₃	0.070 ± 0.012	0.066 ± 0.011	0.059 ± 0.010	0.056 ± 0.010	0.053 ± 0.009
CH ₂ ClCH ₂ Cl	0.153 ± 0.015	0.145 ± 0.014	0.132 ± 0.012	0.125 ± 0.011	0.119 ± 0.011
<i>With TOA as solvent</i>					
CH ₂ Cl ₂	0.147 ± 0.020	0.140 ± 0.018	0.124 ± 0.017	0.117 ± 0.016	0.111 ± 0.016
CHCl ₃	0.214 ± 0.022	0.211 ± 0.021	0.200 ± 0.020	0.196 ± 0.019	0.192 ± 0.019
CCl ₄	0.041 ± 0.015	0.047 ± 0.014	0.056 ± 0.014	0.061 ± 0.014	0.066 ± 0.014
CH ₃ CCl ₃	0.055 ± 0.015	0.050 ± 0.015	0.037 ± 0.013	0.032 ± 0.013	0.027 ± 0.012
CH ₂ ClCH ₂ Cl	0.020 ± 0.014	0.024 ± 0.014	0.032 ± 0.013	0.036 ± 0.013	0.039 ± 0.013

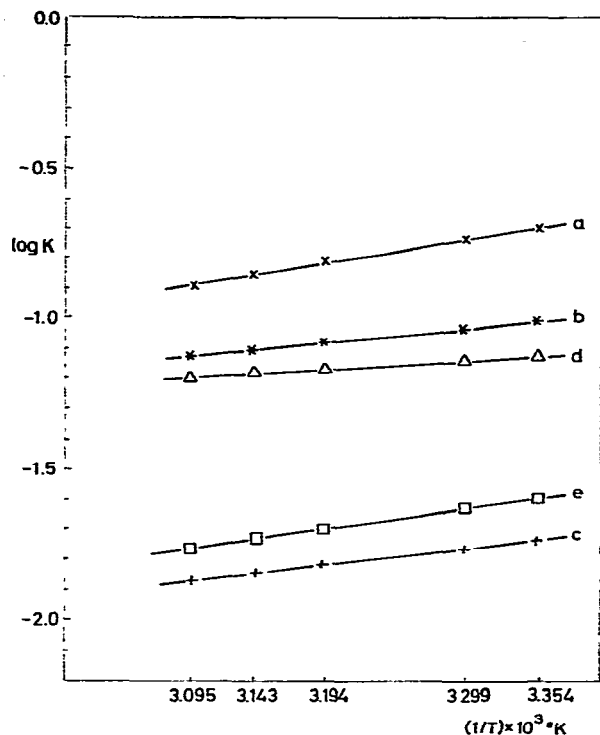


Fig. 2. Dependence of $\log K$ on $1/T$ for TBA as proton-acceptor solvent. (a) = Chloroform; (b) = dichloromethane; (c) = carbon tetrachloride; (d) = 1,2-dichloroethane; (e) = 1,1,1-trichloroethane.

TABLE VIII

ENTHALPIES AND ENTROPIES OF COMPLEX FORMATION

Solute	$-\Delta H_R$, kcal/mole	$-\Delta S$, cal/°K·mole
<i>With TBA as solvent</i>		
CH ₂ Cl ₂	1.95 ± 0.06	11.2 ± 0.8
CHCl ₃	3.30 ± 0.20	14.3 ± 0.3
CCl ₄	2.28 ± 0.26	15.5 ± 0.2
CH ₃ CCl ₃	2.96 ± 0.24	16.8 ± 0.1
CH ₂ ClCH ₂ Cl	1.25 ± 0.07	9.4 ± 0.1
<i>With TPA as solvent</i>		
CH ₂ Cl ₂	2.34 ± 0.12	12.2 ± 0.2
CHCl ₃	3.27 ± 0.70	14.0 ± 0.1
CCl ₄	3.09 ± 0.20	17.2 ± 0.1
CH ₃ CCl ₃	2.41 ± 0.19	14.6 ± 0.1
CH ₂ ClCH ₂ Cl	1.83 ± 0.22	11.0 ± 0.1
<i>With THA as solvent</i>		
CH ₂ Cl ₂	2.57 ± 0.86	11.7 ± 0.2
CHCl ₃	3.83 ± 0.63	14.7 ± 0.3
CCl ₄	2.19 ± 0.20	13.1 ± 0.4
CH ₃ CCl ₃	2.09 ± 0.14	12.3 ± 0.1
CH ₂ ClCH ₂ Cl	1.96 ± 0.10	10.3 ± 0.2
<i>With TOA as solvent</i>		
CH ₂ Cl ₂	2.19 ± 0.15	11.0 ± 0.9
CHCl ₃	0.85 ± 0.09	5.9 ± 0.2
CCl ₄	-3.65 ± 0.51	-6.0 ± 0.1
CH ₃ CCl ₃	5.50 ± 0.84	24.0 ± 0.5
CH ₂ ClCH ₂ Cl	-5.30 ± 1.07	-10.0 ± 0.02

DISCUSSION

It is most important that two requirements concerning the values in eqns. 1 and 3 be fulfilled: the polarizability, α , of the reference and proton-acceptor solvent-pair as well as their molar volumes, v , must be the same^{7,12}. As can be seen from the values in Table I, this condition is obtained for TBA and TD as acceptor-reference solvent pair. However, as we proceed from TBA to TOA, the discrepancy between α and v becomes more pronounced, since TD is always the reference solvent, and the amine molecules change in order from TBA to TOA. The similarity in solvent properties can also be seen from the activity coefficients of the solutes at infinite dilution in the solvents used (see Table III). The values of γ_2^∞ for alkane solutes with TBA and TD as solvents are almost identical. This means that dispersion forces acting between solvent-solute molecule pairs as well as the configuration effects are the same in both solvents; further, the solution mechanism in the two solvents must also be the same. We may conclude, therefore, that non-specific forces are virtually the same for TD-alkane and TBA-alkane pairs, so that TD and TBA should form ideal solutions. This conclusion is supported by the values in Table VI for the activity coefficients of pure proton-accepting solvents. The value for TBA is close to unity, and, since it is determined with respect to TD, (eqn. 3), these two solvents are very similar and should form such solutions. From the foregoing, it is clear that Martire and Riedl's approximation is best fulfilled for the system TBA-TD and least fulfilled for the solvent pair TOA-TD (since the discrepancy between α and v values is greatest for these solvents). An analysis of all the parameters discussed should support this conclusion, and we shall return to it later.

It is well known that, in GLC, the dependence between $\log V_g^0$ and the number of methylene groups in the homologue of the solvent used and for the same solute is linear. This linearity usually starts with the third to fifth members of the homologous series¹³. According to our results (Table II), linear variation of $\log V_g^0$ with the number of methylene groups for the homologous tri-*n*-alkylamines begins with the fifth homologue (TPA).

For V_g^0 values with THA as solvent, our results do not agree with those of Sheridan *et al.*¹⁴, the discrepancy becoming more pronounced with the proton-donating ability of the solute. Our values of specific retention volume for carbon tetrachloride, trichloroethane and *n*-hexane are in good agreement (to within a few per cents.) with those of Sheridan *et al.*; our values, however, are always slightly greater. On the other hand, our values for the strong proton donors chloroform and dichloroethane are considerably higher (even by as much as 20%) than those of Sheridan *et al.* The lower values of V_g^0 on THA given in the literature¹⁴, in comparison with our results, are probably caused by polymerisation of the products of *tert.*-amine decomposition. Unfortunately, Sheridan *et al.* did not explain what precautions they took to avoid decomposition of the amine, except to use fresh distillate. In our experiments, as well as distillation of the amines, we so arranged measurements by GLC that we were able to complete tests with one column within one day.

As can be seen in Table IV, the excess of the partial molar thermodynamic functions of solution becomes more endothermic as the alkyl-chain length of the amine increases; similar behaviour was observed and explained by Kertes and Grauer¹⁵, who examined the effect of chain length on the heats of mixing in tri-*n*-alkylamine-

benzene systems. According to these workers, the heat of mixing became more endothermic with lengthening of the alkyl chain of the amine over the whole mole-fraction range studied. Enhanced endothermy of solution has also been observed by other authors^{16,17}. Increased endothermy with increasing chain length has been attributed by Kertes and Grauer to two effects, acting in opposite directions: (a) the endothermic effect of the disruption of π - π bonds of associated benzene, and (b) the exothermic effect of newly formed bonds between the lone-pair electrons of the nitrogen atom and the π -electrons of benzene.

In our systems, effect (a) is non-existent; instead, non-specific reactions are involved. In systems involving proton-donating solutes, charge-transfer complexation reactions take place, as well as the non-specific reactions. Charge-transfer reaction is governed by two effects with opposite signs: (a) increasing basicity of the nitrogen atom in the amine (caused by increased alkyl-chain length¹⁸), and (b) a shielding effect determined by the geometric properties of the long alkyl chain (the steric-hindrance effect). According to the results in Table IV (which represent over-all effects only), it appears that $\Delta\bar{H}_E$ values for non-specific reactions are similar in order of magnitude to $\Delta\bar{H}_E$ values for complexation reactions. Inspection of these values for the alkane solutes shows an increase in $\Delta\bar{H}_E$ (non-specific) from TBA to TOA in the endothermic direction. For chloroalkane solutes dissolved in THA or TOA, the endothermic contribution of the non-specific interactions overcomes the exothermic contribution of $\Delta\bar{H}_E$ from the complexation process, so that the over-all reaction for THA or TOA is endothermic. As $\Delta\bar{H}_E$ for 1,2-dichloroethane is always endothermic, it seems that the strongest endothermic non-specific interactions occur in systems involving this solute.

As expected, the strongest complexes of all the amines are formed with chloroform, and the weakest with carbon tetrachloride. The order of complexation of all other solutes studied was exactly the same as that found by Sheridan *et al.*¹⁴ for THA as proton acceptor. The main reason for the discrepancy between our results and those of Sheridan *et al.* for stability constants has been discussed above; differences caused by using different reference solvents are negligible. The specific retention volumes of solutes examined on *n*-octadecane¹⁹ (used by Sheridan *et al.*¹⁴) are very close to our results obtained on *n*-tetradecane as reference solvent. This could be because the V_g^0 values were measured on two closely similar stationary phases, both homologous *n*-alkanes.

The nature of the complexes formed between tri-*n*-alkylamines and chloroalkanes can not be discussed on the basis of the results of GLC measurements alone. Most probably, two types of complex-formation mechanism exist^{14,19}, each acting independently and in parallel. These mechanisms are (1) hydrogen bonding of the proton from the chloroalkane to the nitrogen of the amine, and (2) charge-transfer complexation of the n - σ type between nitrogen and chlorine atoms of haloalkane solutes. These two types of reaction can not be resolved, and the stability constants shown in Table VII represent over-all values.

Examination of Table VII shows that the accepting ability of the nitrogen atom increases from TBA to THA, and then decreases for TOA. Thus, the homologous series of tertiary amines acts as if its basicity maximum was to THA. This behaviour can be explained by considering the two antagonistic effects mentioned earlier, *viz.*, enhanced basicity of an amine molecule with a long alkyl chain¹⁸, and an increased steric-hindrance effect acting in the opposite direction. The amine basicity is enhanced

because each added methylene group in the alkyl chain of the amine acts as an electron donor to the nitrogen atom (the hyperconjugate effect)²⁰. Thus, the nitrogen atom becomes a stronger proton acceptor as the length of the alkyl chain increases. This effect is limited in extent and is valid only for the lower members of the homologous series. When a certain number of methylene groups is reached, the hyperconjugate effect ceases, and further methylene groups only increase the shielding effect (steric hindrance effect). According to the results presented, the hyperconjugate effect becomes ineffective at THA. At this point, the basicity of the amine reaches a constant (maximum) value, but the steric effect increases continuously with addition of more methylene groups.

It has been shown that the relationship between the enthalpy of complexation, ΔH_r , and the corresponding entropy, ΔS_r , is linear for a given type of reaction and for compounds of the same homologous series^{5,21}. This semi-empirical relationship is found to be fulfilled for the amines studied. Fig. 3 shows graphs of ΔH_r vs. ΔS_r for the chloroalkanes studied on four amines. Two almost parallel straight lines can be drawn through the experimental points. The upper line connects the points for carbon tetrachloride and trichloroethane, where the $n-\sigma$ type of reaction with amines can be expected to predominate; deviations from the upper line are points for TOA and can be explained as set out above.

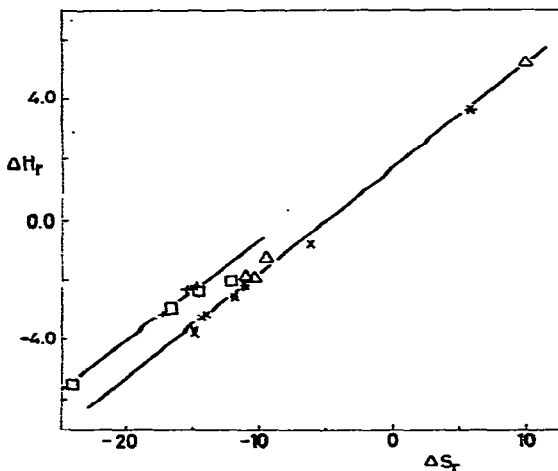


Fig. 3. Relationship between ΔH_r and ΔS_r . \times = chloroform; $*$ = dichloromethane; Δ = 1,2-dichloroethane; $+$ = carbon tetrachloride; \square = 1,1,1-trichloroethane.

The lower straight line connects points for the other three chloroalkanes studied. Although these solutes can react with the amine nitrogen atom through $n-\sigma$ and hydrogen-bonding reactions, the latter type of complexation is more probable. Nevertheless, the lower line represents a mixed type of reaction, which is why there is some scatter of points about the line.

REFERENCES

- 1 J. H. Purnell, in A. B. Littlewood (Editor), *Gas Chromatography 1966*, Elsevier, Amsterdam, 1967.
- 2 A. B. Littlewood, *Anal. Chem.*, 36 (1964) 1441.
- 3 L. Mathiasson, *J. Chromatogr.*, 114 (1975) 39.
- 4 D. F. Cadogan and J. H. Purnell, *J. Phys. Chem.*, 73 (1969) 3849.
- 5 C. Eon, C. Pommier and G. Guiochon, *J. Phys. Chem.*, 75 (1971) 2632.
- 6 D. E. Martire and P. Riedl, *J. Phys. Chem.*, 72 (1968) 3478.
- 7 Hsueh Liang-Liao, D. E. Martire and J. P. Sheridan, *Anal. Chem.*, 45 (1973) 2087.
- 8 D. H. Desty and W. T. Swanton, *J. Phys. Chem.*, 65 (1961) 766.
- 9 D. E. Martire, in L. Flower (Editor), *Gas Chromatography*, Academic Press, New York, 1963, p. 33.
- 10 R. R. Dreisbach, *Physical Properties of Organic Compounds*, American Chemical Society, Washington, D.C., 1959.
- 11 *Handbook of Chemistry and Physics*, Chemical Rubber Co., Cleveland, Ohio, 1952.
- 12 G. Castello and G. D'Amato, *J. Chromatogr.*, 107 (1975) 1.
- 13 A. N. Korol, *Stationary Phases in Gas-Liquid Chromatography* (in Russian), Naukova Dumka, Kiev, 1969, p. 27.
- 14 J. P. Sheridan, D. E. Martire and F. P. Banda, *J. Amer. Chem. Soc.*, 95 (1973) 4788.
- 15 A. S. Kertes and F. Grauer, *J. Phys. Chem.*, 77 (1973) 3107.
- 16 J. Brown, W. Fock and F. Smith, *J. Chem. Thermodynamics*, 1 (1969) 273.
- 17 H. V. Kehiaian, K. Sosnkowska-Kehiaian and R. Hryniewicz, *J. Chem. Phys.*, 68 (1971) 922.
- 18 M. Tamres, S. Searles, E. M. Leighly and D. W. Mohrman, *J. Amer. Chem. Soc.*, 76 (1954) 3983.
- 19 J. P. Sheridan, D. E. Martire and Y. B. Tewari, *J. Amer. Chem. Soc.*, 94 (1972) 3294.
- 20 Dr. D. S. Jeremić, private communication.
- 21 J. E. Leffler, *J. Org. Chem.*, 20 (1955) 1202.