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DETERMINATION OF COMPLEX ASSOCIATION CONSTANTS FROM GAS CHROMATOGRAPHIC DATA

IV. HYDROGEN BONDING OF AMINES, PROPYL MERCAPTAN AND BUTYNE WITH *n*-HEXADECYL CYANIDE AND *n*-HEXADECYL BROMIDE

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SUMMARY

Weak hydrogen bridge complexes have been investigated by gas chromatography. A correction for the influence of dipolar interactions between solvent and solute on the retention of the latter has been evaluated, and applied in the calculation of the association constants. Indications have been found of the existence of very weak complexes between mercaptans or alkynes and *n*-hexadecyl bromide, and the occurrence of complex formation between amines and *n*-hexadecyl bromide has been definitely established. Association constants of the stronger complexes between amines and *n*-hexadecyl cyanide have been evaluated with a precision of about 5%.

INTRODUCTION

In previous work¹, hydrogen bonding between alcohols and a number of hexadecyl derivatives and dioctyl compounds was investigated. In this work, weaker hydrogen bridges have been investigated, *viz.*, between amines, propyl mercaptan and butyne on the one hand, and *n*-hexadecyl cyanide and *n*-hexadecyl bromide on the other.

When weak complexes are investigated by means of gas chromatography (GC), great care must be exercised in correcting for dipolar interactions between the solvent and solute, as the retention of the solute is increased not only by hydrogen bonding, but also by dipolar interactions with the solvent. Therefore, an analysis was made of the influence of dipolar interactions between solvent and solute on the retention of the latter, prior to the investigation of hydrogen bonding.

THEORETICAL

By means of GC, association constants, *K*, for 1:1 complex formation between a volatile solute A and an involatile component B of the stationary phase in the

column can be determined. To do so, the net retention volumes, V , of A, and of a volatile solute, A^* , that is closely related to A but does not form a complex, must be measured for a column containing an inert stationary phase, S, and a series of columns containing mixtures of S and B. K is calculated^{2,3} from the equation

$$\left[\left(\frac{V_A}{V_{A^*}} \right)_{S+B} \left(\frac{V_{A^*}}{V_A} \right)_S F^{-1} - 1 \right] W_B^{-1} = K \left(\frac{f_A f_B}{f_{AB}} \right)_{S+B} \quad (1)$$

where F is a correction factor for dipolar interactions between A and B or A^* and B, W_B is the weight fraction of component B and f is the activity coefficient. By extrapolation and interpolation of the values of the left-hand side, the right-hand side can be determined as a function of W_B over the whole concentration range, including the solvents S ($W_B = 0$) and B ($W_B = 1$). The activity coefficients, f , can be defined as unity either in the solvent S or in the solvent B, depending on the convention chosen. If only the value of the association constant in the solvent B is required, retention data for the solvents S and B suffice.

Influence of dipolar interactions between solvent and solute on retention

The correction factor, F , is given by

$$F = \left(\frac{f_{A^*}}{f_A} \right)_{S+B} \left(\frac{f_A}{f_{A^*}} \right)_S \quad (2)$$

In the general case, where A, A^* and B have a dipole moment, the calculation of F is beyond the reach of theory. However, F can be estimated empirically as described below. It follows from Littlewood's⁴ work that the following equation can be expected to hold for alkanes (alk) and polar solutes (pol) dissolved in *n*-hexadecane (S) or a mixture of *n*-hexadecane and a monofunctional *n*-hexadecyl derivative (S+B):

$$\frac{V_{\text{alk}(S)}}{V_{\text{alk}(B)}} \cdot \frac{V_{\text{pol}(B)}}{V_{\text{pol}(S)}} = \frac{f_{\text{alk}(B)}}{f_{\text{alk}(S)}} \cdot \frac{f_{\text{pol}(S)}}{f_{\text{pol}(B)}} \equiv \frac{1}{r_a} \cdot \frac{f_{\text{pol}(S)}}{f_{\text{pol}(B)}} \equiv r_b = \exp [g(w_B) \mu_B^c \mu_{\text{pol}}^d] \quad (3)$$

where r_a and r_b are symbols used by Littlewood, g denotes a functional relationship, w_B is the concentration of the functional group of B in the solvent, c and d are constants and μ is the dipole moment. When eqn. 3 is applied to the polar solutes A and A^* , then

$$\frac{f_{A(S)}}{f_{A(B)}} \cdot \frac{f_{A^*(B)}}{f_{A^*(S)}} = F = \exp [g(w_B) \mu_B^c (\mu_A^d - \mu_{A^*}^d)] \quad (4)$$

To avoid large errors in the calculation of F from eqn. 4, a reference solute A^* having about the same dipole moment as A should be chosen. In this study, alkyl chlorides ($\mu_{A^*} \approx 2.05$ D) were used as reference solutes for the investigated amines ($\mu_A \approx 1.39$ D). For propylamine, diethyl ether ($\mu_{A^*} = 1.15$ D) was also used as a reference solute, to examine the effect of varying the reference substance. For propyl mercaptan ($\mu_A = 1.58$ D) and butyne ($\mu_A = 0.80$ D), propyl bromide ($\mu_{A^*} = 2.05$ D) and diethyl ether, respectively, were used as reference solutes.

Previously¹, $g(w_B)$ was approximated by $g(w_B) = aw_B$, where a is a constant, and c was set equal to unity, following Littlewood⁴. However, when weak complexes are investigated, as in this work, the correction for dipolar interactions is important and the utmost attention should be paid to the evaluation of $g(w_B)$ and of the constants c and d in eqn. 3.

In the following, w_B is defined as the ratio of the weight fraction of the functional group in the stationary phase to that in the corresponding pure C_{16} compound. We used Littlewood's⁴ retention data at 60° for the stationary phases *n*-hexadecane, *n*-hexadecene, *n*-hexadecyl chloride, *n*-hexadecyl bromide and palmitonitrile, and Littlewood and Willmott's⁵ data (interpolated to 60°) for squalane-lauronitrile mixtures as stationary phases. It appeared that r_a depends slightly on the identity of the alkane*. Therefore, in the calculation of r_b from Littlewood's data, the value of r_a for the alkane homomorph of the polar solute was used, rather than an average r_a value for all investigated alkanes (Littlewood and Willmott⁵ tabulated only average r_a values). We calculated separately for ethyl and propyl derivatives (Tables I and II).

In eqn. 3, $g(w_B)\mu_B^c$ depends only on the identity of the stationary phase (i), and μ_{pol}^d depends only on the identity of the solute (j). Hence eqn. 3 can be written as follows:

$$x_{i,j} = p_i q_j \quad (5)$$

where x represents $\log r_b$, p is proportional to $g(w_B)\mu_B^c$ and q is proportional to μ_{pol}^d . The appropriate mathematical technique for determining the values of p and q that

TABLE I

LOG r_b VALUES OF ETHYL DERIVATIVES, CALCULATED FROM RETENTION DATA OF REF. 4 AT 60° AND REF. 5 INTERPOLATED TO 60°

Stationary phase	Solute						
	Diethyl ether	Ethyl acetate	Methyl ethyl ketone	Ethyl bromide	Ethyl iodide	Nitroethane	Ethyl cyanide
$C_{16}H_{32}$	-0.011	0.080	0.035	0.049	0.048	0.077	0.084
$C_{16}H_{33}Cl$	0.060	0.220	0.259	0.164	0.170	0.384	0.395
$C_{16}H_{33}Br$	0.052	0.225	0.268	0.177	0.196	0.390	0.419
$C_{16}H_{33}N$	0.157	0.458	0.557	0.304	0.280	0.879	0.846
$C_{12}H_{25}N$:							
100%	0.262	0.509	0.666			0.992	1.000
48.4%	0.152	0.316	0.444			0.698	0.666
28.6%	0.121	0.222	0.306			0.529	0.483
14.0%	0.097	0.130	0.189			0.361	0.334

* The mean values of r_a of 10 alkanes investigated by Littlewood⁴, and their standard deviations, are as follows: *n*-hexadecene, 1.004 ± 0.002 ; *n*-hexadecyl chloride, 1.264 ± 0.009 ; *n*-hexadecyl bromide, 1.578 ± 0.019 ; and palmitonitrile, 1.517 ± 0.019 . The standard deviation for *n*-hexadecene is probably caused only by experimental error, but the larger standard deviations for the other stationary phases reflect genuine differences in the individual r_a values. It appears that r_a increases slightly with increasing chain length of the alkane.

TABLE II

LOG r_b VALUES OF PROPYL DERIVATIVES CALCULATED FROM RETENTION DATA OF REF. 4 AT 60° AND REF. 5 INTERPOLATED TO 60°

Stationary phase	Solute						
	Dipropyl ether	Propyl acetate	Propionaldehyde	Propyl chloride	Propyl bromide	Nitropropane	Propyl cyanide
C ₁₆ H ₃₂	0.012		0.053	0.039	0.026		0.100
C ₁₆ H ₃₃ Cl	0.060		0.235	0.142	0.153		0.408
C ₁₆ H ₃₃ Br	0.057		0.253	0.155	0.170		0.416
C ₁₆ H ₃₃ N	0.145		0.515	0.289	0.283		0.872
C ₁₂ H ₂₅ N:							
100%	0.192	0.522		0.339	0.329	0.936	0.957
48.4%	0.129	0.329		0.217	0.198	0.632	0.651
28.6%	0.101	0.244		0.149	0.132	0.478	0.476
14.0%	0.083	0.160		0.087	0.080	0.240	0.362

gives the best description of the experimental value of x is factor analysis⁶. Classical factor analysis can be applied only to complete matrices of $x_{i,j}$ data, but De Ligny *et al.*⁷ have developed procedures that are suitable for incomplete data matrices such as those in Tables I and II. The ensuing values of p and q are given in Tables III and IV**.

Regression analysis of the values of $\log q$ on those of $\mu_{p,01}$ yielded $d = 1.2 \pm 0.2$ for both ethyl and propyl derivatives.

TABLE III

VALUES OF p_i AND q_j DERIVED FROM THE DATA IN TABLE I

Stationary phase	p_i	Solute	q_j
C ₁₆ H ₃₂	0.051	Diethyl ether	0.374
C ₁₆ H ₃₃ Cl	0.235	Ethyl acetate	0.857
C ₁₆ H ₃₃ Br	0.245	Methyl ethyl ketone	1.104
C ₁₆ H ₃₃ N	0.505	Ethyl bromide	0.624
C ₁₂ H ₂₅ N:		Ethyl iodide	0.596
100%	0.593	Nitroethane	1.719
48.4%	0.396	Ethyl cyanide	1.685
28.6%	0.286		
14.0%	0.190		

** Factor analysis also yields the values of r_i, s_j, \dots in the more general equation

$$x_{i,j} = p_i q_j + r_i s_j + \dots \quad (6)$$

However, eqn. 5 gives a good description of the experimental data. Further terms, added to its right-hand side, account only for experimental error, but do not describe any genuine physical effect, as there is no correlation between the values of r_i (or s_j) derived from the data in Tables I and II.

TABLE IV

VALUES OF p_i AND q_j DERIVED FROM THE DATA IN TABLE II

Stationary phase	p_i	Solute	q_j
$C_{16}H_{32}$	0.064	Dipropyl ether	0.309
$C_{16}H_{33}Cl$	0.260	Propyl acetate	0.893
$C_{16}H_{33}Br$	0.275	Propionaldehyde	0.992
$C_{16}H_{33}N$	0.533	Propyl chloride	0.566
$C_{12}H_{25}N$:		Propyl bromide	0.550
100%	0.572	Nitropropane	1.669
48.4%	0.382	Propyl cyanide	1.674
28.6%	0.282		
14.0%	0.182		

In Fig. 1, the ratio of p for squalane-lauronitrile mixtures to p for lauronitrile is plotted as a function of w_B for ethyl and propyl derivatives. This ratio is equal to the ratio of the corresponding $g(w_B)$ values. It follows that the ratio of $g(w_B)$ values is identical for ethyl and propyl derivatives, *i.e.*, it is independent of the solute.

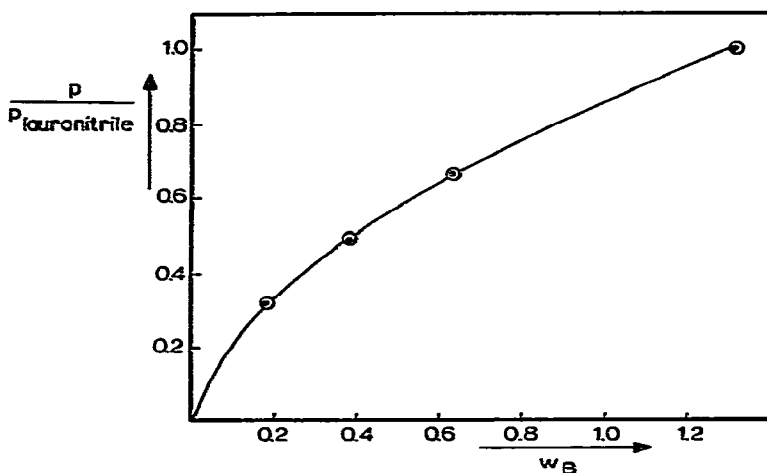


Fig. 1. Influence of solvent composition on dipolar interactions in squalane-lauronitrile mixtures. ●, Ethyl derivatives; ○, propyl derivatives.

To investigate whether the ratio of $g(w_B)$ values depends on the properties of the polar and the apolar component of the solvents, values of $V_{\text{methyl ethyl ketone}} / V_{\text{isopentane}}$ and of $V_{\text{propionaldehyde}} / V_{\text{butane}}$ were determined for mixtures of *n*-hexadecane with *n*-hexadecyl cyanide and with *n*-hexadecyl bromide at 62.6°. From these data, values of r_b for methyl ethyl ketone and propionaldehyde, and values of $g(w_B)/g(w_B = 1)$ can be calculated by means of eqn. 3. The results are given in Tables V and VI and in Fig. 2.

Comparison of the data in the fourth columns of Tables V and VI shows once again that $g(w_B)/g(w_B = 1)$ does not depend on the investigated solute.

TABLE V

RETENTION DATA ON THE SOLUTES METHYL ETHYL KETONE AND ISOPENTANE FOR STATIONARY PHASES CONSISTING OF MIXTURES OF *n*-HEXADECANE WITH *n*-HEXADECYL BROMIDE AND *n*-HEXADECYL CYANIDE AT 62.6°

Stationary phase	$V_{\text{methyl ethyl ketone}}$	r_b	$g(w_b)$
	$V_{\text{isopentane}}$		$g(w_b = 1)$
$C_{16}H_{34}$	1.64		
$C_{16}H_{33}Br$:			
10%	1.71	1.04	0.05
25%	1.93	1.18	0.25
50%	2.38	1.45	0.56
75%	2.76	1.68	0.78
100%	3.20	1.95	1
$C_{17}H_{33}N$:			
10%	2.07	1.26	0.17
25%	2.65	1.62	0.36
50%	3.75	2.28	0.62
75%	4.81	2.93	0.81
100%	5.91	3.60	0.96
Extrapolated, $w_B = 1$		3.80	1

TABLE VI

RETENTION DATA ON THE SOLUTES PROPIONALDEHYDE AND BUTANE FOR STATIONARY PHASES CONSISTING OF MIXTURES OF *n*-HEXADECANE WITH *n*-HEXADECYL BROMIDE AND *n*-HEXADECYL CYANIDE AT 62.6°

Stationary phase	$V_{\text{propionaldehyde}}$	r_b	$g(w_B)$
	V_{butane}		$g(w_B = 1)$
$C_{16}H_{34}$	1.34		
$C_{16}H_{33}Br$:			
10%	1.38	1.03	0.05
25%	1.53	1.14	0.21
50%	1.90	1.42	0.57
75%	2.15	1.61	0.77
100%	2.49	1.86	1
$C_{17}H_{33}N$:			
10%	1.66	1.24	0.17
25%	2.09	1.56	0.35
50%	2.90	2.16	0.62
75%	3.67	2.74	0.81
100%	4.47	3.33	0.97
Extrapolated, $w_B = 1$		3.47	1

Comparison of the data for $g(w_B)/g(w_B = 1)$ for *n*-hexadecane-*n*-hexadecyl cyanide mixtures and for squalane-lauronitrile* mixtures, plotted in Fig. 2, shows that it is immaterial whether the apolar component of the solvent mixture is a straight-

* These data were calculated from the $\log r_b$ values for methyl ethyl ketone in the fourth column of Table I and the r_b value at $w_B = 1$ in the third column of Table V.

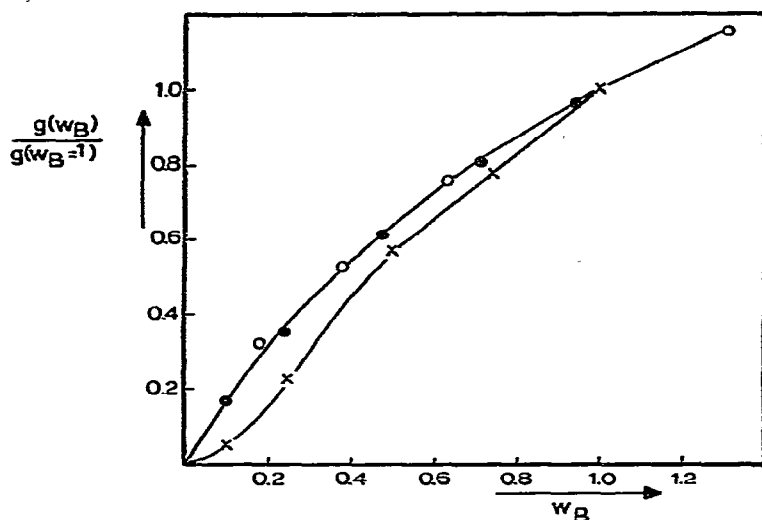


Fig. 2. Influence of solvent composition on dipolar interactions. The effect of changing the type of polar or apolar solvent component is shown. O, Squalane-lauronitrile mixtures; ●, *n*-hexadecane-*n*-hexadecyl cyanide mixtures; X, *n*-hexadecane-*n*-hexadecyl bromide mixtures.

or a branched-chain alkane. However, comparison of the data for $g(w_B)/g(w_B = 1)$ for *n*-hexadecane-*n*-hexadecyl cyanide mixtures and for *n*-hexadecane-*n*-hexadecyl bromide mixtures, either in the fourth columns of Table V or VI, or in Fig. 2, shows that the functional group of the polar component of the solvent mixture has a large influence.

It follows that the influence of the solvent composition on $\log r_b$ (and on F) must be assessed separately for each polar solvent component. It is best estimated graphically, from graphs such as those in Fig. 2.

The value of c was estimated by the following procedure. p , proportional to $g(w_B)\mu_B^c$, was approximated by

$$p = (t + uw_B) \mu_B^c \quad (7)$$

where t and u are constants. Starting with $c = 1$, t and u were estimated by regression analysis of the data for p/μ_B^c for squalane-lauronitrile mixtures from Tables III and IV, on the values of w_B . Using these estimates of t and u , c was estimated by regression analysis of the data for $\log [p/(t + u)]$ for *n*-hexadecane, *n*-hexadecyl chloride, *n*-hexadecyl bromide and palmitonitrile from Tables III and IV on the values of $\log \mu_B$. This procedure was repeated until the values of c , t and u converged. The results were $c = 1.09 \pm 0.05$ for ethyl derivatives and $c = 0.97 \pm 0.05$ for propyl derivatives.

In pure C_{16} compounds as solvents, it holds that

$$r_b = \exp(v\mu_B^c \mu_{\text{pol}}^d) \quad (8)$$

where $v = t + u$. For ethyl derivatives $v = 0.040 \pm 0.004$ and for propyl derivatives $v = 0.04 \pm 0.01$. There is little, if any, difference between the results for ethyl and propyl derivatives. In further calculations we used the values $v = 0.04$, $c = 1.03$ and $d = 1.2$ for all substances.

TABLE VIII
 VALUES OF $K_A^A, f_{AB}/f_{AB}$ FOR 2-SUBSTITUTED DERIVATIVES OF ETHYLAMINE AT 62.6° AND OF PROPYLAMINE, PROPYL
 MERCAPTAN AND BUTYNE AT 40°, 60° AND 80° (CALCULATED FROM THE DATA IN TABLE VII BY EQN. 1)

Stationary phase	Substituted amines				Propylamine			Propyl mercaptan			Butyne			
	-H	-CH ₃	-C ₂ H ₅	=CH ₂	-OCH ₃	40°	60°	80°	40°	60°	80°	40°	60°	80°
C₁₆H₃₃Br:														
10%	-*	-*	-*	-*	-*									
25%	-**	-**	-**	-*	-*									
50%	0.13	0.13	0.16	0.10	0.06									
75%	0.22	0.21	0.17	0.22	0.14									
100%	0.29	0.24	0.29	0.23	0.25	0.61	0.46	0.34	0.06	0.05	0.05	0.06	0.06	0.05
C₁₇H₃₃N:														
10%	0.1	0.2	0.3	0.3	0.1									
25%	0.62	0.57	0.57	0.40	0.40									
50%	0.60	0.56	0.58	0.49	0.46									
75%	0.61	0.49	0.60	0.53	0.45									
100%	0.67	0.48	0.62	0.52	0.49									

* Negative value.

** Zero value.

EXPERIMENTAL

All chemicals were obtained from Fluka (Buchs, Switzerland). A Becker gas chromatograph equipped with a katharometer detector and stainless-steel columns (2 m \times 4 mm I.D.) were used.

The same procedure as described earlier¹ was followed.

RESULTS AND DISCUSSION

The results are given in Tables V–VIII.

The positive entries in the last six columns of Table VIII are an indication that propyl mercaptan and butyne may form very weak complexes with *n*-hexadecyl bromide.

The association of propylamine with *n*-hexadecyl bromide decreases with increasing temperature, as expected. The precision of these data was estimated earlier¹ to be about 5%. The accuracy is not as good, however: when dimethyl ether is used as the reference solute, $Kf_A f_B / f_{AB} = 0.46$ at 60°; when propyl chloride is used, $Kf_A f_B / f_{AB} = 0.24$ at 62.6°.

It is remarkable that the values of $Kf_A f_B / f_{AB}$ for the association of the substituted amines with *n*-hexadecyl bromide are strongly dependent on the solvent composition. On extrapolation to *n*-hexadecane as the solvent, the association constants are found to be about zero. Probably, the association of amines with *n*-hexadecyl bromide is too weak to be assessed quantitatively by gas chromatography.

Association constants for hydrogen bonding of substituted amines with *n*-hexadecyl cyanide were determined by linear regression analysis using the values of W_B^2 as statistical weights. The results are given in Table IX. The standard deviation of the association constants is about 6% in the solvent *n*-hexadecane, and 4% in the solvent *n*-hexadecyl cyanide.

TABLE IX

ASSOCIATION CONSTANTS OF 2-SUBSTITUTED DERIVATIVES OF ETHYLAMINE FOR HYDROGEN BONDING WITH *n*-HEXADECYL CYANIDE AT 62.6° (MOLAR FRACTION SCALE)

Substituent	Solvent	
	$C_{16}H_{34}$	$C_{17}H_{33}N$
–H	0.50	0.67
–CH ₃	0.60	0.48
–C ₂ H ₅	0.54	0.62
=CH ₂	0.49	0.52
–OCH ₃	0.40	0.49

Previously it was found¹, for hydrogen bonding of substituted alcohols with *n*-hexadecyl derivatives, that the 2-methoxy substituent causes a large decrease in the association constant. This was attributed to competition between intermolecular hydrogen bonding of the alcoholic hydroxyl group with the *n*-hexadecyl derivative and intramolecular hydrogen bonding with the 2-methoxy substituent. Inspection of

Table IX shows that the association constant of 2-methoxyethylamine is not particularly small. Apparently, little or no intramolecular hydrogen bonding occurs with this molecule, in contrast to the situation with its alcoholic counterpart.

CONCLUSIONS

Indications have been found that mercaptans and alkynes form very weak hydrogen bonds with *n*-hexadecyl bromide. The association constants found are of the order of 0.05 at 60° (molar fraction scale).

Amines form hydrogen bonds with *n*-hexadecyl bromide. The calculated association constants depend on the reference solute that is used to correct for dipolar interactions between the amine and *n*-hexadecyl bromide, and they also depend strongly on solvent composition. The association is too weak to be assessed quantitatively by GC.

Association constants for hydrogen bonding of amines with *n*-hexadecyl cyanide can be assessed by GC with a precision of about 5%.

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