# 371. *Viscosity and Molecular Association. Part V.* The Association Model, and Hydrogen-bond Enthalpies.*

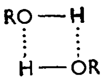
By Leo H. Thomas.

The degree of association of an alcohol or phenol in the pure liquid tends to a finite (non-integral) limiting value at sufficiently low temperature, owing to the formation of an equilibrium mixture of ring polymers. This conclusion (as well as the previously established correlation of degrees of association and molecular structure) is explained largely on the basis of entropy changes accompanying association.

The values derived for the hydrogen-bond enthalpies of the alcohols studied are believed not to depend on the molecular structure of the monomer, but only on the size of the polymer, higher polymers being somewhat more favoured energetically than the dimer.

Association in alcohols is usually regarded as a stepwise process, *i.e.*, $A_1 + A_n = A_{n+1}$. On the assumption that we are dealing with "chain" complexes, each step in the progressive association will be associated with an approximately constant enthalpy change. Successive equilibrium constants therefore will always be temperature dependent, and the degree of association ($\gamma$) will tend to an infinitely high value at sufficiently low temperature.

The author's studies on the other hand lead to the conclusion that in the pure liquid at least, the straight-chain alcohols and also the lower branched-chain alcohols attain constant finite values of the degree of association ($\gamma$) at room temperature, and that other alcohols probably do so at lower temperatures. To explain this, it is assumed that the complexes exist essentially in the form of ring polymers (the concentration of chain polymers being relatively small), *e.g.*, (I) for the dimer, each $A_n$ molecule now having $n$ hydrogen bonds. Therefore, once association has progressed to the point when the concentration of the monomer is negligible and all species exist essentially as ring polymers, further polymerisation can proceed only by passage of smaller rings into larger ones. Subsequent enthalpy changes will therefore be small or even eventually zero. Increasing association, however, would still cause a relatively large decrease in entropy so that $d\gamma/dT$ is still further decreased. Association could therefore proceed to a point where further drop in temperature could (by further increase in orderliness) cause a decrease in entropy large enough, in spite of the


(I)

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* Part IV, preceding paper.

lower temperature, effectively to oppose the (now small) enthalpy change. The free energy ($H - ST$) will then have attained a minimum possible value, and there will virtually be no further increase in $\gamma$.

There is, in fact, evidence from infrared spectroscopic,[1,2] proton magnetic resonance,[3] and matrix isolation[4] studies that the great majority at least of the polymers are in the form of ring polymers. The last method in particular enabled an estimate to be made of the relative strengths of the hydrogen bonding in the several polymeric species; thus the bands in the dimer were weaker than those in the trimer which in turn were weaker than those in higher polymers (in which the bond strength is sensibly constant). This was attributed to formation of ring-polymers, the $O-H \cdots O$ bonds in the lower polymers being markedly non-linear. The formation of a ring polymer is preferred in spite of this nonlinearity because each $A_n$ molecule will have $n$ hydrogen bonds; only $(n - 1)$ such bonds will be present in a chain $A_n$ polymer.

*The Association Model.*—Owing to the comparative smallness of the heat of formation of hydrogen bonds, the enthalpy change characteristic of the conversion of monomer into polymer is relatively small. The entropy change accompanying the formation of a complex is, on the other hand, large because of the decrease in the number of independent units in the system. Entropy considerations will therefore play a major role in determining the position of equilibrium, particularly at low temperature for then the enthalpy change will be very small. Thus entropy requirements will largely dictate the value of $\gamma_{\text{ult}}$.

In addition to the conclusion that $\gamma$ tends to a finite limiting value at sufficiently low temperature, there are two other features of the author's conclusions which require some comment:

(1) Association is a minimum ($\gamma \sim 2$) for straight-chain alcohols, and a maximum when the molecule shows nearest approach to spherical shape about the hydroxyl group. The various relevant factors are (*a*) London interaction forces, (*b*) dipole–dipole interaction between the polar hydroxyl groups, and (*c*) increase in association which necessarily decreases the configurational entropy, and might also restrict the rotational and vibrational freedom.

Straight-chain molecules (quite apart from hydrogen bonding) have a higher internal order at a given vapour pressure than have more spherically shaped isomers, owing to the packing of the molecules with their long axes parallel (close-packing of cylinders[5,6])—an arrangement permitting maximum London interaction. The entropy although low is kept within reasonable limits by an arrangement which allows of disorderly overlap of the chain ends;[7] furthermore there is free rotation of the molecules about their long axes.[5] The formation of alcohol dimers does not involve serious modification of such a structure, although of course the reduction in the number of independent units in the system will lower the entropy, this being generally true irrespective of the nature of the alcohol molecule. Thus the hydroxyl groups of two adjacent molecules can interact *in situ* to form a double-length rod-shaped molecule still capable of free rotation now about a common long axis (II), and still allowing maximum London interaction with neighbouring molecules of the same type. Formation of cyclic higher polymers (III) on the other hand would effectively prevent free rotation, and would not permit the efficient molecular alignment demanded by London forces. For straight-chain alcohols therefore, a barrier to the formation of much polymer of $n > 2$ is readily visualised.

The molecules of those alcohols shown to have the highest degrees of association ($CMe_3{\cdot}OH$, $Et{\cdot}CMe_2{\cdot}OH$, $Pr^i{\cdot}CMe_2{\cdot}OH$) are approximately spherical with the hydroxyl group lying near to the periphery. It is clear that the dispersion energy of two such

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[1] Kuhn, *J. Amer. Chem. Soc.*, 1952, **74**, 2492.

[2] Pimentel and McClellan, " The Hydrogen Bond," Freeman and Co., 1960, p. 96.

[3] Becker, Liddel, and Shoolery, *J. Mol. Spectroscopy*, 1958, **2**, 1.

[4] Van Thiel, Becker, and Pimentel, *J. Chem. Phys.*, 1957, **27**, 486.

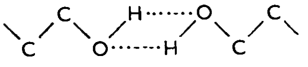
[5] Thomas, *J.*, 1959, 2132.

[6] Moore, Gibbs, and Eyring, *J. Phys. Chem.*, 1953, **57**, 173.

[7] Hildebrand, *J. Amer. Chem. Soc.*, 1937, **59**, 794.

molecules at a given separation will not be very dependent on the direction of alignment (in relation to the C–O bond) of the one molecule relative to the other. The molecules may therefore be rotated *in situ* so as to allow multiple hydroxyl–hydroxyl interaction without serious curtailment in the London interaction, and dimers, trimers, and higher complexes will successively form until the decreasing enthalpy changes are balanced by the decrease in entropy.

The lower association of other branched-chain alcohols (*e.g.*, the drop in $\gamma$ which occurs in the sequence $CMe_3 \cdot OH \longrightarrow Et \cdot CMe_2 \cdot OH \longrightarrow Pr^n \cdot CMe_2 \cdot OH$, etc.) is therefore due to the lengthening long axes and consequent increasing magnitude of the drop in London interaction caused by formation of polymers of $\gamma > 2$.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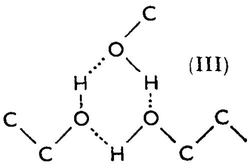
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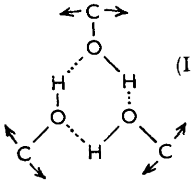
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Another factor may favour formation of higher polymers from spherically-shaped molecules—the angle between the C–O bonds of adjacent units of the complex may be more variable, and high-amplitude rocking (IV) might occur both in and out of the plane of the ring, thereby reducing the orderliness. Such freedom could not be so readily achieved in the bundles of close-packed straight-chain molecules.

(2) The degree of association tends to a non-integral finite value. Such a conclusion can be formally accounted for on the basis either of a finite number of simultaneous equilibria between monomer and different polymers, *i.e.*, $2A_1 \rightleftharpoons A_2$, $3A_1 \rightleftharpoons A_3$, etc., or by the physically equivalent, stepwise process $A_n + A_1 \rightleftharpoons A_{n+1}$. However this does not explain why such a pattern should occur.

In discussing the various factors determining $\gamma_{ult}$ we confined our attention to decreases in entropy occurring through reduction in the number of independent units in the system and through restriction of rotational and vibrational freedom within the complexes. These factors would operate so that the free energy would be least when $\gamma_{ult}$ has a certain integral value, say $n$, depending on the nature of the molecule. It is also clear that the free energies of polymers $A_{n+1}$ and $A_{n-1}$ will be only a little higher.

Another aspect to be considered, however, is how the complexes will pack together in the quasicrystalline liquid state. A liquid consisting entirely of $n$-mer would be expected to form a matrix with a fair degree of order. The presence of a certain amount of $(n - 1)$-mer and $(n + 1)$-mer, however, would give a mixture of molecules of different shape and size and a régime of intrinsically higher disorder [clearly, smaller concentrations of $(n - 2)$-mer and $(n + 2)$-mer and even of chain complexes could also be accommodated in this way]. The free energy is thus less in the latter case, and the average degree of association will no longer (except by chance) be integral; whether it will be $>n$ or $<n$ will of course depend on the relative amounts of $(n - 1)$-mer and $(n + 1)$-mer.

It is concluded therefore that the lowest free energy is attained through conversion of monomer largely into a single ring polymer, but also to a certain but smaller extent into lower and higher polymers. For ethanol, heptan-1-ol, and octan-1-ol, all of $\gamma_{ult} \sim 1 \cdot 9$, this conclusion must imply that the state of minimum free energy is attained through participation of a certain amount of monomer. Methanol is anomalous in having a degree of association much less (1·47) than 2 and it is difficult to see how it fits into the suggested model. On the other hand, its low $\gamma$ value is consistent with the fact that the neighbourhood of its hydroxyl group is particularly open.

*Thermodynamic Evidence.*—Consider a progressive association through the simultaneous equilibria $2A_1 \rightleftharpoons A_2$ and $3A_1 \rightleftharpoons A_3$. Then starting from $N_A$ molecules of monomer in a volume $V$, we have at equilibrium:

$$N_A = N_1 + 2N_2 + 3N_3 = N_1 + 2K_1N_1^2 + 3K_2N_1^3 \qquad (1)$$

and

$$\gamma = N_A/(N_1 + K_1N_1^2 + K_2N_1^3) \qquad (2)$$

where $N_1$, $N_2$, etc., are the numbers of molecules of monomer, dimer, etc., remaining, and $K_1$ and $K_2$ are related to the equilibrium constants $\theta_1$ and $\theta_2$ through $K_1 = \theta_1/V$ and $K_2 = \theta_2/V^2$.

Exact solution of eqns. (1) and (2) is unfortunately not possible.

| $N_2$ | $N_3$ | $N_1$ | $\gamma$ | $N_3/N_2$ | $\gamma'$ | $N_1'$ | $N_{2\cdot74}$ |
|---|---|---|---|---|---|---|---|
| 6·0 | 14·70 | 43·90 | 1·548 | 2·71 | 1·569 | 43·28 | 20·47 |
| 7·0 | 18·52 | 30·44 | 1·787 | 2·73 | 1·803 | 30·08 | 25·39 |
| 7·3 | 19·72 | 26·24 | 1·878 | ,, | 1·891 | 25·96 | 26·93 |
| 8·0 | 22·64 | 16·08 | 2·140 | ,, | 2·143 | 16·03 | 30·63 |
| 8·4 | 24·34 | 10·18 | 2·230 | 2·74 | 2·322 | 10·29 | 32·78 |
| 8·8 | 26·11 | 4·07 | 2·566 | 2·75 | 2·542 | 4·34 | 35·00 |
| 9·05 | 27·22 | 0·24 | 2·739 | | | | |
| | | 0 | 2·750 | | | | |

Assuming that the hydrogen-bond enthalpies ($h$) are the same for both equilibria, and that the value does not vary with temperature, we obtain $\log_e \theta_1 = I_1 - (2h/\mathbf{R}T)$, and $\log_e \theta_2 = I_2 - (3h/\mathbf{R}T)$, where $I_1$ and $I_2$ are constants from which it follows that $\theta_1^3/\theta_2^2 = \exp(3I_2 - 2I_1) =$ a constant ($\alpha$) independent of temperature. But $\theta_1^3/\theta_2^2 = N_2^3/N_3^2V^3$, so that $N_2^3/N_3^2 = \alpha V^3$. On the assumption that the variation in volume can be neglected, the ratio $N_2^{3/2}/N_3$ is then independent of temperature.

Putting $N = 100$ for arithmetic convenience, we may now (from eqns. 1 and 2) calculate the relative quantities of the three molecular species at different values of $\gamma$. These are tabulated. The choice of $\alpha V^3 = 1$ leads to a non-integral ultimate degree of association of 2·750. (Clearly the larger the value of $\alpha$, the closer will the ultimate degree of association approach 3, but concomitantly, the higher will be the ratio $N_3/N_2$ at all values of $\gamma$, and the closer will the process approach a simple monomer–trimer equilibrium.)

In order that these $\gamma$ values can be reproduced by a formal equilibrium of type $mA_1 \rightleftharpoons A_m$, $m$ having a nonintegral value, it is clear that $(2N_2 + 3N_3)$ must equal $mN_m$, and also $(N_2 + N_3) = N_m$, *i.e.*, $(2N_2 + 3N_3)/(N_2 + N_3)$ must equal $m$ or $N_3/N_2 = (2 - m)/(m - 3)$. Such a condition of course cannot in fact hold exactly over a finite temperature range, since the ratio $N_3/N_2$ $(=N_2^{1/2})$ must increase with drop in temperature. Nevertheless, the function is so insensitive that it changes very little (column 5) over the large range in $\gamma$ considered, the average value being $m = 2{\cdot}74$. Subtracting $2{\cdot}74\,(N_2 + N_3)$ from $N_A$ gives a " false " residual monomer concentration ($N_1'$) and a " false " degree of association ($\gamma'$) given by $100/\gamma' = N_1' + (2N_2 + 3N_3)/2{\cdot}74$. Actually $\gamma'$ differs from $\gamma$ by a mean figure of 0·7%—an amount within the uncertainties of my method of determining degrees of association.

Applying the reaction isochore to the equilibrium $2A_1 \rightleftharpoons A_2$ over an arbitrary temperature range from $T_1$ to $T_2$, the corresponding values of monomer concentration being ${}_1N_1$ and ${}_2N_1$, respectively, etc., we have

$$\log\left[\frac{{}_1N_2}{{}_1N_1^{\,2}}\middle|\frac{{}_2N_2}{{}_2N_1^{\,2}}\right] = 2h(1/T_2 - 1/T_1),$$

where $h$ is the " true " value of the hydrogen-bond enthalpy (the complexes being considered as cyclic polymers).

Similarly for the " one-equation " equilibrium over the same temperature range, we get

$$\log\left[\frac{{}_1N_{2\cdot74}}{({}_1N'_1)^{2\cdot74}}\middle|\frac{{}_2N_{2\cdot74}}{({}_2N')^{2\cdot74}}\right] = 2{\cdot}74h'\left[\frac{1}{T_2} - \frac{1}{T_1}\right],$$

where $h'$ is a " false " value of the hydrogen-bond enthalpy. Therefore

$$2h/2{\cdot}74h' = \log\left[\frac{{}_1N_2}{{}_1N^2{}_1}\middle|\frac{{}_2N_2}{{}_2N^2{}_1}\right] \Big/ \log\left[\frac{{}_1N_{2\cdot74}}{({}_1N'{}_1)^{2\cdot74}}\middle|\frac{{}_2N_{2\cdot74}}{({}_2N'{}_1)^{2\cdot74}}\right]$$

Application of this equation to the tabulated values of the variables concerned and within the range $\gamma = 1{\cdot}548$—$2{\cdot}566$ gives a value of $h'$ 1·5% lower than the " true " value, $h$, a figure again within the limits of my method of estimating hydrogen-bond enthalpies.

Similar treatment for the equilibria $3A_1 \rightleftharpoons A_3$ and $4A_1 \rightleftharpoons A_4$ with $N_4/N_3{}^{4/3}$ taken as unity, gives an ultimate degree of association of 3·53. For these equilibria, the equation $3{\cdot}51A_1 \rightleftharpoons A_{3\cdot51}$ reproduces the $\gamma$ results from $\gamma = 1{\cdot}6$ to $\gamma = 3{\cdot}4$ with a mean deviation of 0·7%; $h'$ is 2·3% lower than the " true " value.

The agreement for the equilibria $2A_1 \rightleftharpoons A_2$ and $4A_1 \rightleftharpoons A_4$, with $N_4 = N_2{}^2$, which gives an ultimate degree of association of 3·65 (covering approximately the same range in $\gamma$ as before), is not good. The $\gamma$ values are reproduced to within 1·2%, but $h'$ is now 6·0% lower than $h$.

We may therefore conclude that the description of the progressive association of a liquid by a single equation involving an apparent nonintegral end-polymer can be interpreted as an equilibrium between the monomer and, in the main, with $n$-mer and $(n + 1)$-mer and probably with smaller amounts of other polymers.

When the reaction isochore is applied to the process $mA_1 \longrightarrow A_m + mh$ cal. it is easy to show that [8]

$$\log_{10}\left\{\frac{V^{m-1}(1 - 1/\gamma)}{(1/\gamma - 1/m)^m}\right\} = \text{constant} - \frac{mh}{4{\cdot}571T},$$

where $h$ is now the average hydrogen-bond enthalpy in the process $mA_1 \longrightarrow A_m$, and $V$ is the total volume. By rearrangement, we get

$$\log_{10}(1/\gamma - 1/m) = \log_{10}\left\{\frac{V^{m-1}(1 - 1/\gamma)}{m}\right\} - Q + \frac{h}{4{\cdot}571T}, \tag{3}$$

where $Q$ is a constant.

Application of eqn. (3) to the author's $\gamma$ values for seven alcohols gives the following $h$ and $m$ values. It must be emphasised that $\gamma$ values extended only over the experimental ranges used and that no extrapolation is involved.

| | $m$ | $h/100$ (cal.) | | | $m$ | $h/100$ (cal.) | |
|---|---|---|---|---|---|---|---|
| Heptan-2-ol ............ | 2·5 | 25 | (21) | Butan-2-ol ............... | 4·2 | 31 | (29) |
| 4-Methylpentan-1-ol ... | 2·5 | 21 | (28) | 3-Methylbutan-2-ol ... | 4·4 | 32 | (37) |
| 2-Methylpentan-1-ol ... | 3·4 | 28 | (27) | Pentan-3-ol.............. | 5·2 | 44 | (37) |
| 3-Methylpentan-2-ol ... | 4·0 | 26 | (29) | | | | |

The author's modified $\gamma$ results lead to conclusions similar to those expressed earlier.[8] In all cases, the $\gamma$ values are reproduced by equation (3) to within the limits of error. The accuracy of the $h$ values so derived cannot be high [8] (± ~10%); it is significant however that the mean value (3·0 kcal.) agrees well with the average value (2·9 kcal.) of the hydrogen-bond enthalpies derived directly from viscosity–vapour pressure relationships as such (shown in parentheses). It is difficult to explain this except on the basis that the $\gamma$ values are true measures of the degrees of association. (Clearly, if the $\gamma$ values are linearly related to " true " degrees of association, equation 3 would still give the same values of $h$. On the other hand the values of $h$ derived from the viscosity–vapour pressure behaviour would then no longer agree.) Furthermore, both evaluations, as well as being mutually consistent, lead to $h$ values which agree well with other estimates (see below).

[8] Thomas, *J.*, 1948, 1349.

*Infrared Spectroscopic Evidence.*—Stanford and Gordy[9] found that a series of eight $C_6$ alcohols in dilute solution all gave sharp monomer bands at 2·75 μ and, in the pure liquid, association bands at 2·96 μ (±0·01 μ). Dilution of a solution brings the centre of the association bands progressively nearer to 2·75 μ and it was concluded that the rate of decrease of wavelength with dilution is indicative of the ease of polymer dissociation. The rate was a maximum for hexan-3-ol and a minimum for hexan-1-ol.

It has been shown that decrease in concentration at a fixed temperature has an effect on the position of bands similar to that produced by increase in temperature at constant concentration.[10] We may therefore expect a correlation between (*a*) the rate of decrease of wavelength with dilution, and (*b*) the rate of decrease in $\gamma$ with rising temperature. In the preceding paper it was shown that a high $d\gamma/dT$ (or $d\gamma/d \log p$) appertained to those alcohols showing high values of $\gamma_{\text{ult}}$. Comparison of the difference ($\Delta\lambda$) between the wavelength of the polymer band in the pure liquid and that of the band for a 0·1M-solution with the ultimate degrees of association (Table) tends to confirm the correctness of our arguments.

| Alcohol | $\Delta\lambda$ | $\gamma_{\text{ult}}$ | Alcohol | $\Delta\lambda$ | $\gamma_{\text{ult}}$ |
|---|---|---|---|---|---|
| Hexan-1-ol | 0 * | 2·1 | 2-Methylpentan-2-ol | 0·07 | 3·2 |
| 3-Methylpentan-1-ol | 0 * | 2·6 | 2-Ethylbutan-1-ol | 0·07 | 3·5 |
| 2-Methylpentan-1-ol | 0·02 | 3·2 | 4-Methylpentan-2-ol | 0·08 | 3·8 |
| Hexan-2-ol | 0·05 | 3·2 | Hexan-3-ol | 0·09 | 4·1 |

* Mean of two maxima.

At greater dilution, the association bands for all except hexan-1-ol and 3-methylpentan-1-ol have disappeared.

Badger and Bauer's work[11] on a series of $C_5$-alcohols is at first sight at variance with our deductions regarding the relative associations of these alcohols. They found that the amount of monomer increases in the order primary, secondary, tertiary (and concluded that a steric effect inhibiting association operates in these alcohols). Their subsequent conclusion that high concentration of monomer implies a low degree of association is not, however, necessarily true, and depends on the degrees of complexity of the polymers with which the monomer is in equilibrium. Thus, on the basis of the equilibrium $m\mathrm{A}_1 \rightleftharpoons \mathrm{A}_m$, it can be shown that $N_1/N_{\mathrm{A}} = (m - \gamma)/\gamma(m - 1)$ so that for a 10% molar concentration of monomer, the degree of association will be 1·82, 2·50, 3·08, and 3·57 for $m = 2, 3, 4$, or 5, respectively. Exact comparison with Badger and Bauer's results is unfortunately not possible. It may however be instructive to quote the values of $N_1/N_{\mathrm{A}}$ for the $C_5$ alcohols calculated from $\gamma_{\text{ult}}$ values and the degrees of association at say 25°. These are 0 or very small for pentan-1-ol and 3-methylbutan-1-ol, 1·8% for 2-methylbutan-1-ol, a mean of 4·6% for the three secondary alcohols, and 4·2% for the tertiary alcohol. Badger and Bauer's observations are therefore in agreement (except possibly for the tertiary isomer) with our general thesis.

*Hydrogen-bond Enthalpies.*—The values given in Table 2, column 8, of the preceding paper are for temperatures when the respective vapour pressures are 100 mm., and are calculated on the basis of chain polymers as previously (Parts I and II). On this basis, it can be seen that the hydrogen-bond enthalpy is equal to $x\gamma/(\gamma - 1)$, where $x$ is the heat absorbed in the rupture of all hydrogen bonds per gram-formula weight (Part 3, eqn. 5[12]). We need know only the value of $\gamma$ in order to calculate the hydrogen-bond enthalpy from $x$. This is, however, not true if we are dealing with ring polymers. Thus if we have $N_1$ molecules of monomer in equilibrium with $N_2$ molecules of dimer $\mathrm{A}_2$, $N_3$ molecules $\mathrm{A}_3$ and so on to $\mathrm{N}_n$ molecules of $\mathrm{A}_n$, and writing $h_2, h_3, \cdots h_n$ for the hydrogen-bond enthalpies

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[9] Stanford and Gordy, *J. Amer. Chem. Soc.*, 1940, **62**, 1247.

[10] Liddel and Becker, *Spectrochimica Acta*, 1957, **10**, 70.

[11] Badger and Bauer, *J. Chem. Phys.*, 1937, **5**, 839.

[12] Thomas, *J.*, 1960, 4906.

for the monomer $\rightleftharpoons$ dimer, monomer $\rightleftharpoons$ trimer, etc., equilibria, we can write $x = \sum_2^n nN_nh_n/N_A$, where $N_A$ has the same significance as before. But the average value of the hydrogen-bond enthalpy is clearly given by

$$\bar{h} = \sum_2^n nN_nh_n \Big/ \sum_2^n nN_n = \sum_2^n nN_nh_n/(N_A - N_1).$$

Comparing these two expressions, we get $x = \bar{h}\{1 - (N_1/N_A)\}$, so that $\bar{h}$ cannot be evaluated unless we know the nature of the relevant equilibria. The equation $m\mathrm{A} \rightleftharpoons \mathrm{A}_m$, from which it has been shown that $N_1/N_A = (m - \gamma)/(m - 1)\gamma$, gives

$$\bar{h} = x\gamma(m - 1)/m(\gamma - 1) \tag{4}$$

Values of $\bar{h}$ so calculated are shown in Table 2, 9th column, of Part IV; for those alcohols having $\gamma_{\text{ult}} < 2$, $m$ is put at 2 for reasons already given. The overall spread is less than when the complexes are considered as chain polymers, the mean value being 2·6 kcal. There is now a direct correlation between $\gamma$ and $\bar{h}$, but probably not attributable to any difference in bonding energy between one alcohol type and another. A more likely explanation is that a highly associated alcohol has more molecules in the form of higher polymers, these being characterised by higher enthalpy (cf. ref. 3).

The average hydrogen-bond enthalpy (defined as above) for a given alcohol of $\gamma_{\text{ult}} = m$, is given by

$$m\bar{h} = nh_n(n + 1 - m) + (n + 1)h_{n+1}(m - n), \tag{5}$$

where $n$ is the nearest integral value ($<m$), and $h$ and $h_{n+1}$ are the enthalpies associated with the formation of the $n$-mer and $(n + 1)$-mer, respectively. Graphical solution of equation (5) for the data for 13 alcohols whose $\gamma_{\text{ult}}$ values fall between 2 and 3 gives $h_2 = 2{\cdot}4$ kcal. and $h_3 = 2{\cdot}7$ kcal. The former agrees satisfactorily with the mean hydrogen-bond enthalpies (2·5 kcal.) of methyl, ethyl, n-heptyl, and n-octyl alcohols whose $\gamma_{\text{ult}}$ values are $<2$ and for which we have assumed essentially a monomer $\rightleftharpoons$ dimer equilibrium. Similar treatment of the 11 alcohols whose ultimate degrees of association fall between 3 and 4 shows that within the limits of error $h_3 = h_4 = 2{\cdot}7$ kcal. The data required to evaluate $h_5$ are less extensive, but it is significant that the mean enthalpy value for those 7 alcohols of $\gamma_{\text{ult}}$ 4—5 is again 2·7 kcal. We may therefore write $h_2 = 2{,}400 \pm 100$ cal., with values of $h_3$ ($= h_4 = h_5$) some 300 cal. higher. The latter admittedly lies only just outside the probable limits of error in determination of $h$ (see below); the difference between $h_2$ and $h_3$ is, however, believed to be significant.

The mean hydrogen-bond enthalpies (in kcal.) for a number of phenols and amides have been recalculated on the basis of ring-polymer formation:

| | | | | | |
|---|---|---|---|---|---|
| Phenol | 19 | *p*-Chlorophenol | 20 | Methyl *p*-hydroxybenzoate | 31 |
| *o*-Cresol | 18 | *o*-Methoxyphenol | 15 | Acetamide | 34 |
| *m*-Cresol | 19 | *m*-Methoxyphenol | 24 | Propionamide | 28 |
| *p*-Cresol | 23 | *p*-Methoxyphenol | 28 | n-Butyramide | 23 |

These values are less accurate [12] than those for alcohols, but it is probable from these values and from those for 5-methyl-2-t-butylphenol (19) and 2,6-di-t-butylphenol (22) that the hydrogen-bond enthalpy for the formation of a phenol polymer is ~20% lower than for that of an alcohol polymer. On the other hand, the enthalpy of formation of the NH • • • O bond of amides appears to be higher than of the OH • • • O bond.

*Estimated Accuracy of Results.*—$\gamma$ at any one temperature is given [12] by $\gamma = (a/0{\cdot}220)(E/E')$, where $a$ is the experimentally derived value of the function $\mathrm{d}\log \eta\sqrt{v}/\mathrm{d}\log p$

for the liquid at that temperature, and $E - E' = x$. Uncertainty in the value of $a$ therefore arises from errors in the determination of both viscosity and vapour pressure, and amount [13] on average to $\sim\pm 4\%$ with a maximum error of $\not> 6\%$. However, $E = -\mathbf{R}\,\mathrm{d}\log_e p/\mathrm{d}(1/T)$, so that $\gamma$ can be expressed by $\gamma = (2{\cdot}303\,\mathbf{R}/0{\cdot}220E')(\mathrm{d}\log\eta\sqrt{v}/\mathrm{d}\,(1/T))$. The evaluation of $\gamma$ is therefore independent of error in vapour-pressure measurements. If it is assumed that the experimental error in the determination of viscosity equals that of vapour pressure, then the average error in $\mathrm{d}\log\eta\sqrt{v}/\mathrm{d}(1/T)$ will be 2%. To this we must add uncertainty in the evaluation [5] of $E'$ which is unlikely to exceed $\sim 1\%$. A reasonable figure for the mean error in $\gamma$ is therefore 2—3% with a maximum error of 4—5%.

From equation (4) by putting $x = E - E'$ we obtain $\bar{h} = \{\gamma(m-1)(E-E')\}/m(\gamma-1)$. Errors in $\gamma$ are therefore largely compensated for by corresponding errors in $m$, so that the principal source of uncertainty in $\bar{h}$ values is the evaluation of $E$. For those alcohols showing a linear plot [12, 13] of $\log T$ against $\log T_{\text{benzene}}$ this can be done with an error of $\sim 1\%$, which corresponds to an error in $\bar{h}$ of $\sim\pm 5\%$. Errors in $E$ of between 1 and 2% can be expected for the other alcohols, the corresponding errors in $\bar{h}$ rising to 5—10%.

*Comparison with Other Methods.*—For this comparison, all values of $h$ are evaluated on the basis of chain polymers. At present, no accepted method for the determination of degrees of association of pure liquid alcohols exists, so that independent confirmation of our results is not possible.

The two methods most extensively employed for the determination of hydrogen-bond enthalpies are (*a*) analysis of the second and higher virial coefficients in the gaseous phase and (*b*) studies of infrared intensities mostly on solutions. (Only three values are recorded for pure liquids—4·7 kcal. for methanol,[14] 6·0 kcal. for propanol,[15] and ~4 kcal.[16] for ethanol.) The second method, although generally considered to be the most reliable, carries a number of uncertainties;[2] it is not surprising therefore that the recorded values of $h$ differ widely even for a given alcohol in a given solvent.

It is possible to narrow the limits of error somewhat for methanol and ethanol. The extremes from eleven determinations on methanol are 3·2 and 9·2 kcal. but nine other values are in reasonable concord, and the most probable value is 4·8 kcal. For ethanol there are only 3 values, derived from infrared and virial-coefficients studies—3·4, 4·0, and 7·2 kcal., giving a mean value (4·9 kcal.) virtually identical with that (4·8 kcal.) for methanol. Our hydrogen-bond enthalpies for the first 8 n-alkanols are 5·4, 4·9, 4·7, 4·8, 4·5, 4·3, 4·7, and 4·8 kcal. respectively, giving a mean value of 4·8 kcal. The agreement is therefore very satisfactory.

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