Hydrogen Bonding in Alcohols

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In a recent paper I. S. Wiehe and E. B. Bagley (*1*) discussed the estimation of hydrogen bond energies in liquids. When this estimation is based on the available gaseous data, the results indicate some structure is present for the higher alcohols, and that existence of ring polymers rather than steric hindrance is responsible for observed experimental differences in the energy of hydrogen bonds.

It is possible that ring polymers predominate at low temperatures in liquids and that the hydrogen bond energy which is measured represents more than one bond. Some evidence for the existence of these cyclic bonds can be found from vapor heat capacity data and liquid studies.

VAPOR STATE CORRELATIONS

Heat capacities have been accurately measured in flow calorimeters for six alcohols. All of these data have been found to fit a heat capacity equation of $c_p - c^o_p = A(T)p + C(T)p^3$. Only the model of a mixture of monomers, dimers, and tetramers fits this equation with no additional assumptions. It is interesting that PVT data alone would not distinguish between any association model as the dimer term predominates under the conditions of low amounts of association.

Table 1 presents the vapor correlation constants for the six alcohols corresponding to a mixture of dimers and tetramers. ΔH_2 and ΔS_2 are the enthalpies and entropies of formation of dimers and ΔH_4 and ΔS_4 of tetramers. Weltner and Pitzer (*2*) in proposing the model of a mixture of monomers, dimers, and tetramers indicated that the model did not distinguish between that and an appropriate mixture of n-mers. The success of this model with all six alcohols indicates that the tetramer may indeed be a particularly stable polymer. One remarkable thing about the data is that the energies and entropies of formation for the tetramer are about the same for all of the alcohols while those of the dimer differ. In fact, in fitting the data, it is found that ΔH_4 and ΔS_4 are almost insensitive to ΔH_2. Weltner and Pitzer proposed that the tetramer was cyclic in structure with four hydrogen bonds. The cyclic structure for the tetramer and dimer is compared with an open (linear or chain) structure in Figure 1.

The existence of cyclic or open polymers puts a new variable into the models. The energy of formation/hydrogen bond would be expected to be less for a bent bond than for a straight one. Pauling (*10*) calculated that the strain energy of bending the hydrogen bond in ice was $0.003\delta^2$ kcal./mole where δ is the deviation in degrees from a straight angle at the hydrogen atom. For a straight bond energy of 6 kcal./mole, a model of a mixture of n-mers with equilibrium constants for $n > 2$ equal would predict a δ of 75° or an O—H—O angle of 105° for a cyclic dimer. The tetramer is capable of forming an O—H—O linear bond even in a cyclic structure. Unfor-

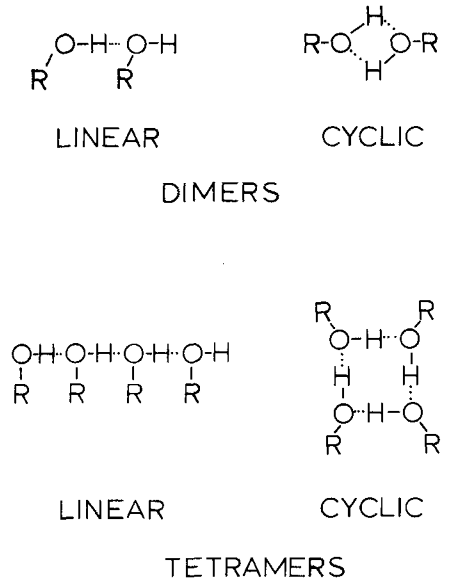

Fig. 1. Linear and cyclic hydrogen bonds.

TABLE 1. ENERGY AND ENTROPY OF FORMATION OF ASSOCIATED COMPLEXES IN VAPOR ALCOHOLS

Alcohol	$-\Delta H_2$ kcal./mole	$-\Delta S_2$ e.u.	$-\Delta H_4$ kcal./mole	$-\Delta S_4$ e.u.
Methanol (*2*)	3.22	16.5	24.2	81.3
(*3*)	4.0	11	22.1	94
Ethanol (*4*)	4.0	11	20.1	88
(*5*)	3.4	16.6	24.8	81.5
n-Propanol (*6*)	3.4	15.4	25.2	75.4
2-Propanol (*3*)	4.0	11	22.6	95
(*6*)	5.3	22.4	22.3	74.2
(*7*)	4.5	19.5	22.9	75.3
2-Butanol (*8*)	5.3	21.4	23.1	74.7
2-Methyl 2-Propanol (*9*)	4.6	19.0	25.1	82.2

tunately, this model predicts a hydrogen bond energy of 8.8 kcal./mole for cyclic dimers which is much higher than the values used to fit the data.

If both cyclic and linear dimers exist, the deviation from ideality due to dimers would consist of three terms. The third term is to account for the van der Waals forces of attraction. At low temperatures, the cyclic term would dominate in the deviations. At intermediate temperatures the linear term becomes significant, and at high temperatures the van der Waals forces dominate. This model accounts for the behavior of 2-propanol, where $\Delta H_2 = 5.3$ kcal./mole fits the data best at the lower temperatures, while $\Delta H_2 = 3.4$ kcal./mole fits best at high temperatures (*6*).

LIQUID STATE CORRELATIONS

In dilute liquid solutions, the same models give similar results for the vapor. Entropies and energies differ from the vapor results due to different temperature and concentration effects, but there is no clear cut choice between cyclic or linear structures. Dunken and Fritzsche (*11*) have recently reviewed this problem.

Thomas (*12* to *15*) in studying the viscosity of the alcohols, used a relationship between an ideal heat of vaporization and the vapor pressure curve for an alcohol. He calculated a degree of association, γ, the average value of n for n-mers. The value of γ approaches a limit for each alcohol at low temperatures.

In order to explain the ultimate constant value of γ, Thomas also concludes that the n-mers are cyclic.

ENTROPY OF VAPORIZATION

A qualitative indication of the structure in the liquid can be obtained from the entropy of vaporization (*16*). For the six alcohols, taken from the references of Table 1 and Fiock et al. (*17*), the entropy of vaporization was determined from the experimental heats of vaporization. Figure 2 shows a plot of ΔS_{vap} vs. the vapor volume. Vapor volumes were calculated from the equation of state and the parameters in Table 1. Hildebrand's rule for normal liquids states that the entropies of vaporization are equal at equal vapor volumes. For other liquids, the entropy of vaporization compared with a normal liquid is an indication of the degree of order in the liquid. Table 2 shows the difference between the entropy of vaporization of the alcohol, and the corresponding hydrocarbon at vapor volumes of 49.5 liters/mole (*18*). At these conditions, the association in the vapor is between 1 and 2% for all six alcohols. The ΔS difference indicates more order and perhaps "longer" polymers in higher molecular weight alcohols. This qualitatively agrees with Thomas.

Hildebrand and Scott (*19*) calculated with less precise data that the entropy of vaporization for methanol and ethanol were 26.5 and 27.0 e.u. at 49.5 liters/mole vapor volume. The greater difference found in the new calculations is in line with the differences found by Thomas and Meatyard and with the entropy of formations determined from dielectric constant data (*20*).

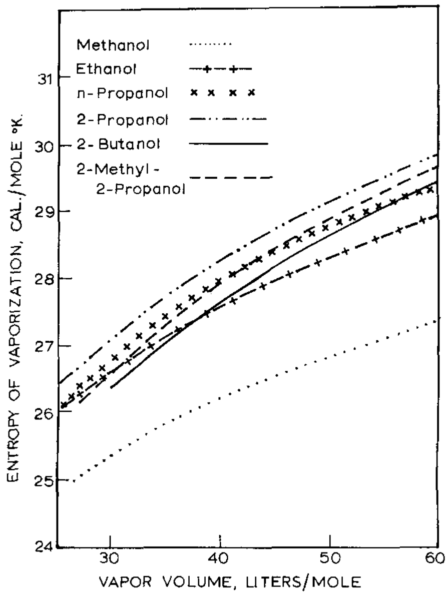

Fig. 2. Entropy of vaporization as a function of saturated vapor volume.

TABLE 2. COMPARISON OF ENTROPIES OF VAPORIZATION IN CAL./G. MOLE °K. OF VARIOUS ALCOHOLS AND HYDROCARBONS AT A SATURATED VAPOR VOLUME OF 49.5 LITERS/G. MOLE

Substance	ΔS_{vap}	ΔS_{vap} (Hydrocarbon) (18)	ΔS (difference)
Methanol (322°K.)	26.8	22.7 (Ethane)	4.1
Ethanol (337°K.)	28.2	22.6 (Propane)	5.6
n-Propanol (356°K.)	28.6	22.3 (Butane)	6.3
2-Propanol (341°K.)	29.1	22.2 (Isobutane)	6.9
2-Butanol (359°K.)	28.5	22.1 (Isopentane)	6.4
2-Methyl-2-Propanol (341°K.)	28.8	21.8 (Neopentane)	7.0

CONCLUSION

Both cyclic and linear dimers exist and higher polymers are present in cyclic form so that a limiting degree of association is reached at low temperatures. Although hydrogen bond energies are nearly the same for all the alcohols, entropy values differ between four types: methanol, other normal alcohols, secondary alcohols, and tertiary alcohols (if steric effects are neglected). At low temperatures, the normal alcohols approach a degree of association of two while secondary and tertiary alcohols associate in larger rings.

The average entropy of association in the liquid was found to be about 8 cal./mole °K. for methanol and about 10 cal./mole °K. for the other alcohols from a model similar to the gaseous model described.

NOTATIONS

c_p = heat capacity
c^o_p = heat capacity in the ideal gas state
H = enthalpy
n = number of moles of monomer and number of monomer units in the n-mer
S = entropy
T = temperature

Greek Letters

ΔH_n = enthalpy change for the formation of n-mer from monomers
ΔS = entropy difference
ΔS_{vap} = entropy of vaporization
δ = deviation in degrees from a straight angle in the structure of the hydrogen bond
γ = degree of association

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Properties of the Transient Heat Transfer (Single Blow) Temperature Response Function

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A theoretical analysis of the transient heat transfer to and from a liquid flowing through a porous medium has been provided by Anzelius (*1*), Nusselt (*2*), Hausen (*3*), and Schumann (*4*). Schumann's analytical solution of the so-called *single-blow problem* was used by Furnas (*5*), and by Saunders and Ford (*6*) to determine the heat transfer characteristics of porous media by matching experimental and theoretical temperature response curves. The value of Schumann's analytical solution of the single-blow problem is somewhat limited as it contains an infinite series of Bessel functions which makes it inconvenient to compute. Locke (*7*) observed that the number of terms of the series, which must be summed to obtain a good approximation, increases with the number of transfer units, N_{tu}. Locke's maximum slope method avoids the computation of the Schumann solution. In their work on the effectiveness of regenerators, Hausen (*8*) and Allen (*9*) have also shunned Schumann's solution and resorted to finite difference methods in solving the single-blow problem.

The purpose here is to derive a simple analytical solution of the single-blow problem which, although it is formally equivalent to the Schumann solution, is computationally much more useful. In our analysis we will use the double Laplace transform method. To exhibit the excellent convergence properties of the new representation of the solution, called *response function*, we will form two se-