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Some Observations on the Structures of Liquid Alcohols and Their Heats of Vaporization

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Abstract: From comparisons of the differences in heats of vaporization of alcohols (ROH) and their analogous hydrocarbons (RCH_3) which turned out to be 6.1 ± 0.1 kcal/mol at 298 K it was concluded that this difference represents the contribution of the hydrogen bond to the value of ΔH_{vap}(alcohol, 298 K). It is further concluded that alcohols are self associated in pure liquids in cyclic clusters each of four alcohols. These conclusions are supported by extensive, earlier studies of PVT relations in vapors, heat capacities, and IR spectra in solutions. Group additivity tables of Ducros et al. are shown to be in excellent agreement with directly measured ΔH_{vap}(298 K) for both alcohols and alkanes. Similar analysis of amines shows a much weaker H-bond with a lower limit of about 2.2 kcal/mol between amines so that amines exist mostly as monomers. Scattered data on diols of lesser accuracy suggest compact sandwich structures with the hydrocarbon tying together two cyclic tetramer rings of H-bonded oxygen atoms.

Introduction

Perhaps the strongest interaction that occurs between neutral molecules is that between Lewis acids and bases. A good example is the interaction between BH_3 and CO which leads to the formation of a complex, BH_3CO, stable at room temperature[1] but with bonds weaker than most single bonds. Hydrogen bonds, which can be placed in this category, are perhaps the weakest of these, with an energy varying from about 7.5 kcal/mol in carboxylic acid dimers[2] to about 5.5 kcal/mol in alcohols and water. All of these are markedly stronger than the typical dipole−dipole or van der Waals' interactions, which are responsible for the energies of vaporization of hydrocarbons and their functionalized derivatives. For hydrocarbons possessing very small or no dipole moments van der Waals' interactions account for all of their energies of vaporization. One consequence of this relation between van der Waals' energies and hydrogen bond energies is that in condensed phase, molecules capable of forming H-bonds will organize themselves so as to maximize the extent of H-bond formation.

In the case of ice, water molecules, which are capable of participating in 4 H-bonds per molecule, form a diamond-type lattice with each molecule sharing in 4H-bonds. The energy of each H-bond in ice is about 5.5 kcal/mol based on assigning 0.2 kcal/mol to the van der Waals' contribution of each such interaction and the remainder to the H-bonds. The melting of ice requires an energy of 1.4 kcal/mol which suggests that about 80% of its H-bonds are still intact in liquid water. In a recent paper we proposed a model to account for this behavior in which liquid water is composed of cubic octamers in equilibrium with cyclic square tetramers.[3] Small units are required in order to account for the fluidity of water and only in polycyclic structures, particularly in cubes, can H_2O share as many as 3 H-bonds per molecule. This is a large percentage of the H-bonds found in ice (4 H-bonds per molecule). This model, for the first time, accounts for the thermochemistry including the heat capacity of water from 0 to 100 °C with a maximum deviation of 2% employing no disposable parameters and using only experimental data.

Carboxylic acids form cyclic dimers and these are the predominant form in the liquid and solid state. Each molecule in the dimer participates in two H-bonds, the maximum possible for the acid CO(OH) group.

Alcohols have been known for a long time to form clusters of 2, 3, or 4 molecules, presumably cyclic or linear.[4−7] The evidence for this has come from infrared studies of dilute solutions of alcohols, from observation of vapor-phase nonideality, and from measurements of C_p (vapor) as a function of density. In recent studies of the X-ray scattering and neutron scattering data of methanol and ethanol[8,9] the authors found evidence for the existence of cyclic hexamers in the pure liquids. In a similar study of liquid *tert*-butyl alcohol[10] it was shown that the X-ray scattering data yield a radial distribution function which is nicely fitted by the structure of a hexamer and not quite as well fitted by the structure of an open chain tetramer. It is the purpose of the present work to show that the data on the heats of vaporization of the organic alcohols provide strong quantitative evidence in favor of small cyclic rings, most probably tetramers.

Heats of Vaporization of Alcohols. If we assume that liquid organic alcohols, ROH, exist in the form of small cyclic clusters, then the smallest of these which involves an unstrained H-bond is the tetramer. It would have 4 O-atoms in the form of a square

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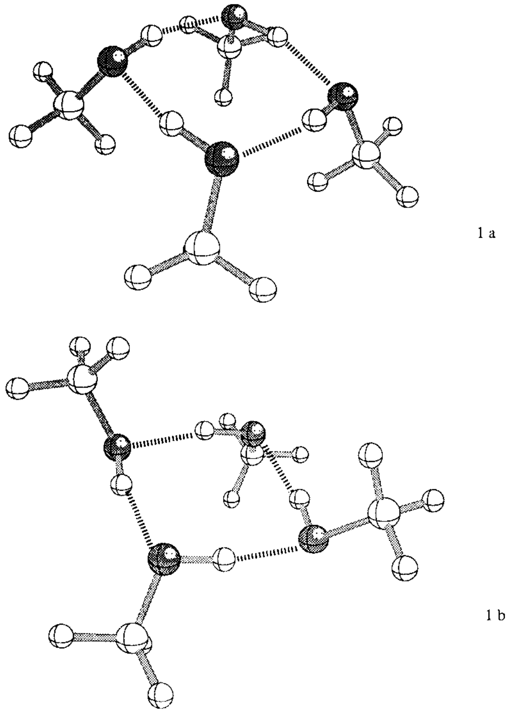

Figure 1. (a) All-cis cyclic tetramer of methanol. Black atoms are oxygen, small white atoms are hydrogen, and larger white atoms are carbon. (b) Alternate cis−trans cyclic tetramer of methanol. The structures shown were obtained by semiempirical calculation using PM3 calculations, (JJP Stewart, *J. Computer Chem.* 1989, 10, 209. Geometry was fully optimized using the program Spartan. The differences in energy between all-cis and cis−trans favored cis−trans for methanol by 0.3 kcal. These differences are so small as to be considered negligible.

Table 1. Differences in Heats of Vaporization at 298 K of *n*-Alkyl Alcohols (*n*-ROH) and their Corresponding *n*-Alkanes, *n*-RCH_3[a]

R	ΔH_{vap}(ROH)	ΔH_{vap}(RCH_3)	$\Delta(\Delta H_{vap}$ ($ROH-RCH_3$))
CH_3	8.94	1.8 (90 K)	(7.1)
C_2H_6	10.2	4.6 (231 K)	(5.6)
		4.2^b $(3.9)^c$	6.0^b $(6.3)^c$
n-C_3H_7	11.3	5.0 (272 K)	6.3 $(6.0)^b$ $(6.2)^c$
		$(5.3)^b$ $(5.1)^c$	
n-C_4H_9	12.5	6.39	6.1
n-C_5H_{11}	13.6	7.54	6.1
n-C_6H_{13}	14.82	8.74	6.1
n-C_7H_{15}	16.0	9.9	6.1
n-C_8H_{17}	17.0	11.1	5.9
n-C_9H_{19}	18.5	12.3	6.2
n-$C_{10}H_{21}$	19.6	13.5	6.1
n-$C_{11}H_{23}$	20.8^c $(19.6)^b$	14.6	6.2 $(5.0)^b$
			[(av) 6.10 ± 0.03]

[a] Values taken from ref 11. ΔH in kcal/mol. [b] Value estimated by group additivity contributions of ref 12. [c] Extrapolated using group additivity values of ref 13. In the case of undecanol, the value of 19.6 kcal/mol is clearly out of line with the extrapolation from the experimental values and tends to favor ref 13.

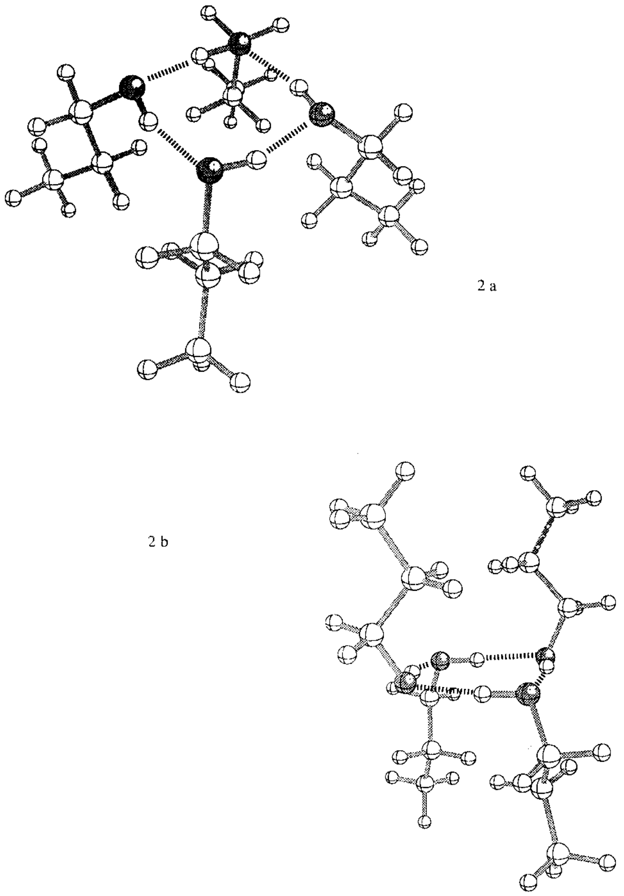

Figure 2. (a) All-cis cyclic tetramer of *n*-propanol. Atoms as indicated for Figure 1a. (b) Alternate cis−trans cyclic tetramer of *n*-propanol. The structures shown were obtained by semiempirical calculation using PM3 calculations, (JJP Stewart, *J. Computer Chem.* 1989, 10, 209. Geometry was fully optimized using the program Spartan. The differences in energy between all-cis and cis−trans favored all-cis for *n*-propanol (0.8 kcal). These differences are so small as to be considered negligible.

with H-atoms oriented about 7° above the edges of the square. With about a 2.8-Å distance between O-atoms, similar to that in ice, the H-atoms on adjacent O-atoms would be 2.1 to 2.2 Å apart, the proper van der Waals' distance to avoid repulsive strain. One would expect the organic groups to pack as closely as possible to benefit from their van der Waals' interactions. In an all-cis geometry this would place the first carbon atoms about 4.7 Å apart, again a strain-free van der Waals' distance. Alternatively, if we assume approximate tetrahedral geometry around each O-atom, we could have adjacent R groups on opposite sides of the oxygen square. The all-cis geometry is shown for a methanol tetramer in Figure 1a while the alternating cis−trans geometry is shown in Figure 1b. For methanol, such clusters would have molar volumes, assuming van der Waals' packing in a simple cubic structure, for the liquid, of about 43 cm^3/mol, close to that observed for methanol of 40.4 cm^3/mol[15] at 20 °C. Figures 2a and 2b show similar structures for *n*-propanol while Figures 3a and 3b illustrate the structures of cyclohexanol.

Most striking about such a cluster is that it would have a relatively weak dipole moment and its interactions with its neighboring clusters in the liquid would be largely van der Waals' in nature. In such case, since as we shall see the van der Waals' intermolecular contributions of O-atoms in molecules are very close to that of CH_2 groups, we might expect that the heats of vaporization of alcohols, ROH, would differ from that of the related hydrocarbon, RCH_3, by a nearly constant amount equal to the energy of one H-bond per molecule.

In Table 1 we list a number of *n*-alkyl alcohols (*n*-ROH) together with the corresponding *n*-alkanes (*n*-RCH_3) and the heats of vaporization of both at 298 K. Omitting for the moment the first three entries for which the hydrocarbons all have boiling points below 298 K we see an astonishing constancy in differences in heats of vaporization at 298 K of 6.10 ± 0.03

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Table 2. Differences in Heats of Vaporization at 298 K of Some Branched Alcohols and Their Corresponding Alkanes[a]

R	ΔH_{vap}(ROH)	ΔH_{vap}(RCH_3)	$\Delta(\Delta H_{vap}(ROH-RCH_3))$
iPr	10.9	4.6[b]	6.3 (6.1)
sec-butyl	11.9	6.0	5.9
2-methyl-*n*-propyl	12.14	6.03	6.1
tert-butyl	11.22	5.35[c]	5.87
2-pentyl	12.56 ± 0.3 (13.15)	7.14	5.4 (6.0)
3-methyl-*n*-butyl	13.15 ± 0.3 (13.31)	7.14	6.0 (6.17)
3-pentyl	12.36 ± 0.3 (13.15)	7.24	5.1 (5.91)
2-methyl-*n*-butyl	13.04 ± 0.3 (13.31)	7.24	5.8 (6.07)
neopentyl	− (12.75)	6.62	− (6.13)
2-hexyl	− (14.34)	8.34	− (6.0)
3-hexyl	− (14.34)	8.4	− (5.9)
4-methyl-2-pentyl	− (14.0)	7.86	− (6.1)
			(av) 5.8 ± 0.3 (6.02 ± 0.10)

[a] Values in parentheses obtained from group additivity (ref 13). Values taken from ref 11. ΔH in kcal/mol. [b] Boiling point 261 K. [c] Boiling point 283 K.

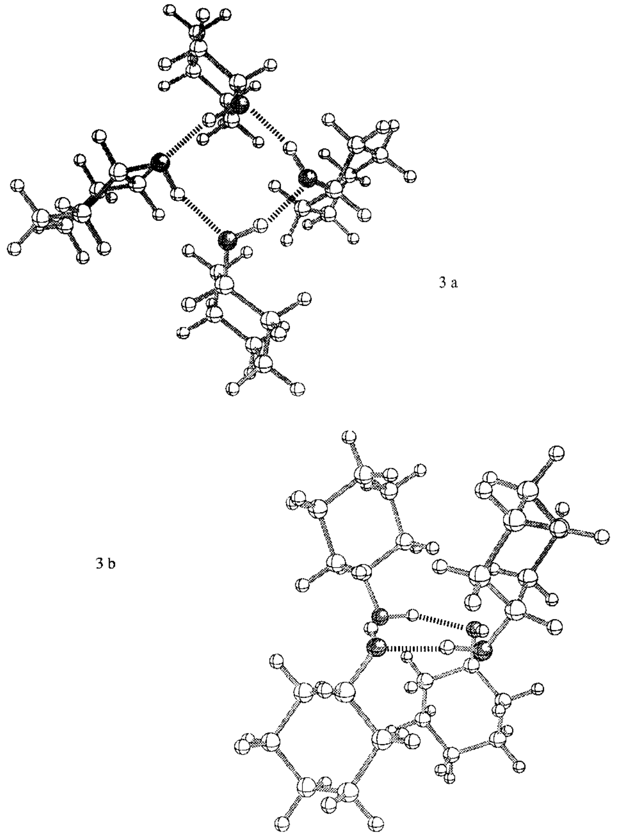

Figure 3. (a) All-cis cyclic tetramer of cyclohexanol. See Figure 1a for the identity of atoms. (b) Alternate cis−trans cyclic tetramer of cyclohexanol. The structures shown were obtained by semiempirical calculation using PM3 calculations, (JJP Stewart, *J. Computer Chem*. 1989, 10, 209. Geometry was fully optimized using the program Spartan. The differences in energy between all-cis and cis−trans favored all-cis for cyclohexanol (0.6 kcal). These differences are so small as to be considered negligible.

Table 3. Differences in Heats of Vaporization at 298 K of Some Cyclic and Some Unsaturated Alcohols (ROH) and Their Corresponding Methyl Analogues, RCH_3[a]

R	ΔH_{vap}(ROH)	ΔH_{vap} (RCH_3)	$\Delta(\Delta H_{vap}(ROH-RCH_3))$
allyl	11.3	4.92	6.4[b]
cyclopentyl	13.74	7.58	6.16
cyclohexyl	14.8	8.5	6.3
2-methylcyclohexyl	15.1 ± 0.5	9.17	5.9
benzyl	14.4[c] (16.4)	10.1	4.3[c] (6.3)
			(av) 5.8 ± 0.6 (6.2 ± 0.14)

[a] Values in parentheses estimated from group additivity (ref 13). All values from ref 11 in kcal/mol. [b] Boiling point of butene-1 is 0.5 °C. [c] This value, measured in 1926,[14] was taken at the boiling point of benzyl alcohol (204 °C) and was reported as 12.1 kcal/mol. The value listed of 14.4 kcal/mol represents an attempt to correct to 25 °C using methods not considered reliable to better than ±2 kcal/mol.[6] Note that the 14.4 value is inconsistant with the 14.8 kcal/mol of cyclohexyl alcohol and the 15.1 kcal/mol listed for 2- methylcyclohexyl alcohol. The boiling points of these last two are 161.1 and 165.6 °C, respectively. Benzyl alcohol with a much higher boiling point must have a higher ΔH_{vap}!

kcal/mol. The claimed accuracy of ΔH_{vap} for the smaller alcohols is about ±0.03 kcal/mol and that for the larger, above C_4, about ±0.15 kcal/mol.

In Table 2 we list values for branched structures. In contrast to the *n*-alkanols there is much less data available, some of it of lesser reliability (the isomeric pentyl alcohols) and surprisingly none available for the isomeric hexyl alcohols or higher alcohols. Despite this the average difference in $\Delta(\Delta H_{vap})$ of the measured values is 5.8 ± 0.3 kcal/mol, very close to that found for the *n*-alkanes. Considering the greater experimental uncertainties they can be taken as essentially the same. Of considerable interest here are the estimates made from the group additivity increments of ref 9 shown in parentheses. These show considerably less scatter and an average value of 6.02 ± 0.10 kcal/mol, again the same as that obtained for the unbranched alcohols. We would conclude that the effect of branching is negligibly small.

Table 3 lists the values of some unsaturated and cyclic alcohols. The average value of $\Delta H_{vap}(ROH-RCH_3)$ is 5.8 ± 0.6 kcal/mol, the same as that found for the branched alcohols (Table 2) but with larger scatter. If we omit or correct by Group Additivity the obviously incorrect value for benzyl alcohol, the average becomes 6.2 ± 0.4 kcal/mol, essentially the same as that found for the other alcohols.

It should be pointed out that the experimental uncertainities in ΔH_{vap} for the alcohols with six more carbon atoms is about 0.15 to 0.3 kcal/mol so that the narrow range of $\Delta(\Delta H_{vap})$ shown in Table 1 is quite astonishing. For all the examples shown which exhausts most of the data available one can take a global average of 5.9 ± 0.3 with only 2 of the 27 examples falling outside this range. Using the values corrected by group additivity would yield an average of 6.1 ± 0.1 kcal/mol.

Discussion

To assess the significance of the near constancy of $\Delta(\Delta H_{vap})$ and its absolute value let us first consider the effect of substituting a CH_2 group for an ether linkage on the heat of vaporization. In Table 4 we list boiling points, molar volumes, and heats of vaporization for a number of ethers ROR′ and their hydrocarbon analogues RCH_2R'. We note that the ethers have

Table 4. Comparison of Boiling Points, Molar Volumes, and Heats of Vaporization of Some Ethers ROR′ and Their Analogous Hydrocarbons RCH_2R'

compound	boiling point[a] (K)	Δ(bp)	V_m[a] (cm/mol)	$\Delta(V_m)$	$\Delta H°_{vap}$[b] (kcal/mol)	$\Delta(\Delta H_{vap})$
CH_3OCH_3	243	12	–	–	3.9[c]	0.1
$CH_3CH_2CH_3$	231		–		3.8[d]	
EtOEt	308	−1	104	−11	6.5	0.1
n-pentane	309		115		6.4	
$O(CH_2)_3CH_2$	340	18	81	−13	7.7	0.8
cyclopentane	322		94		6.9	
>CHOCH<	341	−13	141	−8	7.7	−0.2
>$CHCH_2CH$<	354		149		7.9	
n-Bu_2O	415	−9	169	−10	10.6	−0.5
n-nonane	424		179		11.1	
$O(CH_2)_4CH_2$	361	7	98	−10	8.3	0.4
$CH_2(CH_2)_4CH_2$	354		108		7.9	
$PhOCH_3$	428	19	109	−13	11.2	1.1
$PhCH_2CH_3$	409		122		10.1	
av		5		−10.8		0.2

[a] Data taken from ref 15. V_m taken at 293 K. Values of Δ are for [ether − hydrocarbon]. [b] Data from ref 11. [c] Estimated using group additivity (ref 13). [d] Extrapolated from measured $\Delta H°_{vap}$ at 231 K using $C_p°(\text{liq}) - C_p°(\text{gas}) = 12$ cal/(mol·K). Same value is obtained using group additivity.

uniformly lower molar volumes by 10.8 ± 1.3 cm^3/mol. The molar volume of a CH_2 group can be assigned a volume at 20 °C of 16 cm^3/mol (group additivity) hence the ether group contribution is 5.2 cm^3/mol. While a small part of this can be assigned to the shorter C−O bond (1.43 Å)[15] relative to 1.54 Å for C−C the major part must represent the contribution of the two H-atoms in CH_2.[3]

The boiling points are very close together, within 5 K on average and, most interesting, not consistantly higher for either ether or hydrocarbon. This is not reflected in the differences in ΔH_{vap} which can be positive or negative but generally small in absolute value, about 0.2 kcal/mol, though in sign following Δ(bp). We could infer that the dipole moment of the ethers of about 1.3 D[15] makes little contribution to ΔH_{vap}. For the hydrocarbons we can estimate from group additivity[13] a CH_2 contribution of about 1.2 kcal/mol to ΔH_{vap}(298 K). The ether linkage must be about the same. While alcohols have significantly higher dipole moments (1.7 D) than ethers it seems reasonable to assign about the same excess contribution to ΔH_{vap}(298 K) of the OH group as for the ether group, namely 0.2 ± 0.4 kcal/mol or possibly 0.5 kcal/mol in consideration of the higher dipole moment. The resulting value of $6.1 - 0.5 = 5.6$ kcal/mol is very close to the 5.7 kcal/mol found for the H-bond in ice.

Additional evidence on local structure in liquids comes from their viscosities. In the absence of a quantitative model of viscosity we are confined to qualitative comparisons. In Table 5 we list the coefficients of viscosity of a number of liquid alcohols at 20 °C (293 K) and at 40 °C (313 K), together with the viscosities of analogous hydrocarbons and that of a few other molecules.

If we assume that the viscous drag on a molecule in a dense fluid undergoing Newtonian flow is proportioned to the frequency of collisions then we expect bigger molecules to show a larger drag as is borne out in the growth of η with molecular size (Table 5) both in the ROH series and in the hydrocarbon series. We note also that CH_3OH if it exists as a tetramer should be comparable in viscosity coefficient to *n*-octane, which it is. Similarly C_2H_5OH should have a coefficient similar to that of dodecane, which it does. We note that water which is expected to be a mixture of cyclic tetramers and mostly cubic octamers[3] has a viscosity coefficient (1.00 cP) between that of *n*-octane (0.54 cP) and cyclooctane (2.35 cP).

Table 5. Viscosities of Some Alcohols, Hydrocarbons, and Some Other Liquids at 20 and 40 °C[a]

alcohol	η_{20}[b]	η_{40}	molecule	η_{20}	η_{40}
MeOH	0.60	0.46	*n*-pentane	0.240	–
			n-hexane	0.33	–
EtOH	1.20	0.83	*n*-heptane	0.41	0.34
n-BuOH	2.95	1.78	*n*-octane	0.54	0.43
sec-BuOH	2.88	–	*n*-dodecane	1.35	–
n-octanol	10.6	–	*n*-hexadecane	3.34	–
benzyl alcohol	5.8	–	cyclopentane	0.49	–
2-methyl phenol	20.8	–	cyclohexane	1.02	–
ethylene glycol	19.9	9.1	cyclooctane	2.35	–
			benzene	0.69	0.49
HOH	1.00	0.65	C_2H_5Br	0.40	–
acetic acid	1.26	1.00	$(CH_3CO)_2O$	0.88	–

[a] Data from refs 15 and 16. [b] All values of η in units of centipoise.

In their study of the effect of concentration on the viscosity of C_1 to C_4 alcohols dissolved in hexane or CCl_4, Bamelis et al.[17] were able to interpret their observations in terms of a reversible equilibrium of monomers with cyclic polymers. They also commented on the much higher coefficients of viscosity of ring compounds such as cyclohexane compared to the straight chain *n*-hexane. At 20 °C they are in the ratio of 3.3 to 1, an effect more likely related to cross-section than to molecular weight. In similar fashion benzene finds itself in between hexane and cyclohexane.

Thermochemistry. In one of the first studies of the thermochemistry of association in alcohols, Weltner and Pitzer[7] found that *P, V, T* measurements of methanol vapor could be interpreted in terms of an equilibrium of monomers, dimers, and cyclic tetramers. They found no evidence for trimers. For the dimer formation they found $\Delta H_{dim} = -3.22$ kcal/mol and $\Delta S_{dimers} = -16.5$ cal/(mol·K) (eu). For the tetramerization they found,

$$\Delta H_{tet} = -24.2 \text{ kcal/mol}$$

$$\Delta S_{tet} = -81.3 \text{ eu}$$

From the tetramer data we can calculate an average H-bond strength of 6 kcal/mol but only 3.2 kcal/mol in the dimer.

In a similar study on MeOH, EtOH, and iProH, Kretchmer and Wiebe[18] reported for all three:

$$\Delta H_{dim} = -4.0 \text{ kcal/mol}; \qquad \Delta S_{dim} = -23.0 \text{ eu}$$

while for tetramerization:

$$\Delta H_{tet}(\text{MeOH}) = -22.1 \text{ kcal/mol}$$

$$\Delta H_{tet}(\text{EtOH}) = -20.1 \text{ kcal/mol}$$

$$\Delta H_{tet}(\text{iPrOH}) = -22.6 \text{ kcal/mol}$$

They could not detect any trimer.

For *t*-BuOH, Beynon and McKetta,[19−21] measuring C_p vapor as a function of vapor density, reported:

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$$\Delta H_{\mathrm{dim}} = -4.6 \text{ kcal/mol}; \qquad \Delta S_{\mathrm{dim}} = -19.0 \text{ eu}$$

$$\Delta H_{\mathrm{tet}} = -25.1 \text{ kcal/mol}; \qquad \Delta S_{\mathrm{tet}} = -82.2 \text{ eu}$$

From the studies of water structures[3] it was found that for the vapor phase:

$$\Delta H_{\mathrm{tet}}(\mathrm{H_2O}) = -22 \text{ kcal/mol}$$

$$\Delta S_{\mathrm{tet}}(\mathrm{H_2O}) = -68.4 \text{ eu}$$

These values although showing some 10 to 15% spread for the various alcohols and water in the vapor phase can be taken to give strong support to the values obtained here from heats of vaporization for the H-bond in alcohols.

If we can take a mean value of -80 ± 5 eu for ΔS_{tet}, the entropy change of tetramer formation in the vapor phase:

$$4\mathrm{ROH} \rightleftharpoons (\mathrm{ROH})_4$$

it becomes 20 ± 1.3 eu per alcohol unit. To obtain the equivalent value in liquid phase we use a value of 20.5 eu for the mean entropy change of vaporization (Trouton Constant) at the boiling point for a regular liquid, and the value of -80 ± 5 eu for the gas phase tetra formation is increased by about 61 eu (3×20.5) to -19 ± 5 eu. To further correct for the difference in boiling points of monomer and tetramer[3] we subtract 2 eu. Based on 1 mol of ROH this becomes -5 ± 1.4 eu. This can now be used to estimate the concentration of monomeric ROH in liquid ROH. A further correction of about -5.5 eu to reduce values to standard states of 1 M/L instead of pure liquid gives a final value of $\Delta S_{\mathrm{tet}} = -10.5$ eu.

For the equilibrium:

$$\mathrm{ROH} \rightleftharpoons 0.25(\mathrm{ROH})_4 + 6.1 \text{ kcal}$$

the free energy change $\Delta G^\circ_{298} = \Delta H^\circ_{298} - T\Delta S^\circ_{298} = -2.9 \pm 0.4$ kcal; this gives about 0.02 mol/L or 0.3 mol % of monomer in alcohol at 298 K. It tells us that there is very little monomer in most liquid alcohols.

Because the entropy change for dimerization will be about the same per monomer unit[22] as that for tetramerization while the ΔH will be only -3 kcal/ROH, we expect that the dimer concentration will be slightly greater than the monomer concentration.

There is a rough rule of thumb that when a ring compound opens up to a linear compound there is an entropy gain of about 3.5 eu per internal rotation that is released.[21] For tetramer ring $(\mathrm{ROH})_4$ opening to a linear assembly, three such rotations are released for a gain of 10.5 eu. However, such an opening cleaves one H-bond at a cost of 6.1 kcal/mol for a net free energy change at 298 K of +3.0 kcal. The open chain would thus be about 1% of the ring tetramer in concentration. It is understandable why no evidence was found in the vapor[7,18,19] phase for the existence of trimers which would free only two internal rotations and would involve an open chain conformation to avoid badly strained H-bonds.

Perhaps the strongest argument for cyclic tetramers as opposed to linear structures is the constancy of the value of $\Delta[\Delta H_{\mathrm{vap}}(\mathrm{ROH}-\mathrm{RCH_3})]$. An open chain tetramer for example would give a value of 4.5 kcal/mol very far from the average observed value of 6.1. Similarly an open chain hexamer with only 5 H-bonds would have a value of $\Delta H_{\mathrm{vap}}(\mathrm{ROH}-\mathrm{RCH_3}) = 5.0$ kcal/mol, again very much below the observed value (Table 1).

We can draw an interesting conclusion from the observed constancy of $\Delta H_{\mathrm{vap}}(\mathrm{ROH}-\mathrm{RCH_3})$. If vaporization enthalpy obeys Group Additivity as has been shown[12,13] for both alcohols and hydrocarbons, then the experimental value of 6.1 kcal/mol can be expressed as the difference of the relevant carbon and oxygen groups. The fact that the 6.1 kcal/mol value applies both to branched and unbranched molecules tells us that the packing in the liquid state must be essentially the same for the tetrameric branched alcohols as for their monomeric hydrocarbon analogues.

A casual perusal of ΔH_{vap} of amines ($\mathrm{RNH_2}$ and $\mathrm{R_1R_2NH}$) and the relevant hydrocarbons shows that the strength of the H-bond is much less than that shown by the alcohols. From Group Additivity[13] one can obtain a lower limit on the H-bond interaction of about 2.2 kcal/mol. If the entropy changes are the same as that found for the alcohols, then ΔG° for self-association is positive suggesting that amines are less than 50% associated in the liquid state.

There is very much less data available on the heats of vaporization of diols and triols[23] and what does exist has very large errors due to neglect of association in the vapor and very inaccurate methods of extrapolation of ΔH_{vap} from the very high boiling points to room temperature. However, even these data give values between 10 and 12 kcal/mol for the differences $\Delta(\Delta H_{\mathrm{vap}})[\mathrm{R(OH)_2}-\mathrm{R(CH)_3}]$ for the diols suggesting that both OH groups are fully H-bonded. A compatible structure for ethylene glycol would be a sandwich consisting of two tetramer rings of H-bonded oxygen atoms coupled by the $\mathrm{C_2H_4}$ groups. This would acccount for the astonishingly high density of ethylene glycol (1.109 g/cm^3) compared to ethanol (0.7893 g/cm^3).[15] The molar volume of ethylene glycol of 55.9 cm^3/mol at 20 °C is actually less than that of the smaller ethyl alcohol (58.3 cm^3/mol at 20 °C).

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