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NUCLEAR MAGNETIC RESONANCE STUDIES OF HYDROGEN BONDING. II. ALCOHOLS

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ABSTRACT

The proton magnetic resonance spectra of solutions of methanol, ethanol, i-propanol, and t-butanol in carbon tetrachloride and of ethanol in benzene have been measured over the temperature range 20-60°C. The shifts δ in very dilute solutions yield values of δ_M for the monomeric alcohols. Finite values of $(\partial\delta/\partial x)$ at zero mole fraction are obtained which clearly indicate the presence of a dimeric species. The relationships between these data and the equilibrium constants and enthalpies of dimerization are discussed, but the probable presence of both cyclic and open dimers complicates the interpretation. For ethanol in benzene, where open dimers are believed to predominate, the enthalpy of dimerization is found to be 5.1 ± 1 kcal/mole of dimer.

Only qualitative comments are made concerning the results in concentrated solution where many polymeric species are present.

(End of abstract)

Many physical methods have been used to investigate association of alcohols by hydrogen bonding. A complete review of the very extensive literature is both impractical and unnecessary in view of the recent monograph by Pimentel and McClellan[3]. Although a number of nmr investigations have

(3) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond", W. H. Freeman and Co., San Francisco (1960).

concerned the alcohols, it is desirable to cover a wider temperature range in order to yield information about the various species present. The present investigation was undertaken as a systematic study of the chemical shifts at different concentrations and temperatures with the purpose of broadening the application of nmr techniques to these systems and with the aim of elucidating the nature of the various species and the characteristics of the equilibria.

Experimental

The purification and handling of the reagents have been reviewed previously[4]. All of the alcohols were distilled

(4) J. C. Davis, Jr. and K. S. Pitzer, J. Phys. Chem.

twice from calcium hydride to remove traces of water. All of the solutions were made by dilution of gravimetrically prepared stock solutions.

Shifts were measured at 60 Mcps on a Varian V4300B High Resolution NMR Spectrometer utilizing special apparatus constructed for maintaining the desired sample temperatures as previously described[4]. Shifts were measured by the side-band technique[5]. Some shifts were measured by means of

(5) J. T. Arnold and M. E. Packard, J. Chem. Phys., 19, 1608 (1951).

known fine splittings of adjacent or superimposed peaks as, for example, when the ethanol OH peak was located inside the CH_3 triplet. Shifts were measured to an accuracy of ± 0.5 cps and each reported shift is the result of at least six separate measurements.

Experimental Results. - The chemical shifts of the hydroxyl protons of methanol, ethanol, i-propanol, and t-butanol in CCl_4 and of ethanol in benzene are listed in Tables I - V. The symbol x designates the total apparent mole fraction of alcohol in the solution assuming no association. Shifts are reported in cps measured at 60 Mcps. A positive shift indicates that the hydroxyl resonance occurs at a higher applied magnetic field than that of the reference peak. In all cases the centers of the methyl group resonance were used as references. These peaks were found to be independent of concentration by measurements with both external and internal standards.

Monomer-Dimer Equilibrium. There is considerable evidence that in dilute solutions of alcohols in non-hydrogen-bonding solvents the monomer-dimer equilibrium is of importance[3]. Huggins, Pimentel, and Shoolery[6] have shown

(6) C. M. Huggins, G. C. Pimentel, and J. N. Shoolery, J. Phys. Chem., 60, 1311 (1956).

that for a system containing only monomer and dimer in equilibrium the observed chemical shift is given by the relation

$$\delta = \frac{m}{a}\,\delta_M + \frac{a - m}{a}\,\delta_D = \delta_M + \left(1 - \frac{m}{a}\right)\Delta_D \qquad (1)$$

where m is the number of moles of monomer in the solution, a is the total number of moles of alcohol used to make up the

TABLE I

CHEMICAL SHIFTS OF METHANOL IN CARBON TETRACHLORIDE SOLUTIONS

	δ (cps at 60 Mc from methyl peak)		
x	23°C	35°C	53.5°C
1.00	-92.5	-88.0	-76.1
.742	-87.5	-79.6	-66.0
.502	-74.5	-62.9	-40.1
.249	-48.0	-28.7	8.7
.099	44.8	72.0	133.7
.077	79.1	106.1	147.0
.052	115.4	135.6	158.9
.027	145.5	145.2	167.6
.020	152.8	160.4	168.0
.016	157.0	163.0	168.9
.010	163.4	166.8	170.0
.0082	165.2	167.8	170.5
.0077	165.8	168.1	170.5
.0066	166.7	168.5	170.9
.0052	168.1	169.5	171.0
.0040	169.2	170.0	171.3
δ_M	172.9	172.2	172.1
$\left(\frac{\partial\delta}{\partial x}\right)_o$	950	540	200

CHEMICAL SHIFTS OF ETHANOL IN CARBON TETRACHLORIDE SOLUTIONS

	δ (cps at 60 Mc from methyl peak)		
x	22°C	39°C	56°C
1.00	-250.0	-241.5 (37)	-228.1 (54)
.505	-219.8	-201.5	-176.0
.250	-200.3	-167.8	-134.0
.100	-169.0	-124.2	-83.1
.0775	-160.1	-118.1	-76.6
.0525	-120.0	-77.8	-36.3
.0270	-32.3	4.2	6.0
.0206	-19.0	12.1	21.0
.0165	-9.0	16.9	23.1
.0104	4.0	23.9	27.0
.0083	7.1	25.3	28.1
.0067	13.0	27.5	29.0
.0052	16.7	29.4	29.9
.0042	18.9	30.4	30.1
δ_M	28.2	34.9	32.4
$\left(\frac{\partial\delta}{\partial x}\right)_o$	2250	1070	500

TABLE III

CHEMICAL SHIFTS OF 1-PROPANOL IN CARBON TETRACHLORIDE SOLUTIONS

	δ (cps at 60 Mc from methyl peak)		
x	25°C	38°C	53.5°C
1.00	-237.6	-227.0	-211.6
.746	-235.1	-223.5	-210.0
.507	-203.9	-185.9	-161.5
.254	-166.0	-140.5	-105.6
.101	-113.8	-82.0	-37.6
.078	-95.6	-56.4	-12.2
.053	-86.2	-35.0	3.1
.027	-36.2	3.1	15.3
.021	-10.8	12.1	18.8
.017	-3.0	14.9	19.4
.011	11.8	17.6	20.2
.0084	13.0	19.0	20.8
.0078	13.7	19.0	20.9
.0067	14.2	19.2	21.0
.0053	15.0	19.7	21.1
δ_M	18	21.0	21.9
$\left(\frac{\partial\delta}{\partial x}\right)_o$	400	220	130

TABLE IV

CHEMICAL SHIFTS OF t-BUTANOL IN CARBON TETRACHLORIDE SOLUTIONS

	δ (cps at 60 Mc from methyl peak)		
x	21°C	37°C	53°C
1.00	-210.1	-190.1	-170.0
.745	-198.0	-178.3	-156.8
.505	-168.8	-143.0	-113.1
.252	-130.0	-96.1	-60.0
.100	-70.1	-27.5	-1.0
.078	-34.3	-2.0	9.2
.053	-9.0	10.2	17.3
.027	10.0	17.1	20.0
.0206	15.1	18.9	20.9
.0165	17.5	20.1	21.6
.0104	20.0	21.3	23.0
.0083	21.0	22.2	23.2
.0078	21.4	22.4	23.5
.0067	21.9	22.6	23.6
.0053	22.6	23.1	24.0
δ_M	24.8	24.5	25.0
$\left(\frac{\partial\delta}{\partial x}\right)_o$	430	270	200

TABLE V

CHEMICAL SHIFTS OF ETHANOL IN BENZENE SOLUTIONS

	δ (cps at 60 Mc from methyl peak)		
x	22°C	37°C	54°C
1.00	-250.5	-242.0	-229.5
.504	-229.0	-208.8	-185.0
.276	-201.4	-174.7	-142.2
.145	-156.7	-129.0	-90.1
.0742	-87.0	-58.2	-27.2
.0373	-4.8	8.1	16.0
.0189	9.8	18.0	20.0
.0151	15.3	21.0	24.1
.0076	23.9	25.9	26.0
.0064	24.2	26.9	28.5
.0057	25.0	27.2	28.8
.0047	26.4	28.2	29.1
δ_M	31.0	31.2	31.3
$\left(\frac{\partial \delta_M}{\partial x}\right)_o$	1020	680	440

solution, δ_M and δ_D are the shifts characteristic of the monomer and dimer species, and $\Delta_D = \delta_D - \delta_M$. If the equilibrium constant for the system is expressed in mole fraction units

$$K_2 = \frac{x_D}{x_M^2} \tag{2}$$

then it can be shown that at infinite dilution

$$\left(\frac{\partial\delta}{\partial x}\right)_{x=0} = 2K_2\Delta_D \tag{3}$$

Figure 1 shows a typical set of data in the low concentration region. It is clear that a satisfactory extrapolation can be made to yield both δ_M and the slope $(\partial\delta/\partial \underline{x})_o$. Values of these quantities are given in Tables I - V. Unfortunately the presence of higher polymers makes it impossible to obtain δ_D, and thereby $\underline{K}_2$, from the nmr data.

The assumption that the value of δ_D is independent of temperature, as it seems to be for certain carboxylic acids[4], makes possible a calculation of an apparent $\Delta\underline{H}$ dimerization. From equation (3) we see that, if Δ_D is constant

$$-\Delta H = R \frac{\partial}{\partial(1/T)} \ln \left(\frac{\partial\delta}{\partial x}\right)_o \tag{4}$$

Figure 2 shows the appropriate plot of log $(\partial\delta/\partial \underline{x})_o$ vs $1/\underline{T}$

and Table VI collects the apparent ΔH values. Liddel and Becker[7] measured the infrared spectra of methanol, ethanol,

(7) U. Liddel and E. C. Becker, Spectrochim. Acta, 10, 70 (1957).

and t-butanol in carbon tetrachloride at several temperatures. They assumed that the decrease in the intensity of the characteristic non-bonded O-H stretching band near 3630 cm^{-1} could be taken as a measure of dimerization in the dilute solutions, and from the temperature coefficient of this effect they obtained the apparent ΔH values which are also listed in Table VI. The agreement between the two sets of values is excellent. But we shall indicate later that these treatments are probably oversimplified and that the true ΔH of dimerization is somewhat smaller in some cases.

Higher Polymers.- It is clear that higher polymers are formed in even moderately concentrated solution. Saunders and Hyne[8] have treated their nmr data for several alcohols

(8) M. Saunders and J. B. Hyne, J. Chem. Phys., 29, 1319 (1958).

on the basis of only a single type of polymer in addition to the monomer. They obtained rough agreement for a cyclic tetramer with methanol and ethanol and a cyclic trimer for t-butanol. However, the evidence from various sources for the presence of some dimer is incontrovertible. We tried

extensions of the Saunders and Kyne treatment which considered the monomer, dimer, and a single higher polymer. The inclusion of the dimer changed substantially the size of polymer yielding best agreement. But no case showed agreement within experimental error nor was this result surprising in view of the simplified assumptions.

TABLE VI

DIMERIZATION OF ALCOHOLS IN SOLUTION

	Apparent[a] ΔH, kcal/mole	
	This research	L.B.[7]
CH_3OH in CCl_4	-9.4 ± 2	-9.2 ± 2.5
C_2H_5OH in CCl_4	-7.6 ± 2	-7.2 ± 1.6
C_2H_5OH in C_6H_6	-5.1 ± 1	-
i-C_3H_7OH in CCl_4	-7.3 ± 3[b]	-
t-C_4H_9OH in CCl_4	-4.4 ± 2	-4.8 ± 1.1

[a]See section on Discussion for relationship to true ΔH of dimerization.

[b]The effect of higher polymers so interferes that this value is particularly uncertain.

The dielectric constant data[9] on these systems clearly

(9) K. L. Wolf, H. Frahm and H. Harms, Z. physik. Chem., B36, 237 (1937) gives a summary of such data and reference to earlier papers and to theses.

show that much of the polymeric alcohol must be open ended chains rather than rings, and in that case it is unreasonable to assume a single dominant species. Consequently, we believe any realistic treatment of concentrated solutions must consider an extensive array of associated species such as Coburn and Grunwald[10] assumed in treating their

(10) W. C. Coburn and E. Grunwald, J. Am. Chem. Soc., 80, 1318 (1958).

infrared data on ethanol-CCl_4 solutions. Since nmr data alone do not suffice to show the various species present, a proper interpretation must combine data from additional sources. It is beyond the scope of this paper to attempt such an interpretation for the higher polymers, but the present nmr data should be useful in such a project.

Discussion

The shift between δ_M for the monomer and the δ value for fully hydrogen bonded polymer appears to be roughly 280 cps for each alcohol if we assume some dissociation in

the pure liquids and that this dissociation increases with temperature. There appears to be most dissociation in t-butanol and successively less for the smaller molecules. The reference frequency for the CH_3 protons is, of course, much lower in the case of methanol, and this increases the relative values of δ for that substance as compared to the other alcohols.

The values of δ_M show no significant change with temperature, and this result throws some additional doubt upon the large temperature change of the apparent δ_M values for certain carboxylic acids that we reported previously[4]. The very much smaller dissociation made the δ_M values of the acids much less certain than the present values for the alcohols, but the acids may associate more strongly with the solvent and hence behave differently.

There has been much discussion and speculation about the linear or cyclic nature of polymeric species of alcohols. For example, the dimer species may be either a symmetrical ring, A, with two non-linear hydrogen bonds, or an unsymmetrical open chain, B, with a single linear hydrogen bond.

A B

While there is good reason to believe that the linear hydrogen bond in B is stronger than one bent bond, it is not obvious whether one linear bond gives lower energy than the two bent bonds in A or not. The cyclic form would be expected to have no infrared absorption at the monomeric O-H frequency whereas the open dimer (B) would have one O-H vibration which would still absorb at approximately the monomer frequency. Likewise the nmr chemical shift for the non-bonded proton in the open form would be expected to be about that of the monomer while in the cyclic form both alcohol protons would have shifts affected by the hydrogen bonding. However, only the average shift is observed for the alcoholic protons of all species and there is no independent evidence for this average value in either the open or cyclic form.

In the vapor phase the entropy and enthalpy of formation[11]

(11) W. Weltner and K. S. Pitzer, J. Am. Chem. Soc., 73, 2606 (1951); C. B. Kretschmer and R. Wiebe, ibid., 76, 2579 (1954); G. M. Barrow, J. Chem. Phys., 20, 1739 (1952).

of the dimer indicate the open structure whereas at very low temperatures in inert matrices the spectral data[12] favor

(12) M. Van Thiel, E. D. Becker, and G. C. Pimentel, J. Chem. Phys., 27, 95 (1957).

cyclic structures.

There seems no doubt ~~but~~ that cyclic tetramers and possibly pentamers, hexamers, etc., have special stability. Such a molecule can have linear hydrogen bonds and still close the ring. Coburn and Grunwald[10] fit their infrared data on dilute ethanol-CCl_4 solutions to a model of open dimers and trimers together with ring structures for higher polymers.

Nevertheless, the dielectric constant data[9] for alcohol solutions show that open chain polymers of high dipole moment dominate in moderately concentrated solutions. There is a deep minimum in the molar polarization curve for systems such as methanol or ethanol in cyclohexane at approximately 0.03 mole fraction. For ethanol in CCl_4 the minimum is less deep and lies at approximately 0.05 mole fraction. The results of Coburn and Grunwald indicate that at this concentration the cyclic polymers have become very important species, and they have, of course, small or zero dipole moments. The rise in molar polarization indicates, however, that the still larger polymer species formed at higher concentration must have large dipole moments and are presumably of open structure.

It will require dielectric constant values of extreme precision for very dilute solutions to give a clear decision between open and cyclic dimers. We have not found such data in the literature. It seems to us entirely

plausible that the dimeric species may be partly cyclic and partly open chain at room temperature but with the proportion of the cyclic form decreasing with rise in temperature. In this case the assumption of a constant Δ_D in the calculation of the ΔH values in Table VI is subject to question. The ΔH values calculated from the infrared data of Liddel and Becker[7] are also based upon the assumption of a single type of dimer and are likewise subject to some question. In either case, however, the difference between the true and apparent ΔH values is not likely to be very large.

In the case of ethanol-benzene solutions the molar polarization data[9] show no minimum corresponding to cyclic polymers, hence, it seems safe to assume that the dimer is predominantly open chain and the apparent ΔH value may be adopted as reliable.

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