Infra-red spectroscopic studies of hydrogen bonding in methanol, ethanol, and t-butanol

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Abstract—The infra-red spectra of methanol, ethanol and t-butanol have been investigated in the 3 μ region (fundamental frequency of the OH stretching vibration). The alcohols were studied in CCl_4 solution over a concentration range 0·005–1·0 M and a temperature range −15° to +60°C. Quantitative measurements of the intensity of the sharp OH band near 3630 cm^{-1} yielded values for the equilibrium constants and the following values for the enthalpies of dimer formation: methanol, 9·2 ± 2·5; ethanol, 7·2 ± 1·6; t-butanol, 4·8 ± 1·1 kcal/mole of dimer. Integrated intensities are given for the dimer band near 3500 cm^{-1} and the polymer band near 3350 cm^{-1}. The high values of ΔH, together with the frequency shift and intensity data, suggest that the alcohol dimer is cyclic with two non-linear hydrogen bonds.

THE study of hydrogen bonding (H-bonding) in alcohols has been the subject of numerous investigations, many of them utilizing infra-red spectroscopy. The general spectral characteristics of H-bonded alcohols in the fundamental OH stretching region were established over 20 years ago by ERRERA et al. [1]. Fig. 1 shows spectra of t-butanol at several temperatures and concentrations. The plots are typical of all the lower alcohols. The sharp band in the region of 3630 cm^{-1} decreases in peak height with increasing concentration and is clearly assigned to the OH stretching mode of alcohol monomers. The broad bands at lower frequencies (3300–3500 cm^{-1}) increase in intensity with increasing concentration and are assigned to OH stretching vibrations in H-bonded alcohol molecules.

Following ERRERA's work FOX and MARTIN [3] made extensive studies of the spectra of benzyl alcohol, while MECKE and his collaborators [4, 5] have investigated the OH stretching modes of alcohols in both the fundamental and overtone regions. Both groups interpreted their results in terms of chemical equilibria between various H-bonded species. SMITH and CREITZ [6] studied the spectra of several sterically hindered alcohols, and COGGESHALL and SAIER [7] determined equilibrium constants for H-bond formation in some of the lower alcohols. KUHN [8] examined the spectra of a large number of alcohols and diols. Recently ENS and MURRAY [9] studied the first overtone spectra of several alcohols, and FISHMAN and DRICKAMER [10] reported the effect of pressure on the spectrum of n-butanol. Measurements of the intensity and frequency of infra-red bands attributed to H-bonded alcohol molecules have been given by TSUBOMURA [11] and by FINCH and LIPPINCOTT [12].

Other physico-chemical measurements have also provided information on H-bonding in alcohols. WELTNER and PITZER [13] deduced values for the energy of H-bonds from measurements of the gas phase heat capacity of methanol;
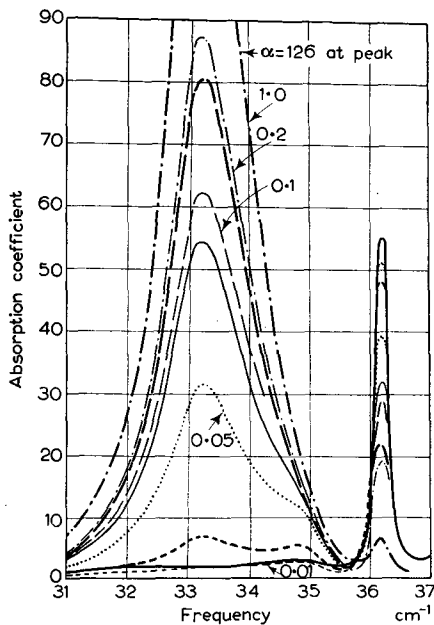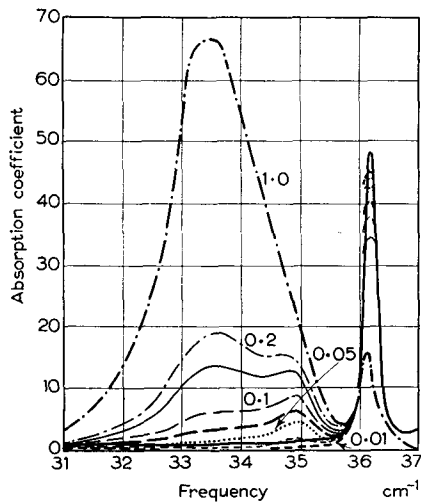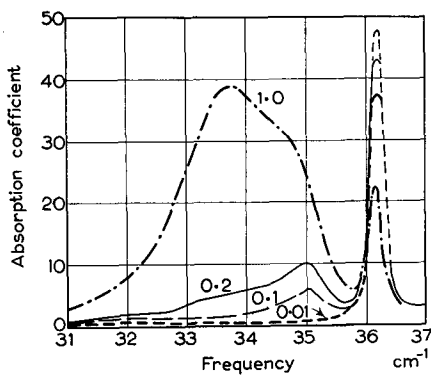
Fig. 1(a)

Fig. 1(b)

Fig. 1(c)

Fig. 1. Absorption spectrum of *t*-butanol. (a) −12°C; (b) 25°C; (c) 50°C. Absorption coefficient (α or ε) is defined as $(1/Cd)(\log_{10} I_0/I)$, C in moles/l., d in cm. (This figure has appeared in the Transactions of the New York Academy of Sciences [2].

STAVELY and TAYLOR [14] reported on the viscosities of dilute solutions of alcohols in "inert" solvents; CALDWELL and BABB [15] studied diffusion in the methanol–benzene system; BOUD et al. [16] investigated the molecular polarization of alcohol solutions in non-polar solvents; SCATCHARD et al. [17] measured the vapor pressure of methanol dissolved in CCl_4; BROWN, FOCK and SMITH [18] determined the heats of mixing of ethanol and isopropanol with several non-polar solvents; SAROLÉA-MATHOT [19], KRETSCHMER and WIEBE [20], and BARKER and SMITH [21] applied statistical theories of association to alcohols in CCl_4; and BONDI and SIMKIN [22] estimated H-bond energies from the heats of vaporization of aliphatic alcohols.*

Virtually all investigators agree that a solution of an alcohol in a non-polar solvent such as CCl_4 consists of a variety of H-bonded species, as well as unassociated monomers. However, there is controversy over the sizes, shapes and relative numbers of H-bonded molecules. Viscosity data [14] indicate an absence of dimers, with only trimers and higher polymers as H-bonded species. Likewise, the infra-red data of KREUZER and MECKE [4a] show that there are practically no dimers, and MECKE [4b] proposes that cyclic trimers are the smallest stable H-bonded alcohol molecules. On the other hand, a number of investigations have provided strong evidence for the existence of dimers. Fox and MARTIN [3] were able to show that the peak height of the band at 3500 cm^{-1} in benzyl alcohol varied as the square of the total alcohol concentration and assigned it to a dimer. SMITH and CREITZ [6] confirmed the assignment for the corresponding band in 2,4-dimethyl-3-ethyl-3-pentanol. They used the concentration variation of the height of this band as well as that of the monomer band (3625 cm^{-1}) to calculate the equilibrium constant for formation of dimers. COGGESHALL and SAIER [7] studied the concentration dependence of the peak heights of the monomer bands in several simple alcohols and determined equilibrium constants for formation of dimers and higher polymers.

The structure and shape of the hydrogen bonded species of alcohols have also been a matter of some controversy, with advocates of both cyclic and open (chain) structures. Of particular interest is the structure of the dimer (assuming that it exists) since a cyclic structure would require non-linear H-bonds. Fox and MARTIN [3] presented evidence against an open dimer, but SMITH and CREITZ [6] strongly favor an open dimer because of the presence of a band at 3619 cm^{-1} in 2,4-dimethyl-3-ethyl-3-pentanol, which they attribute to the non-bonded hydrogen of the dimer. (In this alcohol the monomer OH absorption is at 3627 cm^{-1}.) VAN THIEL, BECKER and PIMENTEL [23] have recently used the novel matrix isolation technique [24] to study the hydrogen bonding in methanol at 20°K in a solid nitrogen matrix. By varying the ratio of nitrogen to methanol they were able to assign the observed frequencies in the 3 μ region to various H-bonded species, and from the pattern of frequency shifts between species they concluded that the dimer is very probably cyclic and that the trimer is also likely to be cyclic.

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* References 1–22 are not intended to provide a comprehensive account of work in this field. The cited articles should be consulted for references to earlier work. Several reviews of H-bonding (L. KELLNER *Rep. Progr. Phys.* 1952 **15** 1; M. DAVIES *Chem. Soc. Ann. Rep.* 1946 **43** 1; and L. HUNTER *Ibid.* 1946 **43** 141) also provide valuable literature references.

In the present work we have used conventional infra-red techniques to study H-bonding of methanol, ethanol and *t*-butanol solutions in CCl_4 over the temperature range $-15°$ to $+60°C$. This investigation differs from previous studies primarily in the coverage of a considerably broader temperature range and in the emphasis that we have placed on the spectral and thermodynamic properties of a single species, the dimer. Many earlier workers have presented treatments which led to the calculation of average properties for a variety of H-bonded species.

Experimental

All spectral measurements were made with a Perkin-Elmer Model 13 spectrophotometer (double beam) that had been modified to scan and record linearly in frequency [25]. A calibrated LiF prism was used with an estimated frequency accuracy of ± 4 cm^{-1}. The spectral slit width was about 9 cm^{-1} at 3600 cm^{-1} and 6 cm^{-1} at 3000 cm^{-1}. A scanning rate of 125 cm^{-1}/min was used. Transmission accuracy is estimated at ± 0.5 per cent in the region 30–50 per cent T, where most measurements were made, giving an optical density accurate to about 1·5 per cent. The zero and 100 per cent transmission values were measured for each spectrum. A correction was applied for the false energy, which was found to be one per cent in the 3500 cm^{-1} region. The spectrometer was desiccated with P_2O_5 or $Mg(ClO_4)_2$ to reduce water vapor absorption.

The cell employed for most of the measurements* had CaF_2 windows, was water jacketed, and could be varied in thickness from 0·1 mm to 10 mm by use of appropriate lead spacers or copper spacers and teflon gaskets. The 0·1 mm spacer was measured by interference fringes; the others (0·5 mm or greater) were measured with a micrometer. The temperature of the cell could be varied by passing through the jacket water or gylcol solution from baths maintained about $-15°$ and $+60°C$. Spectra at intermediate temperatures were obtained as the cell warmed or cooled. In these cases the temperature change was small and was always measured, while scanning the spectral region of interest, with a copper-constant and thermocouple placed in the solution or soldered in the copper spacer that formed the body of the cell. Estimated temperature accuracy is $\pm 2°C$.

The alcohols were distilled from sodium prior to use. Considerable difficulty was encountered with the absorption of atmospheric water by the CCl_4, and a special procedure was devised to dry it. The CCl_4 (Eastman spectro grade) was placed in an open beaker in an evacuated desiccator over P_2O_5 and was allowed to stand at least 24 hr prior to use. In order to minimize exposure to atmospheric water all transfers of CCl_4 and of solutions were made with hypodermic syringes or with pipettes. Solutions were prepared by successive dilutions from a concentrated solution (usually 1 M) made from a weighed amount of alcohol. Concentrations should be accurate to one per cent. Solutions were prepared just before use in order to minimize evaporation of the alcohol [26].

Each of the eight concentrations between 0·005 M and 0·2 M (and in some cases 1·0 M) was studied as a function of temperature in a cell of appropriate thickness. For each cell thickness a CCl_4 blank was run, and optical densities were determined by a point-by-point calculation. The optical densities were corrected for the variation in the number of molecules in the light path due to density change of the solvent with temperature, and an apparent molar absorption coefficient, ε, was calculated from the relation $\varepsilon \equiv (1/Cd) \log_{10} (I_0/I)$, where C is the total concentration of alcohol in moles/l. and d is the cell length in cm. The values of ε at the peaks of the bands of interest (CH and OH stretching modes) were plotted vs. temperature for each concentration and values read from the resultant smooth curves at temperature intervals of about 10° from $-10°$ to $+45°C$. These interpolated values of ε served as the working data for the calculation of equilibrium constants.

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* Spectra of ethanol at concentrations higher than 0·2 M were obtained in standard Perkin-Elmer microcells fitted with BaF_2 windows. Thicknesses were measured by interference fringes. The temperature was not measured but is estimated be to $27° \pm 3°C$.

Results

Calculation of K and ΔH. The feature of primary interest is the sharp band near 3630 cm^{-1} (Fig. 1) and the variation of ε for this band (designated ε_m) with temperature and with concentration. The frequency of the band varies from one alcohol to another and is slightly dependent on temperature, as indicated in the first two columns of Table 1. This band is unquestionable due primarily

Table 1. Frequencies of OH stretching modes

Alcohol	Monomer		Dimer		Polymer	
	Frequency at 25°C	$\Delta\nu/\Delta T$ (cm^{-1}/deg)	Frequency at 25°C	$\Delta\nu/\Delta T$ (cm^{-1}/deg)	Frequency at 25°C	$\Delta\nu/\Delta T$ (cm^{-1}/deg)
Methanol	3643	0·08	3528	0·2	3332	0·85
Ethanol	3634	0·06	3509	0·3	3336	0·8
t-Butanol	3616	0·06	3492	0·25	3352	0·85

to absorption by monomers, although it is possible that non-bonded hydrogen atoms of open dimers or polymers absorb at this frequency also [8, 23]. In 0·005 M solutions, which are sufficiently dilute to preclude formation of an appreciable number of alcohol-alcohol H-bonded species, ε_m displays a marked temperature coefficient, as shown in Fig. 2 for a typical case. We reported this variation of
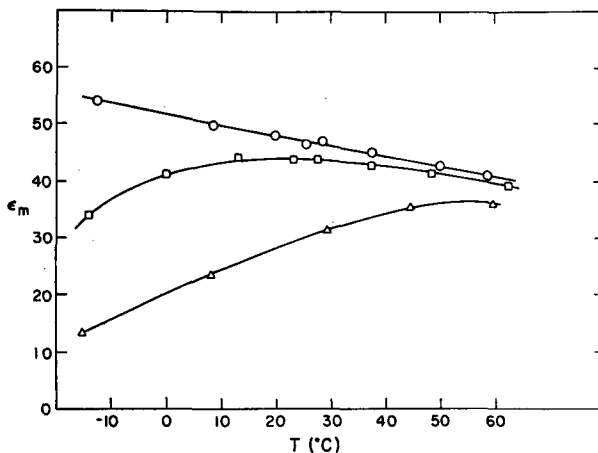

Fig. 2. Apparent absorption coefficient, ε, for the 3635 cm^{-1} (monomer) band of ethanol as a function of temperature at various concentrations.
○ 0·005 M; □ 0·05 M; △ 0·20 M.

intensity with temperature previously and attributed it to a temperature-dependent solvent perturbation resembling very weak H-bonding to the solvent [27]. HUGHES, MARTIN and COGGESHALL [28] reported a similar effect in long-chain alcohols. In more concentrated solutions ε_m is decreased, especially at lower

temperatures, as a result of the depletion of monomers and formation of H-bonded species which absorb at other frequencies. The net result, as indicated in Fig. 2, is the superposition of these two effects, giving, in general, a maximum value of ε_m at an intermediate temperature.

Values of ε_m at various temperatures were plotted vs. concentration and smooth curves drawn through the points. Typical examples are shown in Fig. 3. The
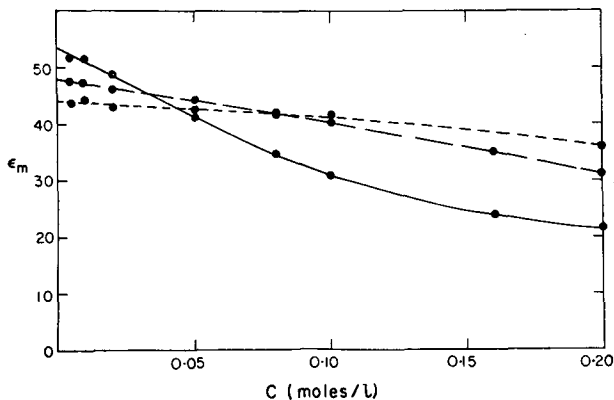
Fig. 3. Apparent absorption coefficient, ε, for the 3635 cm^{-1} (monomer) band of ethanol as a function of concentration at various temperatures.
———— 0°C; — — — 25°C; - - - - 45°C.

extrapolation to zero concentration gives the value of ε_m when all alcohol molecules are in the form of monomers, and is designated $\varepsilon_m{}^o$. This quantity is, as we have noted, temperature-dependent, but is assumed to be independent of concentration (i.e. to obey Beer's Law) over the concentration range of interest.*

Analysis of the chemical equilibrium expression for formation of dimer and polymer (appendix, 1 and 4) shows that the limiting slope of the ε_m vs. C curve is related to the equilibrium constant for dimer formation. If only monomer contributes to ε_m, the relation is

$$(d\varepsilon_m/dC)_{C=0} = -2K_C\varepsilon_m{}^o = -K_X\varepsilon_m{}^o/5,$$

where $K_C = C_d/C_m{}^2$, $K_X = X_d/X_m{}^2$, C_d, C_m, X_d, X_m are concentrations and mole fractions of dimer and monomer, and $K_X = 10K_C$ for CCl$_4$. Such a condition would be applicable in the low concentration region, where higher polymers are unimportant, if the dimer is cyclic. For an open dimer the non-bonded hydrogen might absorb at almost the same frequency as monomer [8, 23] and thus would presumably contribute to the monomer band. If the non-bonded hydrogen of the open dimer has the same absorption coefficient as the monomer, $\varepsilon_m{}^o$, then it is easily shown (appendix, 2) that the value of K calculated above should be multiplied by 2. (If its absorption coefficient is $r\varepsilon_m{}^o$, then K should be multiplied

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* The effects of finite resolution discussed by RAMSEY [29] result in a correction factor that is independent of optical density in the range studied.

by $2/(2 - r)$.) The dimer equilibrium constant can alternatively be found from the limiting slope of a plot of $C(\varepsilon_m/\varepsilon_m{}^o)^2$ vs. $(1 - \varepsilon_m/\varepsilon_m{}^o)$ [4], or from the extrapolation of the function $[C(\varepsilon_m/\varepsilon_m{}^o)^2]/[1 - \varepsilon_m/\varepsilon_m{}^o]$ to zero concentration [7]. We actually used all three methods to obtain K's for some temperatures and found
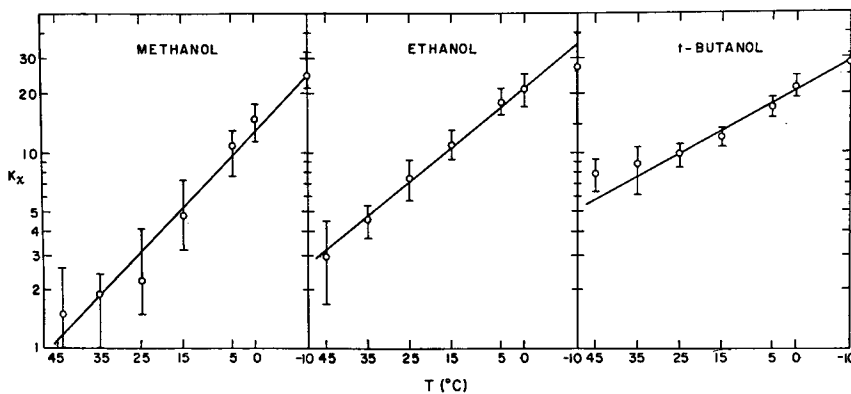

Fig. 4. Variation of the equilibrium constant for dimer formation, K_x, with temperature.

agreement within the accuracy of the data. Since $(1 - \varepsilon_m/\varepsilon_m{}^o)$ is a small quantity at low alcohol concentrations, there is considerable scatter in the plots using that function.

Equilibrium constants for formation of cyclic dimers were calculated and $\log_{10} K$ plotted vs. $1/T$ to obtain the heat of formation, as shown in Fig. 4. It should be noted that a similar plot for open dimer K's would yield the same slope and same ΔH since all K's would be a constant (~ 2) times the K's given for a

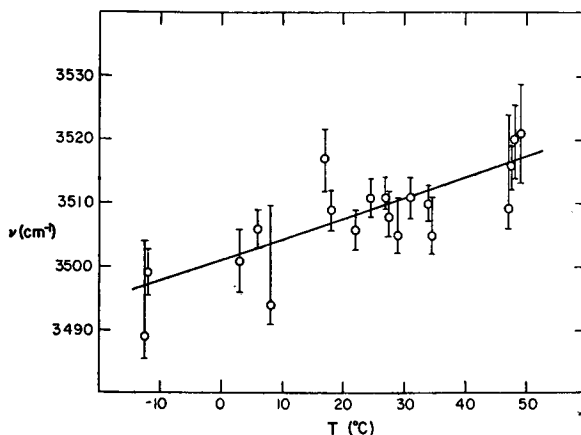Fig. 5. Frequency of the band near 3510 cm^{-1} in ethanol as a function of temperature.

cyclic dimer. We shall attempt to identify ΔH with the energy of the dimer H-bond (or bonds). This requires the assumption that the difference in solvation energy between the dimer and two monomers is negligible. The calculated ΔH's are listed in Table 2, along with H-bond energies reported by other workers.

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We have not calculated equilibrium constants for formation of higher polymers.

Dimer and polymer bands. The calculations of K and ΔH have used data only for the height of the "monomer" band near 3630 cm^{-1}. Additional information is contained in the bands due to associated species at approximately 3500 cm^{-1} and 3350 cm^{-1}. The former feature has been attributed to dimers [3, 6] and hence is of considerable interest in connection with the foregoing calculations. This band is difficult to study in detail, since it is weak in comparison with the features

Table 2. H-bond of energy of alcohols

Alcohol	Solvent	Species	Energy*	Investigators	Method
Methanol	CCl$_4$	Dimer	$9 \cdot 2 \pm 2 \cdot 5$	This work	i.r.
	Vapor	Dimer	$3 \cdot 2$	WELTNER and PITZER [13]	Gas heat capacity
	Vapor	Tetramer	$6 \cdot$	WELTNER and PITZER [13]	Gas heat capacity
	Liquid	Polymer	$5 \cdot 5$	BONDI and SIMKIN [22]	Heat of vaporization
	CCl$_4$	Polymer	$4 \cdot 72$	MECKE [4b]	i.r.
	C$_6$H$_6$	Polymer	$3 \cdot 67$	MECKE [4b]	i.r.
	CCl$_4$	Polymer	$5 \cdot 15$	MECKE [4b]	Heat of solution
	CCl$_4$	(Dimer) (Polymer)	$3 \cdot 6 \pm 0 \cdot 4$	SAROLÉA-MATHOT [19]	Statistical; i.r. data of ref. 5
Ethanol	CCl$_4$	Dimer	$7 \cdot 2 \pm 1 \cdot 6$	This work	i.r.
	Liquid	Polymer	$5 \cdot 5$	BONDI and SIMKIN [22]	Heat of vaporization
	Cyclo-hexane	Polymer	$5 \cdot 4 \pm 1 \cdot 0$	KRETSCHMER and WIEBE [20]	Statistical; thermo-dynamic data
	CHCl$_3$	Polymer	$6 \cdot 74$	BARKER and SMITH [21]	Statistical; thermo-dynamic data
t-Butanol	CCl$_4$	Dimer	$4 \cdot 8 \pm 1 \cdot 1$	This work	i.r.
	CCl$_4$	Polymer	$5 \cdot 3 \pm 0 \cdot 5$	HOFFMANN [5]	i.r.

* The values given under this heading for the present work are the enthalpy changes (ΔH) per mole of dimer. For other studies, where polymers are involved, the figure given is generally ΔH divided by the average number of monomeric units in the polymer. The original articles should be consulted for more details.

at 3630 and 3350 cm^{-1}. There is only a small region of temperature and concentration in which this band is of sufficient intensity to be accurately measurable and yet is not submerged in the very broad band at 3350 cm^{-1}. The frequency of the 3500 cm^{-1} band was carefully measured for the most favorable conditions of concentration and temperature for the three alcohols. A plot of ν vs. T for ethanol is shown in Fig. 5. Although there is considerable scatter due to the

inherent breadth of the band and small interference by water vapor, there is no
doubt that the frequency is a function of temperature. Such a relation is predicted
by the theory of hydrogen bonding of LIPPINCOTT and SCHROEDER [30] and
correlates with the studies of alcohol polymers by FINCH and LIPPINCOTT [12].
The frequencies and temperature coefficients for the three alcohols are given
in Table 1.

In less favorable cases where the 3350 cm^{-1} band is appreciable, an attempt
was made to resolve graphically the 3500 and 3350 cm^{-1} bands and to determine
their areas separately. The intensities of the band at 3500 cm^{-1} are known with
much less accuracy than the peak heights of the monomer band. These values may,
however, be used to check the assignment of this band to the dimer, as well as
to make a rough check on the consistency of the dimer equilibrium constants at
different temperatures. The integrated intensities of this band were plotted vs.
temperature for each concentration and values read from the best smooth curves
through the points at temperatures corresponding to those used in the calculation
of the dimer K's. At a given temperature the variation of the dimer concentration
with total alcohol concentration can be found from the relation

$$C_d = KC_m{}^2 = KC^2(\varepsilon_m/\varepsilon_m{}^o)^2$$

(assuming only monomer contributes to the 3630 cm^{-1} band.) From the integrated
intensity, B_d, of the 3500 cm^{-1} band and the calculated dimer concentration
the true integrated molar absorption coefficient, $B_d{}^o$, can be determined at each
concentration and checked for constancy. In both ethanol and t-butanol an
approximately constant value was found, but in methanol the calculated dimer
absorption coefficient increased with concentration at each temperature. Such
behavior indicates either that the 3500 cm^{-1} band is increasing with concentration
more rapidly than expected for a dimer absorption or that the concentration
of monomer has been underestimated at the higher concentrations of alcohol.
The latter is highly improbable, since absorption by other species (non-bonded
hydrogens of open dimers or polymers) at the monomer frequency would cause
the calculated monomer concentration to be too high, rather than too low. The
3500 cm^{-1} band does not increase rapidly enough with concentration to be due
only to trimer, but it is possible that two species, dimer plus, presumably, trimer,
absorb at this frequency. No separate band was found for any of the alcohols
studied in this work which could be correlated with the band found in the matrix
isolation studies at 3445 cm^{-1} and attributed to trimer [23]. It is conceivable that
dimer and trimer bands overlap so as to be unresolvable in the temperature
range used in the present work.

A rough check on the rate of change of equilibrium constants with temperature
(hence a check on the calculated ΔH) is obtained by comparing the values of $B_d{}^o$
found for each temperature. For ethanol $B_d{}^o$ approximately independent of
temperature could be obtained with equilibrium constants appropriate to a ΔH
of about 5–7 kcal/mole; for t-butanol best agreement is obtained for ΔH in the
range 4·5–6 kcal/mole. The failure of $B_d{}^o$ to remain constant with concentration
at a given temperature prevented us from using this method to check ΔH for
methanol. Values of $B_d{}^o$ for ethanol and t-butanol are listed in Table 3. The

best values of $B_d{}^o$ obtained for an open dimer with an assumed absorption coefficient of $\varepsilon_m{}^o$ for the non-bonded hydrogen were approximately half that for the cyclic dimer, giving approximately the same intensity per bonded OH. The calculated concentration variation of the open dimer did not vary sufficiently from that of the cyclic dimer to permit a definite assignment of the 3500 cm^{-1} band to either species.

Measurements of the intensity of the broad polymer band near 3350 cm^{-1} are influenced by the presence of dimers, and accurate measurements of the area of the polymer band are possible only in our most concentrated solutions (≥ 0.2M).

Table 3. Frequency shifts, band widths and absorption coefficients

Species	Alcohol	$v_m - v$ (cm^{-1})	$v_{1/2}$ (cm^{-1})*	$B^\circ \times 10^{-3}$ (l./mole cm^2)†
Monomer	Methanol	0	22	4·7
	Ethanol	0	24	4·6
	t-Butanol	0	15	3·3
Dimer	Methanol	115 ± 3	80 ± 30	———
	Ethanol	125 ± 5	90 ± 20	15 ± 5
	t-Butanol	124 ± 4	75 ± 15	11 ± 2
Polymer	Methanol	311 ± 6	205 ± 15	54
	Ethanol	298 ± 6	195 ± 15	55
	t-Butanol	264 ± 6	160 ± 15	53

* $v_{1/2}$ the band width at half maximum, has been corrected for finite resolution according to the methods given by RAMSEY [29].

† B^o is the integrated molar absorption coefficient *per* OH *bond*;
$B_i{}^o \equiv (2 \cdot 3/NC_i d) \int \log_{10} (I_0/I) \, dv$, where C_i is the concentration of the species in question in moles/l., d is the cell thickness in cm, and N is the number of OH oscillators per molecule contributing to the band. For monomer a Lorentzian shape was assumed, giving

$$B_m{}^o = 2 \cdot 3/C_m d \cdot (\log I_0/I)_{max} \, v_{1/2} \, K,$$

where $K(\sim \pi/2)$ is given by RAMSEY [29]. For the H-bonded species B^o was determined by graphical integration.

The calculation of the number of alcohol molecules existing as polymers is also subject to uncertainty since the band at 3630 cm^{-1} might contain an appreciable contribution from non-bonded hydrogens of dimers or polymers. Calculations for the two limiting cases—an open trimer, in which 1/3 of all the OH's in the polymer are assumed to contribute to the 3630 cm^{-1} band with intensity $\varepsilon_m{}^o$, and an infinite (or cyclic) polymer, in which none of the hydrogens of the polymer contribute to the 3630 cm^{-1} band—show that the intensity per *bonded* OH is approximately independent of the effect of end group OH's (exactly independent if the amount of dimer is negligible). The polymer intensity data are summarized in Table 3. Most of the data were obtained from solutions less concentrated than 1 M, but for ethanol results at room temperature were obtained up to a concentration of 9 M.

The frequency of the polymer band varies with temperature for all three alcohols, as indicated in Table 1. Our values for the temperature coefficients, $\Delta v/\Delta T$, are 2–3 times those found by FINCH and LIPPINCOTT [12] for these

alcohols. We cannot account entirely for this discrepancy, but it presumably reflects a difference in behavior between the relatively small polymers that are probably present in our system and the very large polymers that would be present in the undiluted alcohols studied by FINCH and LIPPINCOTT.

Other spectral effects of H-bonding. In addition to the pronounced spectral changes with extent of H-bonding that we have discussed thus far, two other spectral features were found to vary with temperature and concentration. In both methanol and ethanol some of the bands attributable to CH stretching modes intensified slightly with decreasing temperature in dilute solutions [27] and exhibited a pronounced intensification with increasing concentration, especially at low temperature. This effect, which is certainly an indirect result of hydrogen bonding, is being studied in more detail. The results will be published soon.

Another feature which seems to be associated with formation of H-bonds in the alcohols, and which has apparently not been previously discussed, is the appearance of two weak bands near 2600 cm^{-1} in concentrated solutions ($\geq 0 \cdot 1$ M) at low temperature ($\leq 0°$). Although these bands are too weak to permit accurate measurement, their intensities correlate qualitatively with the amount of polymer as indicated by the intensity of the 3350 cm^{-1} polymer band. The weakness of the features and their location at ~ 2600 cm^{-1} suggest the possible assignment as a combination mode of the polymer. The bands could arise as a difference between the strong 3350 cm^{-1} band and a fundamental (unobserved in the present work) about 750 cm^{-1}. The closest frequency to 750 cm^{-1} that has been reported is a band at 670 cm^{-1} found in a large series of alcohols by STUART and SUTHER-LAND [31]. They showed it to be due to a vibration of associated molecules and assigned it to the out-of-plane OH deformation. Coupling between this out-of-plane mode and the OH stretching vibration is expected to be quite weak. Another serious drawback to the assignment of the 2600 cm^{-1} bands as a difference is that the corresponding sum was not observed. No reasonable alternative assignments have occurred to us.

Discussion

It is shown in the appendix that the limiting slope of the ε_m vs. C curve is proportional to the equilibrium constant for dimer formation and that a non-zero value of $(d\varepsilon_m/dC)_{c=0}$ implies that dimers are stable. This treatment is subject only to the requirement that Beer's Law hold over the range in which the slope is calculated. In applying the equations it is, of course, necessary to find the true limiting slope. By expanding the expression for $d\varepsilon_m/dC$ in a power series in C it can be shown that for only monomers and dimers $d\varepsilon_m/dC$ will first deviate appreciably from its limiting value at a concentration $>0 \cdot 01$ M (for K's in the observed range) and that the initial deviation will tend to decrease the absolute value of the observed slope. The presence of higher polymers in this region would, on the other hand, tend to increase the slope (in absolute value). Even at the lowest temperatures studied there appears to be virtually no polymer (as indicated by the 3350 cm^{-1} band) in the concentration region below 0·02 M. We believe, therefore, that our measurements extend to a sufficiently low concentration to permit direct observation of the limiting slope, and that the non-zero slope found

for all three alcohols at all temperatures shows conclusively that alcohol dimers are stable in CCl_4 solution.

As noted in the introduction, other workers have reached the conclusion that alcohol dimers are not stable. This disagreement is not too surprising in view of the complexity of the system and the practical impossibility of building up an appreciable concentration of a given H-bonded species without considerable interference from other species. For instance, STAVELEY and TAYLOR [14] tested for the presence of dimers by noting the linearity of a function of viscosity plotted vs. concentration. They do not give examples of the plots but indicate indirectly that their data extended to 0·1 or 0·2 M (at 20°C). In this range of concentration and temperature our results predict that any effect of dimers would probably be masked by the larger concentration of higher polymers. HOFFMANN [5] has also concluded from infra-red data that dimers are absent ($K = 0$). However, we have replotted HOFFMANN's data on an ε vs. C curve and from the limiting slope obtain equilibrium constants in reasonable agreement with ours (e.g. ethanol at 21–25°C; HOFFMANN's data, $K_x = 5 \cdot 3 – 11 \cdot 6$; our data, $K_x = 5 \cdot 8 – 9 \cdot 2$). Such a large variation dependent upon the method of plotting the data is quite disturbing and demonstrates the sensitivity of the equilibrium calculations to small errors in the data. A significant increase in the accuracy of determination of K by this method will probably have to await an order of magnitude improvement in the accuracy of photometry. We feel that our conclusions on the presence of dimers are materially strengthened by the inclusion of experiments over a wide range of temperature, particularly below room temperature, where the limiting slope is certainly not zero.

The exact values obtained for the dimer equilibrium constants are dependent on the structure of the dimer and the extent of contribution, if any, of the non-bonded hydrogen of the open dimer to the monomer band. The various alternatives are discussed in the appendix. Because of this ambiguity the K's themselves can contribute little information to our knowledge of the structure of the dimer. The mean values of ΔH obtained from the temperature dependence of K's, as listed in Table 2, are quite high for a single OH—O hydrogen bond, especially one which causes a frequency shift of only 125 cm^{-1} [32]. These values, therefore, suggest that the dimer is formed from two H-bonds (necessarily non-linear) and exists in the cyclic form. An energy of 2·5–4·5 kcal per bond is probably reasonable for such a non-linear bond. The precision of determination of ΔH is not great enough to rule out the single bonded open dimer, but only to make it appear less plausible than the cyclic form. It is conceivable that both open and cyclic dimers co-exist. If so, the K found in this work actually represents the sum of the constant for a cyclic dimer, K_{cd} and half the constant for an open dimer, K_{od} (appendix, 3). In that event, the calculated ΔH would represent an average heat of formation of the two types of dimer and would probably be temperature-dependent. It is unlikely that both cyclic and open dimers would absorb at exactly the same frequency. At high concentrations the absorption of the open dimer (for example) might be hidden under the polymer band, but at lower concentrations there seems to be insufficient absorption in that region to permit the presence of an appreciable amount of dimer.

Table 2 shows that ΔH for dimer formation decreases in absolute value with increasing size of the alcohol. These figures indicate an unusually large variation in the strength of the hydrogen bond(s) of the dimer for molecules that are very similar chemically. Furthermore, the frequency differences between the monomer and dimer bands are nearly the same for the three alcohols, and a large difference in H-bond energy among the three is unexpected in view of the generally accepted correlations between frequency shift and H-bond energy [32]. Some of the discrepancy may be the result of the presence of both cyclic and open dimers, which would give an apparent ΔH that is temperature-dependent. On the other hand, the margin of error in these determinations is almost large enough to permit a more nearly constant ΔH of about 6–7 kcal/mole to be consistent with our data for the three alcohols.

HUGGINS and PIMENTEL [33] have recently published data on frequency shifts, band widths and integrated intensities for a large number of H-bonding systems and have shown that these quantities can be correlated for many such compounds. The frequency and band-width data for all three alcohols given in Table 2 agree rather well with the straight line of HUGGINS and PIMENTEL. There are discrepancies, however, in the intensity-frequency shift correlations. Our intensity values for the 3500 cm^{-1} (dimer) band in ethanol and t-butanol are far below that predicted by the H–P curve. Part of the discrepancy might be due to error in measurement of the band intensity and in the calculation of dimer concentration. However, if the 3500 cm^{-1} is due to the cyclic dimers, the deviation from the predicted behavior may represent the effect of non-linear H-bonds [33]. Further studies of spectral systematics among systems that are known to form bent H-bonds are needed.

Our values for the intensity of the polymer bands also lie below the H–P curve, but are probably well within the combined limits of error of our measurements and of the curve itself. It should be noted, however, that the intensity datum given by H–P for methanol is far from their curve and from our value. Their intensity is evidently in error, probably as a result of interference by dimers.

Appendix

Assume that the alcohol molecules exist in the form of monomer, dimer, trimer and higher polymers. The concentrations of the first three species (C_m, C_d, C_t) are related by the equilibrium expressions

$$K_d = C_d/C_m^2; \qquad K_t = C_t/C_m^3.$$

(1) Suppose that ε_m represents the apparent absorption coefficient of the band due *only* to monomer. Then

$$\varepsilon_m = \varepsilon_m{}^0(C_m/C)$$

$$= \varepsilon_m{}^0[(C - 2C_d - 3C_t - nC_p)/C],$$

where C is the total concentration of alcohol and C_p is the concentration of the higher (n-fold) polymers. Then

$$\varepsilon_m = \varepsilon_m{}^0[(C - 2K_d C_m^2 - 3K_t C_m^3 - \text{terms in higher powers of } C_m)/C].$$

Neglecting the terms in powers of C_m greater than 3, and making the approximation that $C_m \approx C^*$, we have

$$\varepsilon_m = \varepsilon_m{}^0[(C - 2K_dC^2 - 3K_tC^3)/C]$$
$$= \varepsilon_m{}^0[1 - 2K_dC - 3K_tC^2]$$
$$d\varepsilon_m/dC = \varepsilon_m{}^0[-2K_d - 6K_tC]$$
$$\lim_{C \to 0} (d\varepsilon_m/dC) = -2K_d\varepsilon_m{}^0.$$

(2) Suppose that ε_m represents not only monomer absorption $\varepsilon_m{}^0$ but also absorption by the non-bonded OH of an open dimer, $r\varepsilon_m{}^0$. Then

$$\varepsilon_m = \varepsilon_m{}^0(C_m/C + rC_d/C)$$
$$= \varepsilon_m{}^0[(C - 2K_dC_m{}^2 + rK_dC_m{}^2)/C]$$
$$\approx \varepsilon_m{}^0[1 - (2 - r)K_dC]$$
$$\lim_{C \to 0} (d\varepsilon_m/dC) = -(2 - r)K_d\varepsilon_m{}^0.$$

Thus K_d is seen to be $2/2 - r$ times as large as in the case 1, and for $r \approx 1$, K_d is about twice that for case 1.

(3) Suppose both cyclic dimers (cd) and open dimers (od) exist, with the non-bonded OH of the latter contributing to ε_m with an absorption coefficient $\varepsilon_m{}^0$. Then

$$K_{cd} = C_{cd}/C_m{}^2; \qquad K_{od} = C_{od}/C_m{}^2$$
$$\varepsilon_m = \varepsilon_m{}^0(C_m/C + C_{od}/C)$$
$$= \varepsilon_m{}^0[(C - 2K_{cd}C_m{}^2 - 2K_{od}C_m{}^2 + K_{od}C_m{}^2)/C]$$
$$\approx \varepsilon_m{}^0[1 - 2K_{cd}C - K_{od}C]$$
$$\lim_{C \to 0} (d\varepsilon_m/dC) = -2(K_{cd} + K_{od}/2)\varepsilon_m{}^0.$$

(4) The monomer-dimer equilibrium can be expressed either in concentration or mole fraction,

$$K_C = C_d/C_m{}^2; \qquad K_X = X_d/X_m{}^2.$$

It is easily shown that the equilibrium constants are related by the expression

$$K_X = K_C/V_s \approx 10K_C$$

where V_s, the molar volume of the solvent, is about 0·1 l. for CCl_4.

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* The justification of this assumption at low C can be shown by a detailed exact treatment or by development in a power series in C, as has been done for the monomer-dimer case by BONO [34].

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