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NUCLEAR-MAGNETIC-RESONANCE STUDIES OF HYDROGEN BONDING

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Jefferson Clark Davis, Jr.

(Thesis)

October 26, 1959

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Contents

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Lawrence Radiation Laboratory and Department of Chemistry
University of California, Berkeley, California

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ABSTRACT

The nuclear-magnetic-resonance spectra of several hydrogen bonding systems in noninteracting solvents have been studied at several concentrations and in the temperature range of 20° to 100° C. A specially constructed dewar insert and heating apparatus was constructed for maintaining the samples at the desired temperatures.

Chemical shifts were measured at 60 Mc for the carboxyl protons of formic, acetic, and benzoic acids in benzene. The shifts characteristic of the monomer and dimer species were calculated. Shieldings of the monomer species were calculated to be of the same order as those of alcohol monomers. At the lower end of the temperature range, the monomer shieldings were even higher than those of the alcohols. The decrease of the monomer shieldings with increasing temperature may indicate an association of the monomer molecules with the solvent, although a limited number of measurements of benzoic acid in carbon tetrachloride indicate a similar high shielding. The dimer shieldings were found to be in the range of 300 to 400 cps below the benzene reference. The dimer shieldings increase with the strength of the hydrogen bond.

Chemical shifts were also measured for methanol, ethanol, isopropanol, and tertiary butanol in carbon tetrachloride and for ethanol in benzene.

The enthalpies of dimerization were estimated from the change in the limiting slopes of shift vs. concentration curves with temperature and found to be -9.3 ± 2.5, -7.4 ± 2.0, -6.5 ± 1.5, -5.4 ± 1.8, and -5.6 ± 1.6 kcal per mole of dimer respectively. These are in good agreement with infrared results. The dimer shielding in ethanol was estimated from infrared and NMR data and used to calculate equilibrium constants for ethanol. At 22° C, the dimerization constant for ethanol in carbon tetrachloride is 11.0 for a cyclic dimer and twice this for a linear dimer. Probable higher polymers were estimated for the ethanol system, and the experimental data were fitted by adjusting polymer shieldings and equilibrium constants. This analysis does not definitely prove the existence of a particular higher polymer, but the presence of dimers is strongly indicated.

NUCLEAR MAGNETIC RESONANCE STUDIES OF HYDROGEN-BONDING

I. INTRODUCTION

Hydrogen bonding systems in noninteracting solvents have been studied by a variety of methods in recent years.[1] Refined freezing-point techniques, ebullioscopy, dielectric-constant studies, vapor-pressure measurements, and solvent-distribution methods have been used to establish the various species and the equilibria involved. Probably the most thoroughly studied systems have been those involving the O - H....O bond in alcohols and in carboxylic acids. Of particular interest in recent years has been the application of infrared spectroscopy to such studies.[2,3] It has been observed that the O - H stretching frequency is shifted when hydrogen bonding takes place,[4] and the band due to the dimeric species has been rather definitely established, at least in the case of carboxylic acids and alcohols. Higher polymers give a broad band which cannot be separated into various species. The relative amounts of the various molecular forms in solution from the band intensities have been estimated.[5-7]

The effect of hydrogen bonding on proton-magnetic-resonance spectra was first observed by Arnold and Packard who discovered that the peak corresponding to the resonance of the hydroxyl protons in ethanol shifted to a higher externally applied magnetic field when the temperature was raised.[8] Cohen and Reid also observed a similar shift of the hydroxyl peak when ethanol was diluted in carbon tetrachloride.[9] This effect was interpreted by Ramsey and Liddel as being caused by a change in the time-average magnetic environment of the hydroxyl protons as a result of the shift in the equilibrium between the monomer and higher polymers caused by varying temperature and dilution.[10]

Since these initial observations, nuclear-magnetic-resonance (NMR) techniques have been used increasingly to study hydrogen bonding.[11] Attempts have been made to evaluate equilibrium constants for phenols;[12,13] alcohols;[9,13,14] and systems such as chloroform with acetone,[15,16] with triethylamine,[15] with benzene and other olefins,[16,17] and with diethyl ether;[16] and acetic acid with acetone[15] and with dimethyl sulfoxide.[18] More qualitative studies have also been made to elucidate the various species involved, particularly in acetic acid[19] and in various hydrides.[20]

In general, it has been observed that when a hydrogen bond is formed there is a shift of the proton resonance to a lower applied magnetic field.[11] Separate peaks are not observed for each species involved, presumably because there is a sufficiently rapid redistribution of a proton between bonded and nonbonded states. It has been proposed that in such cases the position of the observed signal is a weighted average of the positions of the individual species present.[21]

In spite of the numerous investigations made of hydrogen bonding in inert solvents by a variety of methods, and information obtained about similar equilibria in the vapor phase and in solids, there is considerable uncertainty about the species present and the important equilibria. For example, it has been difficult to determine the exact structure of the dimers in alcohols, and in both acids and alcohols very little is known about the sizes of the higher polymers. In addition, it would be interesting to know more about the exact nature of the hydrogen bond itself in such systems.

Most notably lacking are extensive studies made at different temperatures. Only a few infrared investigations have been made with this in mind (for example, Reference 6) and no systematic temperature studies have been reported that use NMR methods. As a result there is little information about heats and entropies of polymerization for such systems. It was for this purpose that the present study was undertaken. In addition, it was hoped to learn more about the various species and the important contributions to hydrogen bonding.

Systematic temperature studies required the construction of an apparatus for the accurate control of the sample temperature in the high-resolution NMR spectrometer. This equipment is described in Part II, along with pertinent information about the preparation of the samples and the measurements. In Part III the spectra of several carboxylic acids are discussed followed by a study of alcohols in Part IV.

II. EXPERIMENTAL PROCEDURE

Preparation of Samples

Of primary concern in this work was the removal of water from the samples since hydrogen bonding of the alcohols and acids with water might seriously change the observed chemical shifts. The individual purification procedures were as follows:

Benzene: twice distilled from anhydrous calcium sulfate; bp 80.0 to 80.1°C.

Carbon tetrachloride: twice distilled from anhydrous calcium sulfate; bp 76.7 to 76.8°C; stored over P_2O_5.

Benzoic acid: c.p. acid recrystallized from benzene and dried 10 hr at 80°C under vacuum; m.p. 122.3°C.

Formic acid: 98% c.p. acid distilled from anhydrous calcium sulfate, twice vacuum distilled from anhydrous sodium sulfate, and stored as solid to avoid decomposition.

Acetic acid: c.p. acid distilled from anhydrous calcium sulfate and vacuum distilled from anhydrous sodium sulfate.

Maleic acid: c.p. acid recrystallized from water and dried in vacuum oven at 100°C; m.p. 136°C.

Methanol, ethanol, tertiary butanol, isopropanol: all alcohols distilled twice from calcium hydride.

All materials were stored in a water-free atmosphere and samples were prepared in a dry-box. The alcohol solutions were all prepared by dilution of a stock solution which was gravimetrically prepared.

The carboxylic acid solutions were all made up by weight. The concentrations of the solutions are given in mole-fraction units to avoid temperature dependence.

Measurement of Chemical Shifts

All of the spectra were obtained on a Varian Associates V-4300B high-resolution NMR spectrometer operating at 60 Mc and equipped with a Model V-K3606 super-stabilizer system. A number of the acid solutions were also observed at 40 Mc, the shifts agreeing exactly with those obtained at 60 Mc.

Chemical shifts were measured by the side-band technique[22] with a Hewlett-Packard Model 200J audio oscillator which was calibrated with a Hewlett-Packard Model 524B electronic counter. All shifts were reported in cycles per second, measured at 60 Mc.

In the more concentrated solutions, the shifts were measured visually on the oscilloscope by superimposing the audio sidebands of the reference peak directly on the peaks of interest. In the very dilute solutions, the peaks were recorded with the reference sidebands placed on either side during the recording. The actual positions of the peaks were then obtained by graphical interpolation between the sidebands. In a few cases the shifts were obtained from 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.

Variable-Temperature Apparatus

The studies of chemical shifts at temperatures other than room temperature required the design of an apparatus that would permit control of the sample temperature while still allowing the cylindrical sample tubes to be spun rapidly. This spinning enhances the field homogeneity as required for high-resolution spectra.

The V4331A probe of the Varian spectrometer, positioned between the pole faces of the magnet, contains transmitter coils mounted with their axis horizontal and perpendicular to the primary field of the magnet. These coils produce the oscillating field at the sample which is contained in a cylindrical 5-mm-o.d. glass tube passing vertically between the two sets of coils and perpendicular to their axis. The reorientations of the nuclear moments at resonance are detected as a voltage induced in a small receiver coil wound on a 10-mm o.d. glass cylinder (called an insert) around the sample tube. The receiver coil is connected to the rest of the probe circuitry by a coaxial connector at the bottom of the insert. This connector also serves to hold the bottom of the insert rigid. The top of the insert is held rigid by a Teflon ring. On the top of the probe, an air turbine is mounted on a threaded O-ring to provide a means for spinning the sample tubes. The space inside the transmitter coils allows the use of inserts up to 18 mm o.d. for large samples, but only the small insert using 5-mm sample tubes allows spinning.

The apparatus constructed for the variable-temperature studies is shown in Figs. 1 and 2. It consisted primarily of a special pyrex insert (Fig. 1) which had a dewar jacket to prevent heat loss to the probe. The receiver coil was wound around the inner tube and the connecting wires were led through a Teflon plug to a coaxial connector at the bottom. The Teflon plug was inserted for mechanical strength and to provide as much heat insulation as possible. The bottom of the inner tube was provided with a Teflon cushion on which the sample tube rests. Holes in the ground joint at the top of the insert allowed heated or cooled nitrogen to flow into the space between the dewar jacket and the inner tube, through the holes in the bottom of the inner tube, up around the sample tube, and out the top.

On top of the probe was mounted an aluminum and Teflon housing (Fig. 2) which was held in place by the O-ring on the probe that normally holds the air turbine. This housing served to support the air turbine and also to trap the nitrogen coming out of the insert and direct it out through a dewar-walled tube; this gas passed around the heated nitrogen coming into the insert. The ground-joint arrangement on the insert had a groove connecting the entrance holes which allowed the nitrogen to flow regardless of how the insert was turned relative to the top, doughnut-shaped, distributing chamber through which the nitrogen first passed. This allowed the insert to be turned in the probe for proper balancing of the rf leakage between the receiver coil in the insert and the transmitter coils in the probe.

The dry nitrogen was brought to the desired temperature by means of a nichrome-coil heater wound in a pyrex tube and mounted in a dewar-walled jacket. The nitrogen flow rate was regulated by means of a Victrometer flow gauge and the temperature was varied by regulating the current in the heater with a Variac transformer.

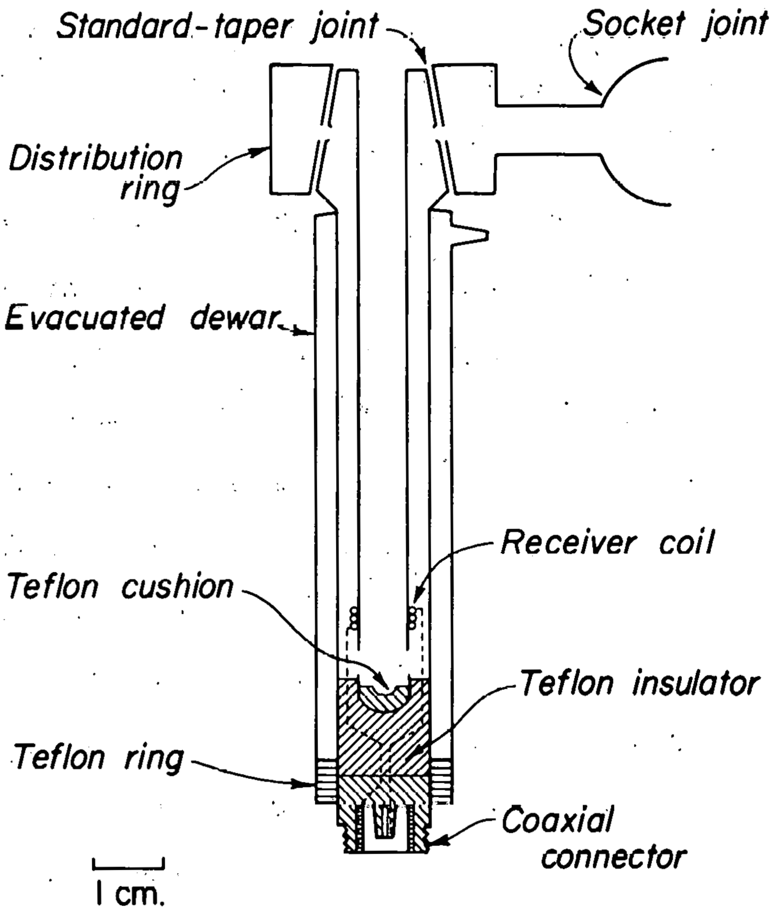

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Fig. 1. Variable-temperature, high-resolution insert.

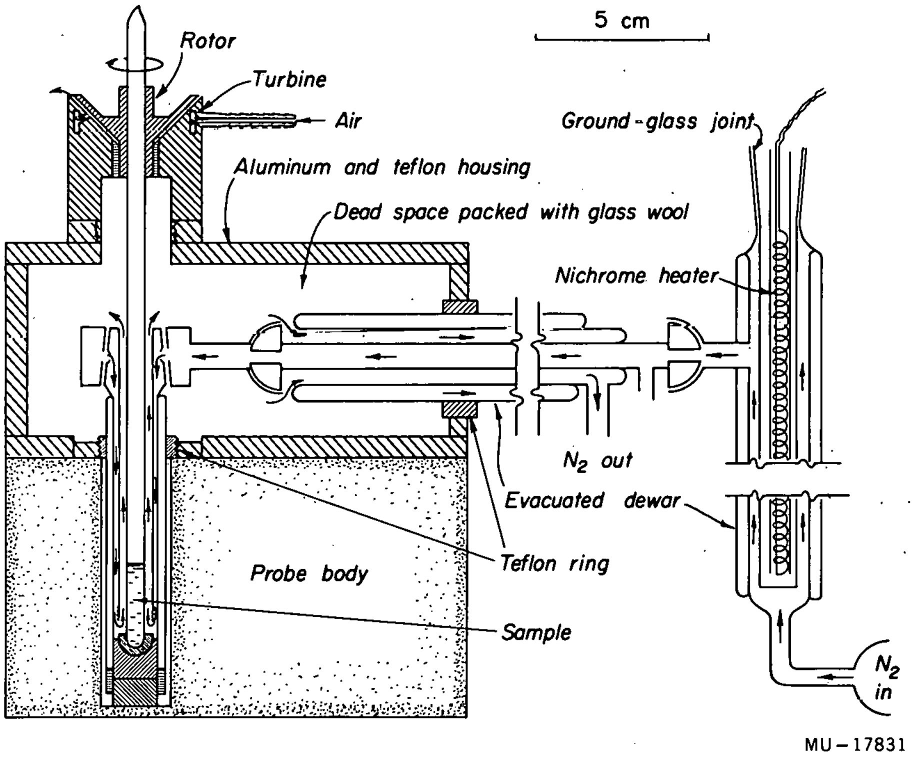

Fig. 2. Variable-temperature apparatus.

Thermocouples were placed in the nitrogen stream at the points at which the nitrogen enters and leaves the insert. Both points were monitored continuously to within ± 0.05°C. It was not possible to place a thermocouple in the vicinity of the receiver coil in these experiments, but a sample tube containing a thermocouple was used to determine the sample temperatures as related to the temperatures in the nitrogen stream over a period of time. This sytem provided an accurate and reliable indication. It is believed that the sample temperatures are known within ± 1°C.

The probe, aluminum housing, heater, and dewar transfer tube were all mounted on an aluminum supporting bar which was attached to the magnet's traversing mechanism. This allowed the position of the sample to be adjusted in the field for maximum homogeneity at any time without disturbing the heating equipment.

Spectra of a standard acetaldehyde sample indicate that the signal-to-noise ratio is less for this insert than for the standard insert. This is because difficulty in winding a coil of sufficiently high Q and because the filling-factor of the coil is less than in the standard insert. However, the resolution obtained closely approaches that of the standard insert, indicating that the coil was accurately wound and mounted.

III. HYDROGEN BONDING IN CARBOXYLIC ACIDS

The association of carboxylic acids has been investigated for many years.[23] Accurate vapor-density measurements and several infrared studies have established equilibrium constants for monomer-dimer equilibria in the vapor,[24-27] and electron-diffraction studies have shown that the dimers are cyclic with two hydrogen bonds.[28] Over the temperature and pressure ranges studied, the experimental data have been closely fitted if we assume only monomers and dimers in the systems, but some indications of higher polymers have been found.[25,27] The nature of the trimers and tetramers proposed in these cases has not been elucidated, however.

For the solid state, considerably less information is available. It is known that aromatic acids and dicarboxylic acids also exhibit a cyclic structure in the solid[29,30] but it has been shown that formic and acetic acids, and presumably related aliphatic acids, form infinite chains in which each acid molecule is hydrogen bonded to two other acid molecules.[31] These higher polymers exhibit considerably shorter O---O distances and lower OH stretching frequencies than the monomers and cyclic dimers.[32]

The association of carboxylic acids in inert, nonhydrogen-bonding solvents has also been the subject of extensive investigation.[23] Cryoscopic studies at the freezing point of the solvent and boiling-point-elevation studies were among the first methods used in investigating these systems, and these techniques have been refined in recent years. Accurate vapor-pressure measurements have also been employed. A number of systems have been studied by following the dielectric constants of solutions of various concentrations. The cyclic dimers have a considerably smaller dipole moment than the monomers.[33,34] Another technique has been to study the distribution of acids between water and an inert solvent,[35] but the effect of the solubility of water in the solvent on the equilibrium is uncertain. Attempts have also been made to deduce monomer-dimer equilibrium constants from the intensities of bands in the infrared spectra attributed to various species.[36-38]

NMR techniques have not been widely used to study acid systems in inert solvents. Although the ionization constants of several acids have been calculated from shifts observed in aqueous solutions,[21,39] and the equilibrium between various species in acetic acid - acetone solutions has been studied,[12] there are only two reported investigations involving inert solvents. Huggins et al. observed no shift in solutions of acetic acid in carbon disulfide, but their measurements were not extended to very dilute solutions.[12] Reeves and Schneider studied the shifts of acetic acid in several noninteracting solvents of varying dielectric constant and observed that there was a pronounced shift to high field when the concentration of acid was reduced below 0.1 M.[19] However, the dilute region was not studied thoroughly. A slight shift to low field was observed as the pure acid was diluted to 0.1 M and an approximate dimer shift was obtained by extrapolating this trend to infinite dilution. No quantitative calculations of the equilibria were made, however.

In the present investigation, benzoic acid shifts have been measured at a variety of concentrations in benzene and at several temperatures. This system was chosen since it has been established that only a monomer - dimer equilibrium is present and the equilibrium constant and ΔH are well known.[23] A limited number of measurements in carbon tetrachloride solutions were also made. In addition, formic acid and acetic acid in benzene have also been studied.

Benzoic Acid

The shifts observed for the carboxyl proton of benzoic acid in several benzene solutions and at several temperatures are listed in Table I. The symbol x designates the total apparent mole fraction of solute in the solution. The shifts are given in cycles per second measured at 60 Mc. A negative shift indicates that the carboxyl peak lies at a lower applied magnetic field than the reference peak from which the shift is measured. The peak of the benzene solvent was used as a reference since the ring protons of the acid were obscured by the solvent peak and it was felt that any changes in the bulk susceptibility of the solution would be experienced equally by the acid and solvent molecules. This was verified in the case of acetic acid - benzene solutions where the methyl peak of the acid remained unaffected by dilution relative to the solvent peak. In solutions of benzene and cyclohexane it was observed that the cyclohexane peak did not shift more than ± 2 cps relative to the benzene in the concentration range of interest. The use of external references is less satisfactory because bulk susceptibility corrections of unknown accuracy are required, especially at higher temperatures where less susceptibility data are available.

Table I

Chemical shifts of benzoic acid in benzene solutions

x_{acid}	δ (cps from benzene) 22°C	37.5°C	52°C	77°C	98°C
0.0594	-371.0	-357.2	-340.9	-304.0	-271.1
0.0369	-366.0	-354.0	-334.1	-296.0	-263.4
0.0289	-355.1	-339.3	-323.0	-282.1	-245.9
0.0222	-343.4	-323.7	-306.1	-261.5	-218.0
0.0183	-339.0	-320.1	-301.0	-255.4	-208.1
0.0147	-338.0	-319.1	-298.4	-252.0	-202.5
0.0132	-323.0	-317.2	-284.1	-232.2	-180.9
0.0107	-310.2	-288.7	-266.0	-212.5	-154.8
0.0103	-310.2	-288.7	-266.0	-212.5	-154.8
0.0087	-298.9	-275.0	-250.0	-192.2	-127.5
0.0074	-287.0	-262.3	-235.0	-168.2	- 88.1

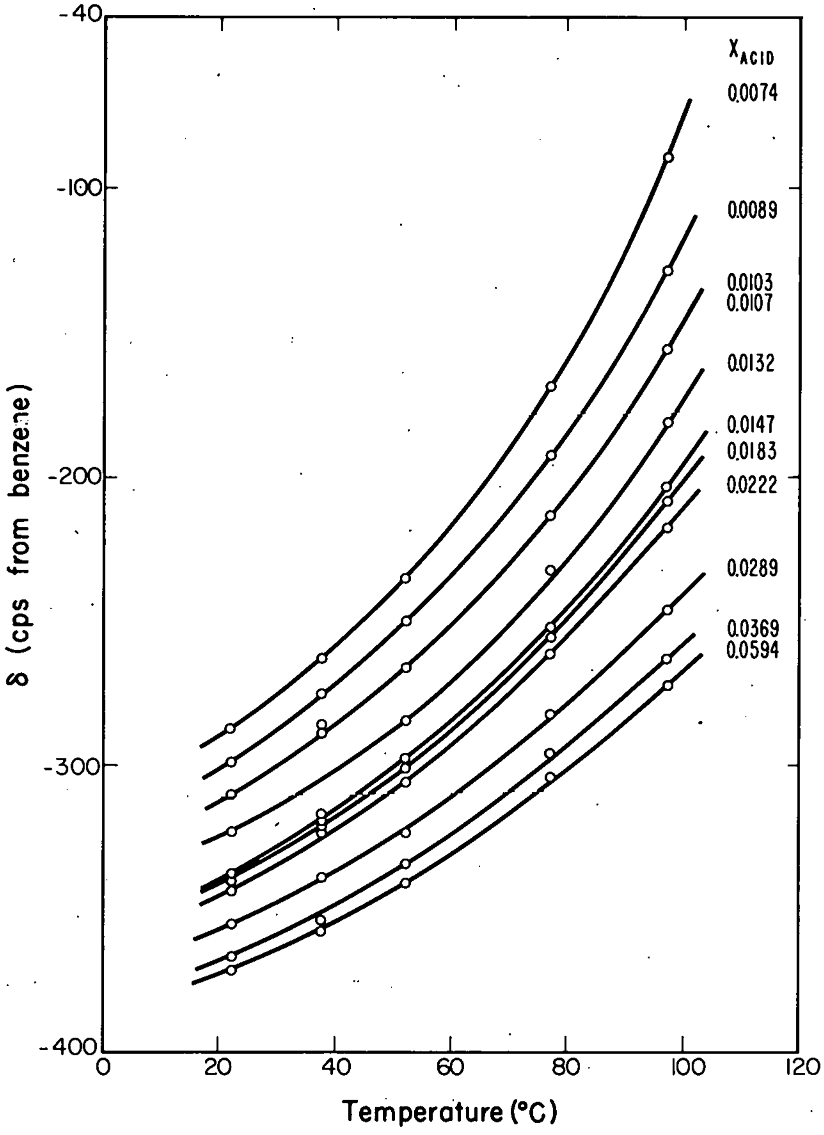

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Fig. 3. Chemical shifts of benzoic acid in benzene solutions.

The data of Table I are illustrated in Fig. 3 where the effect of temperature on the shift for each solution is shown and in Fig. 4 where the effect of concentration on the shift is illustrated at one temperature.

Neither the monomer nor dimer shifts of benzoic acid were observed directly. The high-concentration measurements were limited by the solubility of the acid in benzene, and the low-concentration measurements by the signal-to-noise ratio of the spectrometer. At the lowest concentration observable (mole fraction of acid ~ 0.0074) and at the highest temperature (98°C), about one-third of the acid protons were calculated to be in a monomer environment.

Although these two shifts were not observed, it is possible to calculate them. As described by Gutowsky and Saika[21] and illustrated by Huggins et al.,[12] the observed shift in a rapidly exchanging system is a weighted mean of the shifts of the various species present. If a is the total moles of acid and m is the moles of acid in the monomer form at equilibrium, the observed chemical shift δ for this system is given by

$$\delta = \frac{m}{a}\,\delta_M + \frac{(a - m)}{a}\,\delta_D , \tag{1}$$

where δ_M and δ_D are the characteristic monomer and dimer shifts. The quantity m/a is the fraction of acid molecules in the monomer form and (a - m)/2a is the fraction of dimer molecules, but since there are two hydrogen bonds in the dimer, the latter weight must be multiplied by two to give the resulting expression.

The equilibrium constant for the association in terms of m, a, and s is

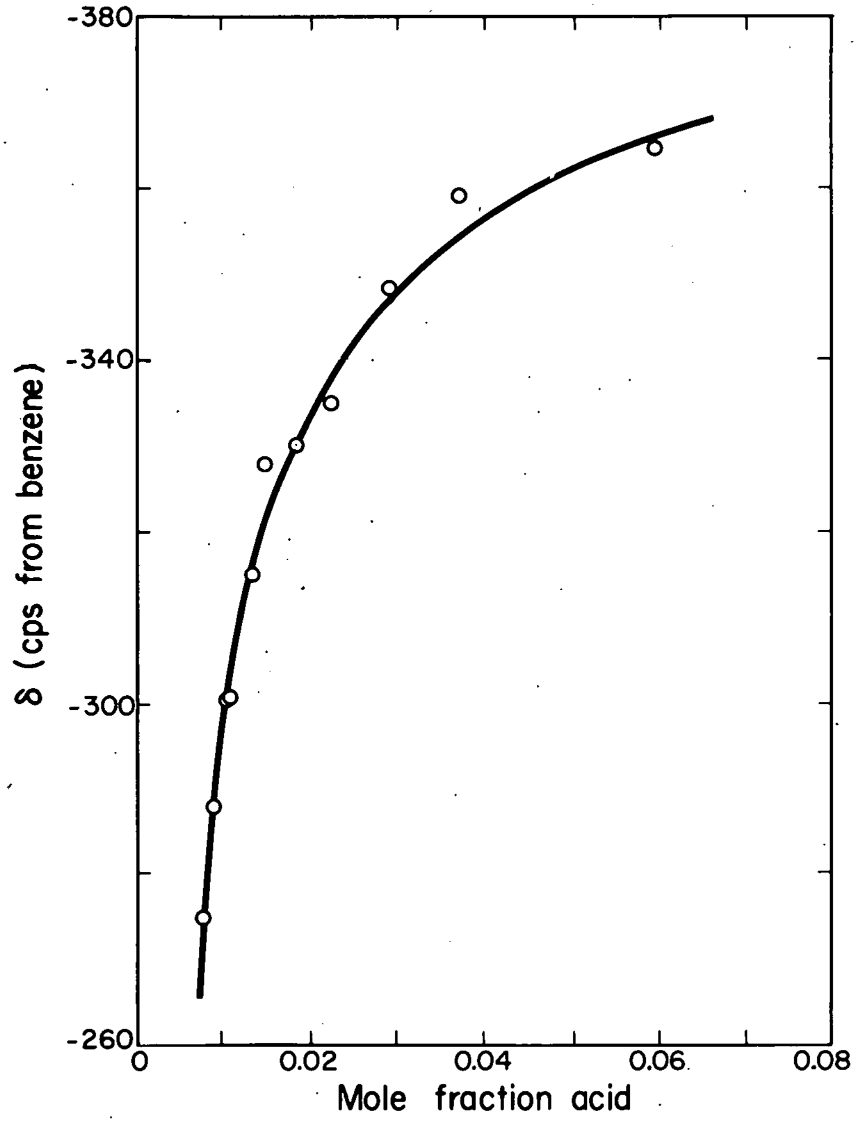

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Fig. 4. Effect of concentration on shifts of benzoic acid in benzene.

$$K_2 = \frac{x_D}{x_M^2} = \frac{(a - m)(2s + a + m)}{4m^2} , \qquad (2)$$

where s is the moles of solvent in the solution and x_D and x_M are the mole fractions of dimer and monomer in solution, respectively. Rearrangement of this expression leads to expressions for $\frac{m}{a}$ and $\frac{(a - m)}{a}$ so that these two terms can be calculated for any solution for which a, s, and K_2 are known. The equation for $\frac{m}{a}$ is

$$\frac{m}{a} = \frac{-s + [s + a(4K_2 + 1)(a + 2s)]^{1/2}}{a(4K_2 + 1)} , \qquad (3)$$

and that for $\frac{(a - m)}{a}$ follows directly.

The equilibrium constant for the benzoic acid - benzene system has been determined at several temperatures by a number of investigators.[33,40-42] All of the data except the dielectric-constant measurements[33] are in excellent agreement, consistent with a ΔH of -8.4 ± .5 kcal mole^{-1}. The equilibrium constant has been calculated for every 10° interval from 30°C to 100°C. For each solution, $\frac{m}{a}$ and $\frac{(a - m)}{a}$ have been calculated by the use of Eq. (3) from these K's and the weights of solvent and acid used in making up the solutions.

With values of the measured shift δ, $\frac{m}{a}$, and $\frac{(a - m)}{a}$ for each solution at each temperature, it is now possible to obtain values of δ_M and δ_D by solving two simultaneous equations of the form of Eq. (1) for these two unknown quantities. This has been done by solving the equations for 32 different pairs of solutions at a given temperature, the same pairs being used at every temperature. Closely adjacent pairs of solutions were not included, since errors would be unnecessarily magnified in these cases.

The resulting δ_M's and δ_D's have been averaged and tabulated in Table II. The indicated errors are the average deviations of the calculated δ's from the means. The data of Table II are also illustrated in Fig. 5.

It is seen that at 30°C the calculated δ lies in the region usually measured for carboxylic acid shifts,[11] but that the value of δ_M is extremely high. In fact, it is shifted to a much higher field than has ever been reported for any proton. However, with an increase of temperature, δ_M drops rapidly and appears to approach the range also measured for alcohol monomers -- a field that is about 400 cps higher than that of benzene. On the other hand, δ_D is little affected by temperature, shifting to a higher field by only about 25 cps.

The behavior of the monomer shifts is strongly suggestive of an interaction of the monomer with the solvent. It is well-known that molecules with acidic protons associate with benzene,[17,43,44] and extensive NMR studies[17,45] indicate that in such an association the proton is drawn into the face of the benzene molecule rather than around the edge.[17,45] It has been shown that the benzene molecule exhibits an anisotropic diamagnetic susceptibility which can be viewed as arising from a circulation of the mobile π electrons around the ring induced by the external magnetic field.[46,47] These circulating electrons give rise to a secondary magnetic field around the benzene molecule. The magnitude of this field averaged with time over all orientations of the benzene molecule has been calculated by various means.[47-49]

If a molecule is associated in some definite region around the benzene ring, a proton in this molecule will experience the secondary field from the benzene in addition to the external field. This will

Table II

Calculated monomer and dimer shifts for benzoic acid in benzene

($\Delta H = -8.4$ kcal mole^{-1})

T ($^{\circ}$C)	K_2	δ_M (cps from benzene)	δ_D (cps from benzene)
30	5,250	915 ± 89	-423 ± 7
40	3,390	740 ± 70	-416 ± 7
50	2,290	655 ± 72	-413 ± 9
60	1,510	556 ± 69	-407 ± 11
70	1,050	498 ± 59	-402 ± 11
80	676	448 ± 59	-400 ± 14
90	525	460 ± 62	-398 ± 15
100	380	442 ± 61	-400 ± 18

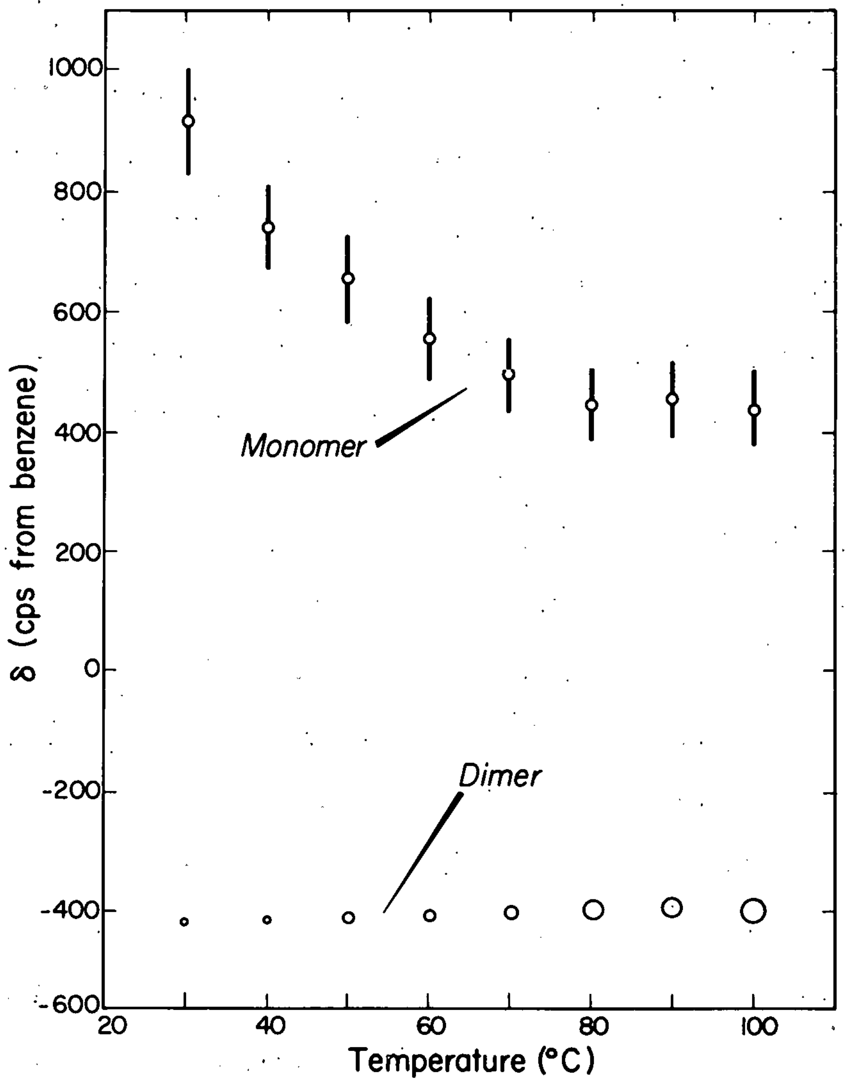

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Fig. 5. Calculated monomer and dimer shifts of benzoic acid in benzene.

result in a shift of the proton's resonance. In the case where the proton is located in the face of the ring near the symmetry axis, the secondary field opposes the external field so that a larger external field is required for resonance. In other words, the resonance is shifted to a higher external field. As the temperature is raised, this association is weakened, the proton is withdrawn from the region of the benzene ring, the second field therefore is reduced in the vicinity of the proton, and the resonance is shifted to lower fields. This is the behavior observed for δ_M in Fig. 5.

An accurate calculation of the time-average field distribution was made by Johnson and Bovey.[49] Previous approximate calculations considered the field arising from the magnetic dipole at the center of the benzene ring that would be produced by the circulating electrons in a loop at a radius of that of the benzene molecule.[47] A second type of calculation considered the field arising directly from the circulation of the electrons in such a loop.[48] Johnson and Bovey improved the calculation by putting the circulating electrons in two loops above and below the plane of the ring as they actually must be in the π orbitals of the molecule. The distance between the loops was adjusted by matching the calculated shifts for protons on the ring and on substituents with those experimentally observed. The time-average field distribution around the benzene molecule was then obtained by averaging the fields for each orientation of the molecule in the external magnetic field over all possible orientations. Johnson and Bovey have published tables of the time-average field so that it is possible to see what shift would be produced by this field at a nucleus in any position relative to the benzene molecule.

If it is assumed that the carboxyl proton is drawn toward the benzene face exactly along the symmetry axis and that the unassociated δ_M is about 400 cps at 30°C, then from the tables it is found that the time-average secondary field distribution produces this shift at the carboxyl proton at a distance of approximately 1.1 A from the plane of the benzene ring. Since this is an extremely close approach, it is more likely that the acid proton may be located between the faces of two benzene molecules and (or) that the molecular motions leading to an averaging over all possible orientations in space of the benzene molecules may be restricted in this system, which would result in higher secondary fields.

Such an association with the solvent would not be anticipated for the cyclic dimer which has no free, acidic protons, and indeed no unusual shifts are observed. It would be expected that the hydrogen bond is weakened at higher temperatures, which might account for the small shift of δ_D to higher field.

Despite the plausibility of the effect of association with benzene on the calculated δ_M, it is also desirable to investigate the effect of varying K_2 on δ_M and δ_D. In particular, it would be of interest to see what equilibrium constants and ΔH would give a monomer shielding around 450 cps at all temperatures.

At 30°C, a K_2 of 2.2×10^3 gives a δ_M of 450 cps and a δ_D of -425 cps. With this K_2 and the previous K_2 at 100°C, a new ΔH of -5.62 kcal mole^{-1} was estimated. This ΔH was used to calculate K at the intermediate temperatures, and monomer and dimer shifts were calculated. These are listed in Table III. The deviations are of the same magnitude as those given in Table II. There is again an increase

Table III

Calculated monomer and dimer shifts of benzoic acid in benzene after adjustment of equilibrium constants.

($\Delta H = -5.62$ kcal mole^{-1})

T (^{o}C)	K	δ_M (cps from benzene)	δ_D (cps from benzene)
30	2200	450	-425
40	1622	413	-419
50	1230	388	-415
60	955	381	-410
70	741	380	-407
80	589	398	-405
90	468	424	-403
100	380	442	-400

in δ_D over the temperature range studied, while δ_M decreases and then increases again although the total fluctuation is of the order of the average deviations in the calculated values. Apparently a set of equilibrium constants which would make δ_M exactly the same at all temperatures will not fall on a straight-line log K vs 1/T plot.

It is interesting to note that the value of K_2 at 30°C which brings δ_M down to 450 cps is closer to that determined by the dielectric measurements (1.41×10^3).[33] However, the disagreement with the freezing point, isopiestic, and boiling point studies both in K_2 and ΔH leaves the low value in doubt. It is also possible that the limited concentration of monomer in the low-temperature solutions might lead to large errors in the calculated monomer shift, but the average deviations from the mean of the calculated values are not much larger at the lower temperatures than at the higher. Thus it is difficult to see why an error should necessarily fall preferentially toward higher shieldings.

An infrared determination of the equilibrium constant for the dimerization of benzoic acid in carbon tetrachloride solution has recently been reported.[7] The K_2 at 25°C converted to mole-fraction units was calculated to be 4.56×10^4. In this investigation an attempt was made to calculate δ_M and δ_D for this system from NMR measurements, but the limited solubility of the acid ($X \sim 0.019$) restricted the measurements to a narrow concentration range in which the calculated fraction of molecules in the monomer environment varied only from 0.024 to 0.040. The estimated δ_M and δ_D from these measurements (five solutions) are 2267 ± 302 and -399 ± 9 cps from benzene after correction for the bulk susceptibility differences in carbon tetrachloride and benzene.

This monomer shift is even higher than those calculated for the benzene solutions while the dimer shift is about the same. There is no reason to expect solvent effects to produce a large shielding for the monomer in this system, but the accuracy of this estimate is unknown since such a limited range was accessible for the NMR measurements, and because the K_2 is of unknown accuracy. Unfortunately, there are no other measurements of the benzoic acid-CCl_4 system, but comparison of the distribution and infrared studies of acetic acid in CCl show that the infrared K is about ten times that obtained from distribution measurements.[23] A K_2 of 4.2×10^3 would bring δ_M to about 440 cps and δ_D to -396 cps. Again, the high δ_M may result in both the benzene and carbon tetrachloride systems when the concentration of monomer is very small for all the solutions, although, as pointed out, it is not clear that the error should be predominantly in one direction rather than random.

Formic and Acetic Acids

The shifts of several solutions of formic acid and of acetic acid in benzene have also been studied over the temperature range 20 to 100°C. The observed shifts are recorded in Tables IV and V. These shifts are again measured with benzene used as an internal reference.

Only one investigation of the monomer-dimer equilibrium for formic acid has been reported.[33] A value for K_2 of 1.41×10^3 was calculated at 30°C in benzene from dielectric-constant measurements. Because it is the only available value, there is some uncertainty as to its accuracy, particularly since the K calculated from similar data for benzoic acid in benzene does not agree with those of other methods. However the agreement is good for the toluic acids. Since no values for ΔH have been reported, it was only possible to calculate δ_M and δ_D for this system at 30°C by the use of the method outlined for benzoic acid. A total of 46 different pairs of solutions were used to solve Eq. (1) for δ_M and δ_D. The average values and the average deviations from the means are listed in Table VI. It is seen that in the cyclic dimer, the carboxyl proton is more shielded than in benzoic acid. Since benzoic acid apparently forms a stronger hydrogen bond, it might be expected that the proton would be less shielded in the benzoic acid dimer. The monomer shift is again seen to be high for formic acid as it was for benzoic acid, but since this may result from association with the solvent, and because the errors are large, comparisons with benzoic acid are not likely to be significant.

Table IV

Chemical shifts of formic acid in benzene solutions

x_{acid}	δ (cps from benzene)				
	23°C	40°C	53°C	71°C	110°C
0.0088	-120	-87.3	-66.0	-37.5	obscured by benzene peak
0.0115	-147.3	-117.0	-75.0	-45.0	"
0.0136	-163.8	-134.1	-112.5	-75.0	"
0.0159	-173.1	-142.8	-116.7	-75.0	"
0.0171	-177.3	-147.6	-117.0	-82.5	-22.5
0.0227	-209.1	-177.3	-150.3	-112.5	-55.8
0.0268	-215.7	-187.5	-157.8	-123.0	-61.2
0.0304	-219.0	-190.8	-165.3	-129.6	-64.8
0.0354	-229.8	-200.7	-172.5	-130.5	-68.7
0.0395	-235.2	-208.5	-183.6	-146.7	-85.5
0.0464	-236.7	-211.2	-184.5	-153.0	-90.3
0.0555	-241.5	-216.6	-192.0	-157.2	-97.8
0.0660	-249.6	-225.3	-201.8	-157.8	-112.5
0.0752	-250.5	-229.8	-210.3	-181.5	-127.8
0.0854	-250.5	-226.8	-211.5	-183.5	-131.7
0.0977	-250.8	-232.5	-213.9	-184.8	-130.8
0.1225	-247.5	-231.3	-217.8	-198.0	-151.8
0.1416	-242.4	-235.5	-209.4	-190.8	-140.7
0.1587	-238.5	-225.0	-208.5	-190.5	-129.3

Table V

Chemical shifts of acetic acid in benzene solutions

	δ (cps from benzene)			
x_{acid}	23°C	49°C	53°C	77°C
0.870	-298.0	-272.5	-267.1	-236.0
0.705	-291.2	-267.1	-260.9	-229.1
0.580	-284.1	-256.0	-252.2	-217.8
0.429	-278.0	-250.0	-244.0	-208.0
0.360	-272.8	-242.8	- -	-200.2
0.271	-262.1	-231.0		-187.1
0.223	-246.0	-209.1		-156.3
0.151	-232.3	-194.3		-135.1
0.131	-204.1	-163.1		-101.5
0.114	-197.0	-155.0		- 92.2
0.100	-196.0	-152.0		- 88.0

The acetic acid-benzene system has been investigated by two methods -- measurement of the dielectric constant[33] and study of the distribution of acetic acid between water and benzene.[35] The values of K_2 obtained at 30°C by these two studies are 4.17×10^3 and 1.29×10^3, respectively. The effect of the solubility of water in benzene on the latter value is uncertain; however, the constants obtained by distribution methods generally appear to be lower than those obtained by other means. For this reason, the dielectric value was used to calculate δ_M and δ_D for acetic acid in benzene at several temperatures. A ΔH of -8.2 kcal mole^{-1} obtained from both the distribution studies and thermodynamic methods was used to calculate K_2 at temperatures other than 30°C. The results of these calculations for 34 pairs of solutions at each temperature are given in Table VII.

Again, the cyclic dimer shift is at a higher field than for benzoic acid and at slightly lower field than for formic acid, consistent with the picture of shift as a function of hydrogen-bond strength. The monomer shifts are also at a much higher field than that usually measured for protons, and again there is a rapid drop of δ_M to a lower field as the temperature is raised. This is similar to the behavior observed for benzoic acid.

The deviations in the δ_M and δ_D calculated for formic and acetic acids are larger than for benzoic acid. In the formic acid and acetic acid systems, higher polymers are known to form, and the presence of small amounts of higher polymers may cause less-consistent monomer and dimer shifts. However, no particular trends were observed for the calculated shifts dependent on whether pairs of solutions in the high or

Table VI

Calculated monomer and dimer shifts for formic acid in benzene

T (°C)	K_2	δ_M (cps from benzene)	δ_D (cps from benzene)
30	1,410	908 ± 141	-333 ± 19

Table VII

Calculated monomer and dimer shifts for acetic acid in benzene

($\Delta H = -8.2$ kcal mole^{-1})

T (^{o}C)	K_2	δ_M (cps from benzene)	δ_D (cps from benzene)
30	4,170	1232 ± 173	-344 ± 17
40	2,692	1005 ± 121	-343 ± 15
50	1,779	849 ± 108	-340 ± 11
60	1,230	720 ± 100	-329 ± 12
70	851	628 ± 92	-323 ± 12
80	603	547 ± 90	-320 ± 18

low concentration ranges were used. This would seem to indicate that at the concentrations used in the calculations, the amount of higher polymers may not be important, and the calculated monomer and dimer shifts are fairly reliable.

Shifts of Higher Polymers

Although the cause of the shift of the proton towards lower shielding with the formation of hydrogen bonds is not clearly understood, there is some evidence that it is primarily an electrostatic effect. Marshall and Pople have calculated the effect of the electric field of a point charge on the shielding of a hydrogen atom. They have shown that the resulting shift is of the correct order of magnitude and in the right direction.[50] Essentially, what happens then is that the electrons from the second oxygen atom repel the electrons in the OH bond and the resulting electronic asymmetry causes a decrease in the proton shielding.

It would be expected that a stronger hydrogen bonds would result in larger shifts, and in general this has been observed. The proton shift on dimerization of alcohols is considerably smaller than that observed for acids, and a similar difference in shift is observed for the O-H stretching frequency.[4] It would thus be expected that the formation of higher polymers, which are seen from infrared shifts to have stronger hydrogen bonds than the dimer, would exhibit correspondingly larger shifts of the proton resonance. This has generally been observed. In the alcohols, for example, the higher polymers appear to have a shift about three times that of the dimer. This is considered in greater detail in Part IV.

In carboxylic acid systems, a somewhat different situation appears to exist. Reeves and Schneider[19] observed that in acetic acid solutions the proton shielding decreases on dimerization but that above a mole fraction of about 0.1 the shielding again increases. This behavior was observed in this investigation also where the shifts were measured relative to both the benzene signal and the methyl peak of acetic acid. It was observed that there was a total shift of about 40 cps to higher field from the lowest measured shift. Similar behavior was detected in the formic acid solutions.

This behavior is not that to be expected from the electrostatic effect of the electrons on the approaching carbonyl oxygen. In this case, the closer approach of the electrons would produce a larger field at the proton and repel the bonding electrons even more than in the dimer, giving a smaller shielding. Reeves and Schneider have suggested that the hydrogen bonds in the higher polymers are not as strong as in the dimer, but such an argument does not seem reasonable because the polymers are formed preferentially at higher concentrations and the infrared shifts show the higher polymers to have much stronger hydrogen bonds.

It is also possible that monomer-like protons on the end of a polymer chain would bring the average observed shift back toward the higher shielding. However, polymers of any reasonable size would contain several more bonded protons than unbonded protons, and unless the bonded proton shifts were little more than in the dimer, they should outweigh the unbonded contributions.

A third possible explanation may lie in the fact that in the higher polymers the O--O distance is considerably smaller than in the dimer (formic acid dimer is 2.73 A, polymer (solid) is 2.58 A). In such a case the electrons of the second oxygen actually contribute towards shielding the proton in addition to the electrostatic effect. Whether the extent to which the second oxygen's electrons actually bond with the proton and contribute to the shift is significant remains to be seen. It would be interesting to observe the proton shifts of systems in which the O--O distance is extremely short and determine whether the shielding is at higher field than observed for greater O--O distances. Several molecules are known in which the bond is short because of steric reasons. Examples are maleic acid (2.46 A) and Ni-dimethylglyaxime (2.44 A).

It has not been possible to observe these compounds in nonhydrogen-bonding solvents, even at high temperatures, because of the limited solubilities. It would be convenient to do so, since then only the hydrogen bonds of the molecule of interest would be observed. Several solutions of maleic acid in acetone have been measured and an extrapolation of the shifts toward pure maleic acid indicates that the shift in the absence of bonding with acetone is about 250 cps below a benzene reference. This is a little higher than is usually observed for hydrogen-bonded acids (300-400 cps), but not appreciably so. Since this average shift includes the internally bound hydrogen as well as the hydrogen bond in the dimer, the higher observed shielding may reflect a higher shielding in the internal bond.

IV. HYDROGEN BONDING IN ALCOHOLS

Although the association of alcohols in the vapor phase and in solids has been studied by several investigators,[51] systems of alcohols in solution have been of primary interest. Infrared methods have been used most widely, and it has been possible to distinguish inter- and intramolecular hydrogen bonds.[4] Spectra of numerous alcohols in solvents such as carbon tetrachloride show a characteristic OH stretching band at about 3650 cm^{-1}. A second band at 3500 cm^{-1} has been attributed to dimers, while a broad band centering around 3380 cm^{-1} is presumably due to several indistinguishable higher polymers. Matrix isolation investigations have thrown some light on individual polymers.[52]

Alcohol association has been a popular subject for NMR investigation.[11] Several qualitative studies have been made of the shifts caused by concentration and temperature variations. Becker et al have studied the ethanol-CCl[4] system and estimated the extent of the monomer-dimer equilibrium.[14] More recently Saunders and Hyne have analyzed several alcohol-CCl_4 systems in terms of the predominant equilibria.[13] There have been no systematic temperature studies using NMR methods, however.

In the present study shifts have been measured for the hydroxyl protons of methanol, ethanol, isopropanol, tertiary butanol, in CCl_4 at several temperatures. In addition, the ethanol-benzene system has been investigated. The shifts measured for these solutions are listed in Tables VIII to XII. All of the shifts have been reported relative to the methyl protons of the alcohol under investigation. This reference was chosen since the methyl resonances were found by measurements with both external and internal references to be unaffected by changes in hydrogen bonding. Hence they are more satisfactory as an internal reference than bulk susceptibility corrections with an external reference. For comparison, external references will be cited later.

There have been two approaches to the analysis of NMR shifts for alcohol systems. The first of these considers the monomer-dimer equilibrium at low concentrations for which there is considerable infrared data available. The second approach assumes that there is only one predominant equilibrium (say monomer-trimer) and the data is fit with an appropriate equilibrium constant and polymer shift. The present results have been analyzed by both methods. Since the monomer-dimer equilibrium is unique at very low alcohol concentrations, it is convenient to attempt to obtain as much information as possible about this system and apply this knowledge to the analysis at higher concentrations.

Table VIII

Chemical shifts of methanol in carbon tetrachloride solutions

x_{alc}	δ (cps from methyl peak) 23°C	35°C	53.5°C
1.00	-92.5	-88.0	-76.1
0.742	-87.5	-79.6	-66.0
0.502	-74.5	-62.9	-40.1
0.249	-48.0	-28.7	8.7
0.099	44.8	72.0	133.7
0.077	79.1	106.1	147.0
0.052	115.4	135.6	158.9
0.027	145.5	145.2	167.6
0.020	152.8	160.4	168.0
0.016	157.0	163.0	168.9
0.010	163.4	166.8	170.0
0.0082	165.2	167.8	170.5
0.0077	165.8	168.1	170.5
0.0066	166.7	168.5	170.9
0.0052	168.1	169.5	171.0
0.0040	169.2	170.0	171.3

Table IX

Chemical shifts of ethanol in carbon tetrachloride solutions

	δ (cps from methyl peak)		
x_{alc}	22°C	39°C	56°C
1.00	-250.0	-241.5 (37°)	-228.1 (54°)
0.505	-219.8	-201.5	-176.0
0.250	-200.3	-167.8	-134.0
0.100	-169.0	-124.2	- 83.1
0.0775	-160.1	-118.1	- 76.6
0.0525	-120.0	- 77.8	- 36.3
0.0270	- 32.3	4.2	6.0
0.0206	- 19.0	12.1	21.0
0.0165	- 9.0	16.9	23.1
0.0104	4.0	23.9	27.0
0.0083	7.1	25.3	28.1
0.0067	13.0	27.5	29.0
0.0052	16.7	29.4	29.9
0.0042	18.9	30.4	30.1

Table X

Chemical shifts of ethanol in benzene solutions

	δ (cps from methyl peak)		
x_{alc}	22°C	37°C	54°C
1.00	-250.5	-242.0	-229.5
0.504	-229.0	-208.8	-185.0
0.276	-201.4	-174.7	-142.2
0.145	-156.7	-129.0	- 90.1
0.0742	- 87.0	- 58.2	- 27.2
0.0373	- 4.8	8.1	16.0
0.0189	9.8	18.0	20.0
0.0151	15.3	21.0	24.1
0.0076	23.9	25.9	26.0
0.0095	24.7	27.0	28.0
0.0064	24.2	26.9	28.5
0.0057	25.0	27.2	28.8
0.0047	- 26.4	- 28.2	- 29.1

Table XI

Chemical shifts of isopropanol in carbon tetrachloride solutions

	δ (cps from methyl peak)		
x_{alc}	25°C	36°C	53.5°C
1.00	-237.6	-227.0	-211.6
0.746	-235.1	-223.5	-210.0
0.507	-203.9	-185.9	-161.5
0.254	-166.0	-140.5	-105.8
0.101	-113.8	- 82.0	- 37.6
0.078	- 95.6	- 56.4	- 12.2
0.053	- 86.2	- 35.0	3.1
0.027	- 36.2	3.1	15.3
0.021	- 10.8	12.1	18.8
0.017	- 3.0	14.9	19.4
0.011	11.8	17.6	20.2
0.0084	13.0	19.0	20.8
0.0078	13.7	19.0	20.9
0.0067	14.2	19.2	21.0
0.0053	15.0	19.7	21.1

Table XII

Chemical shifts of t-butanol in carbon tetrachloride solutions

x_{alc}	δ (cps from methyl peak) 21°C	 37°C	 53°C
1.00	-210.1	-190.1	-170.0
0.745	-198.0	-178.3	-156.8
0.505	-160.8	-143.0	-113.1
0.252	-130.0	- 96.1	- 60.0
0.100	- 70.1	- 27.5	- 1.0
0.078	- 34.3	- 2.0	9.2
0.053	- 9.0	10.2	17.3
0.027	10.0	17.1	20.0
0.0206	15.1	18.9	20.9
0.0165	17.5	20.1	21.6
0.0104	20.0	21.3	23.0
0.0083	21.0	22.2	23.2
0.0078	21.4	22.4	23.5
0.0067	21.9	22.6	23.6
0.0053	22.6	23.1	24.0

The Monomer-Dimer Equilibrium

Infrared studies indicate that the monomer-dimer equilibrium is most important at low concentrations of alcohol in an inert solvent. If it is assumed that the concentration of higher polymers is insignificant, then the observed shift in such a system is again given by Eq. (1), for two hydrogen bonds in each dimer molecule. The equilibrium constant will again be given by Eq. (2). In very dilute solutions we have $2s \gg a + m$, so that

$$K_2 \sim \frac{(a - m)\, s}{2m^2} \quad . \qquad (4)$$

Substituting this expression for $(a - m)$ into Eq. (1) and noting that as the concentration of alcohol approaches zero we have $m \sim a$ and $x \sim a/s$, we obtain for Eq. (1)

$$\delta = \delta_M + 2\, x\, K_2\, (\delta_D - \delta_M) . \qquad (5)$$

Taking the partial derivative with respect to the mole fraction of alcohol, we obtain

$$\left(\frac{\partial\, \delta}{\partial\, x} \right)_{x=0} = 2\, K_2\, (\delta_D - \delta_M) = 2K_2\, \Delta_D \quad . \qquad (6)$$

It is seen that if only the monomer-dimer equilibrium is involved, a plot of δ as a function of the mole fraction of alcohol should approach a straight line at infinite dilution. From the slope of this line and the values of δ_M and δ_D, the equilibrium constant can be calculated by Eq. (6).

The monomer shift δ_M can be estimated from the extrapolation of δ to infinite dilution, if it is assumed that the alcohol is completely in the monomer form. The dimer shift, however, cannot be obtained directly, since higher polymers form at moderate concentrations, and the shift measured for the pure alcohol, for example, is largely the result of several polymer shifts. It should be pointed out that even if the dimer contains only one hydrogen bond, the linear relation (6) is still valid so long as δ_D represents the "average" shift of a dimer molecule.

Although it is not possible to calculate K_2 without knowledge of the dimer shift, it is still possible to estimate the ΔH of dimerization since a plot of log K_2 vs 1/T is equivalent to a plot of log $(\partial\delta/\partial x)$ vs 1/T. If we assume δ_M and δ_D to be essentially unchanged by a moderate change in temperature, the term log $(1/2\Delta_D)$ is only an additive constant for any given alcohol system, so that the log K vs 1/T plot is equivalent to a plot of log $(\partial\delta/\partial x)$ vs 1/T. Thus if the slopes of the shift vs concentration curves at several temperatures are obtained, ΔH can be estimated from the slope of the log $(\partial\delta/\partial x)$ vs 1/T plot.

This has been done for each of the alcohol systems studied and the slopes, monomer shifts, and heats of dimerization obtained are listed in Tables XIII to XVII. A typical δ vs x curve at low concentrations is illustrated in Fig. 6 and the log $(\partial\delta/\partial x)$ vs 1/T curves are illustrated in Fig. 7. In addition to slopes obtained from the experimentally measured shifts, similar δ vs x curves were drawn at 10° intervals, the shifts at these temperatures being obtained from δ vs T curves for each solution. These results are included in the data. The reported errors in ΔH are compounded from the estimated errors in measuring the slopes and the resulting deviations in the slopes of the log $(\partial\delta/\partial x)$ vs 1/T curves.

The calculated heats of dimerization are interesting in several respects. It is seen that ΔH decreases with increasing molecular weight of the alcohol. This behavior was observed by Liddel and Becker.[6] These results, in fact, agree remarkably well with the calculations of ΔH for methanol, ethanol, and tertiary butanol in carbon tetrachloride from infrared data which were -9.2 ± 2.5, -7.2 ± 1.6, and -5.4 ± 1.8 kcal mole^{-1}, respectively. The ΔH for isopropanol lies between those of ethanol and tertiary butanol; it was not measured by infrared studies.

The cause of this variation is not clear. It is conceivable that the trend may only be apparent since the limits of error estimated for the heats of all of the alcohols might be considered to have a ΔH of about -7 kcal mole^{-1}. On the other hand, this decrease of ΔH with increasing size of the alcohol molecule may reflect either steric or electronegativity effects on the strength of the hydrogen bond. It is possible, for example, that the formation of a dimer is less favorable sterically when there are larger hydrocarbon chains attached to the hydroxyl group. This might be particularly important if the dimer is cyclic, in which case a special orientation of the molecules would be required for the most favorable bonding. However, the O-H stretching frequency does not shift appreciably differently for the different alcohols, as might be expected if the strength of the hydrogen bonds varied greatly. In fact, the O-H stretching frequency shifts slightly further in the case of the larger alcohol molecules indicating stronger hydrogen bonding.[6]

It is also possible that differences in heats of solvation of the monomer and dimer species for the various alcohols might lead to the observed trend, although there is no considerable evidence to anticipate

Table XIII

Limiting slopes of methanol in carbon tetrachloride solutions, monomer shifts, and calculated enthalpy of dimerization ($\Delta H = -9.3 \pm 1.5$)

T($^\circ$C)	($\partial\delta/\partial x$) (cps/mole fraction alcohol)		δ_M (cps from methyl peak)
20	1120		173.0
25	970		173.2
30	648		172.2
35	510		172.1
40	410		173.1
50	261		172.7
53.5	220		172.2
60	156		172.0
		Average	172.6

Table XIV

Limiting slopes of ethanol in carbon tetrachloride solutions, monomer shifts, and calculated enthalpy of dimerization

($\Delta H = -7.4 \pm 2.0$)

T (^{o}C)	($\partial\delta/\partial x$) (cps/mole fraction alcohol)	δ_M (cps from methyl peak)
20	2320	23.5
22	2250	28.5
30	1410	31.8
39	1170	35.7
40	1100	35.3
50	700	33.3
56	500	32.4
60	480	32.2
	Average	31.6

Table XV

Limiting slopes of ethanol in benzene solutions, monomer shifts, and calculated enthalpy of dimerization

($\Delta H = -5.6 \pm 1.6$)

T (^{o}C)	($\partial\delta/\partial x$) (cps/mole fraction alcohol)	δ_M (cps from methyl peak)
20	1100	30.9
22	1050	31.2
30	833	31.8
37	630	31.4
40	600	30.8
50	462	31.1
54	440	31.4
60	375	31.4
	Average	31.3

Table XVI

Limiting slopes of isopropanol in carbon tetrachloride solutions, monomer shifts, and calculated enthalpy of dimerization

($\Delta H = -6.5 \pm 1.5$)

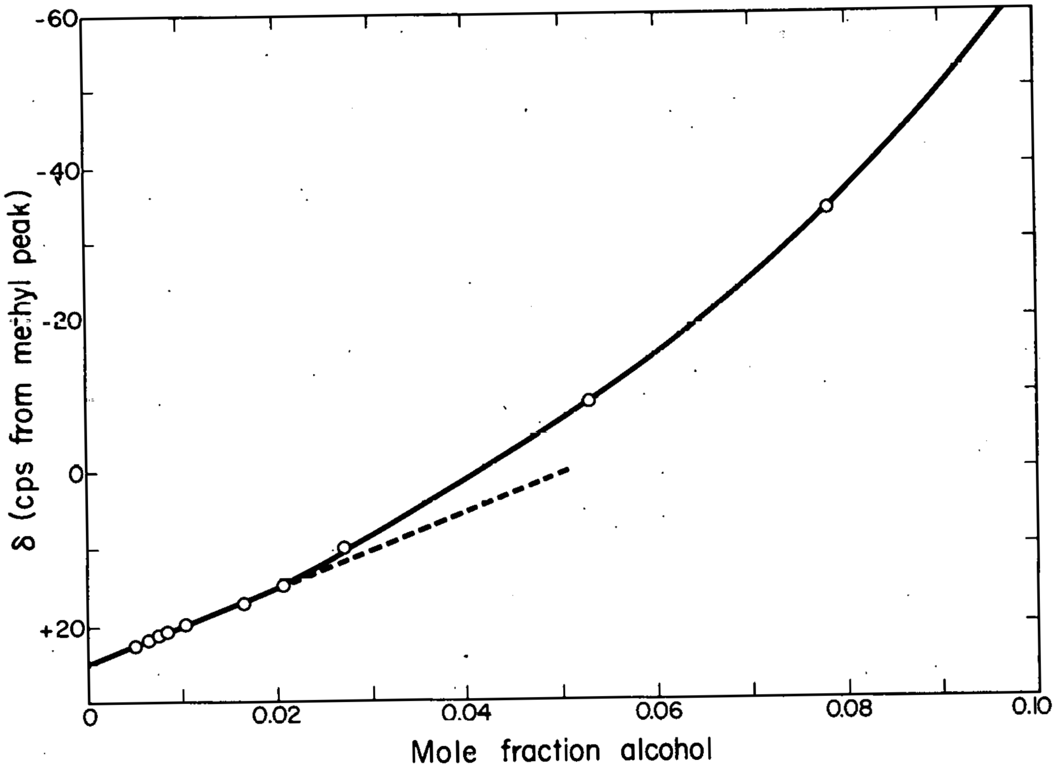
T (°C)	$(\partial\delta/\partial x)$ (cps/mole fraction alcohol)	δ_M (cps from methyl peak)
20	490	18.0
25	430	17.4
30	338	20.0
36	260	22.0
40	230	21.5
50	185	22.1
53.5	160	22.0
60	140	21.8
	Average	20.5

Table XVII

Limiting slopes of tertiary butanol in carbon tetrachloride solutions, monomer shifts, and calculated enthalpy of dimerization

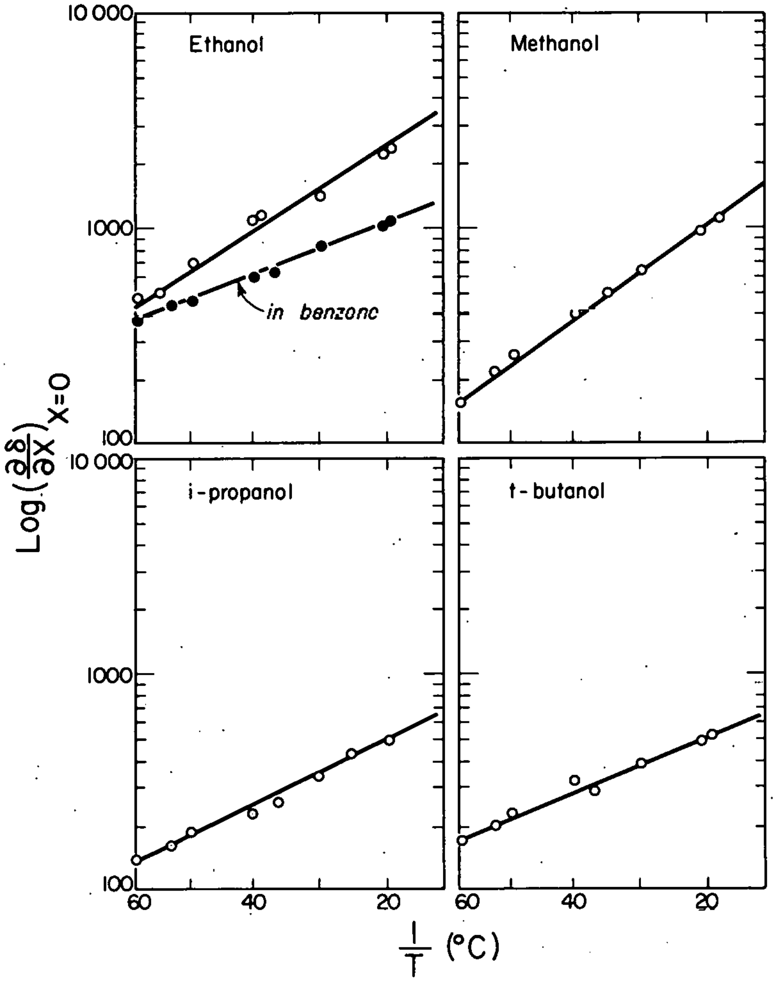
($\Delta H = -5.4 \pm 1.8$)

T ($^\circ$C)	($\partial\delta/\partial x$) (cps/mole fraction alcohol)	δ_M (cps from methyl peak)
20	520	25.4
21	500	25.3
30	390	24.8
37	290	24.7
40	320	25.1
50	230	24.9
53	200	25.0
60	170	25.2
	Average	25.1



MU-17834

Fig. 6. Chemical shifts of tertiary butanol in CCl_4 solutions at 21°C.



MU-17835

Fig. 7. Effect of temperature on monomer-dimer equilibria in alcohols in CCl_4.

such an effect. It has been suggested that the presence of various amounts of both cyclic and linear dimers with their own characteristic heats of dimerization might bring about such a trend as observed here.

In addition to the trend observed for the different alcohols it is also seen that the heat of dimerization of ethanol is less in benzene than in carbon tetrachloride. This behavior is not unexpected because a number of hydroxyl systems are known to associate to some degree with benzene. Such an association of the ethanol monomer with the benzene solvent would necessarily lower the heat of dimerization if the dimer molecules were not equally solvated.

Another interesting observation is that these heats of dimerization are rather larger than would be expected for systems of this sort. The heat of dimerization of carboxylic acids which form stronger hydrogen bonds, for example, is of the order of 7 to 8 kcal mole^{-1} of dimer in carbon tetrachloride. Liddel and Becker have suggested that the high ΔH is evidence for a cyclic dimer in which two hydrogen bonds, although each is weaker than the usually preferred linear bond, contribute to give a larger total heat of dimerization.[6]

The calculation of K_2 from Eq. (6) is a more difficult problem because δ_D cannot be measured directly. As a first approximation, it has been common to assume that the chemical shifts in hydrogen-bonded systems are roughly proportional to the infrared stretching frequency shifts. However, Becker et al have suggested a method of estimating δ_D more exactly.[14] In their spectroscopic measurements of the band intensities of methanol, ethanol, and tertiary butanol, they obtained values of ϵ_m/ϵ_m^o for the band near 3630 cm^{-1} at a number of concentrations and temperatures. Here ϵ_m is the apparent absorption coefficient and ϵ_m^o

is the true absorption coefficient obtained at infinite dilution. Assuming that this band measures all the unbonded alcohol protons, whether on a monomer molecule or on the end of a polymer chain, they could calculate the fraction of nonbonded protons, μ, from ϵ_m/ϵ_m^0 and x.

If Eq. (1) is expressed in terms of unbonded and bonded proton shifts, it becomes

$$\delta = \mu\delta_M + (1 - \mu)\,\delta_b = \delta_M + (1 - \mu)\,\Delta_b \qquad (7)$$

where it is assumed that all nonbonded protons experience the shielding of the monomer and δ_b is the average shielding of a bonded proton. Since μ can be obtained from the infrared measurements and δ is measured by NMR, Δ_b can be calculated for each solution. This has been done for ethanol at 25°C by the use of Becker's infrared data. The values of μ and Δ_b are included in Table XVIII. It can be seen that at higher concentrations at 25°C, Δ_b is fairly constant, but below about 0.02 mole fraction of alcohol, it drops suddenly to a lower value. In this case at 25°C, Δ_b fluctuates around an average of 102 cps. This behavior is a strong indication of two quite different kinds of polymer shifts, and since the monomer-dimer equilibrium is of greater importance at the lower concentrations, it seems reasonable to assume that the Δ_b in this region represents the actual value of Δ_D. On this assumption, K_2 can now be calculated from Eq. (6).

The monomer shifts are essentially unchanged by temperature. Without further information, it is impossible to tell whether the dimer shift would be affected by temperature. The calculated dimer shifts for the carboxylic acids were reasonably constant, but the weaker alcohol dimers might show a greater temperature effect. If it is

Table XVIII

Calculated μ and Δ_b for ethanol in carbon tetrachloride at 25°C from infrared measurements[14]

x_{alc}	δ (cps from methyl peak)	μ	Δ_b (cps)
1.00	-246.0	0	276.0
0.505	-216.2	0.037	255.6
0.250	-190.0	0.090	241.7
0.100	-154.3	0.210	233.2
0.0775	-146.1	0.258	237.3
0.0525	-105.8	0.348	208.3
0.027	- 17.7	0.549	105.7
0.0206	- 4.4	0.646	97.2
0.0165	2.6	0.721	98.4
0.0104	13.3	0.842	105.7
0.0083	15.0	0.877	150.0
0.0067	20.4	0.903	99.0
0.0052	22.4	0.928	105.5
0.0042	24.1	0.943	103.5

assumed that δ_M and δ_D are both constant, then Δ_D is about 102 cps at all temperatures and K_2 can be calculated at each temperature. The values obtained with these assumptions are listed in Table XIX. In this calculation cyclic dimers with two hydrogen bonds have also been assumed. Linear dimers would have a Δ_D half as great, since one of the two protons would have a monomer shielding, and the resulting equilibrium constants would be twice those in Table XIX.

The monomer shifts for ethanol in benzene appear to be the same as in carbon tetrachloride, which indicates that any solvent effects are not apparent in the monomer shift as opposed to the carboxylic acids, where a strong effect is believed to be indicated. It seems reasonable to assume that δ_D would be the same in this solvent, and on the assumption that Δ_D is constant at all temperatures, the values of K_2 obtained from Eq. (6) are listed in Table XIX. These are again for the cyclic dimer.

There is insufficient data to determine the dimer shieldings for the other alcohols studied. It would be tempting to assign a dimer shift on the basis of the infrared shifts, but without absorption-coefficient data of the sort used to calculate Δ_b for ethanol, it does not seem warranted to calculate constants for the other alcohols. Certainly the dimer shifts should be of the same order of magnitude, and it is obvious from the slopes of δ vs concentration that in such a case the equilibrium constants for dimerization at room temperature increase in the order isopropanol, tertiary butanol, methanol, and ethanol, with the constant for ethanol in benzene less than in carbon tetrachloride.

The increase in constant from methanol to ethanol is in agreement with the infrared results obtained by Liddel and Becker[6] and with the slopes obtained from the NMR data at room temperature by Saunders and Hynes.[13]

Table XIX

Equilibrium constants for dimerization of ethanol in carbon tetrachloride and benzene

T (°C)	K_2 in CCl_4	K_2 in benzene
20	11.4	5.4
22	11.0	5.3
30	6.9	4.1
37	- -	3.1
39	5.7	- -
40	5.4	2.9
50	3.4	2.3
54		2.2
56	2.4	
60	2.4	1.8

However, the results for tertiary butanol are quite different; both the previous investigations found the tertiary butanol equilibrium to be slightly higher than that for ethanol. It is difficult to account for the discrepancy. It is possible that the presence of water in the tertiary butanol samples brought the average shift to an equilibrium value at greater concentrations resulting in a nearly flat slope even at room temperature. It is interesting that the slopes in this case give such good agreement with the infrared results for the heat of dimerization.

It must be emphasized that all of the preceding analysis is dependent upon the limiting slopes of the shift vs mole-fraction curves at infinite dilution. The measurements were limited in the low-concentration region by the signal-to-noise ratio of the variable-temperature insert, and it is quite possible that despite the apparently good straight lines that could be drawn, lower limiting slopes would have been obtained if measurements could have been made at lower concentrations. On the other hand, at the higher temperatures it seems more likely that higher polymers would have interfered to a much less extent. If the lower-temperature slopes should actually have been less, then the resulting heats of dimerization would be smaller than reported. Nevertheless, the data fitted reasonably good log (slope) vs 1/T lines.

Monomer Shieldings

A comparison of the monomer shifts obtained by extrapolation to infinite dilution is also of interest. The measured shifts are collected in Table XX. Also shown are the monomer shifts of the respective alcohols in dilute carbon tetrachloride solution measured from an external water reference contained in a coaxial annular cylinder and the monomer shifts measured relative to an internal benzene reference. It is seen that the monomer proton is progressively less shielded as the size of the alcohol increases except that isopropanol is very slightly below tertiary butanol. A similar decrease of the O-H stretching frequency of the monomer has been observed for the series. While the infrared frequencies are consistent with the common view that the electronegativities of the hydrocarbon groups decrease in the order methyl, ethyl, isopropyl, tertiary butyl, the monomer shifts do not fit this pattern in that the more electronegative group would be expected to lessen the proton shielding because of the smaller penetration of the proton into the electron cloud of the bond. It would appear that the shielding of the hydroxyl proton is greatly affected by other electronic circulations in the molecule and is not a simple function of the extent to which the proton is surrounded by the electrons in the O-H bond. Another indication of such an effect may be the apparently high monomer shieldings in the carboxylic acids (the benzoic acid curve in Fig. 5 levels off between 400 and 450 cps above benzene), which appear to be at least as high as those of the alcohols. One would expect the more ionic protons of the acids to be less shielded.

Table XX

Comparison of monomer shifts of the alcohols

Alcohol	δ_M (benzene ref.)	δ_M (methyl peak ref.)	δ_M (H_2O ref.)
Methanol	411.0	172.6	254.8
Ethanol	402.6	31.6	246.4
Isopropanol	393.5	20.5	237.3
Tertiary butanol	395.1	25.1	238.9

Higher Polymers in Ethanol

It is possible to analyze the shifts of these alcohols in terms of equilibria involving polymers larger than the dimer by a method somewhat similar to that used for the carboxylic acids but having the advantage that a more complete concentration range can be covered. That is, suppose that there is only one important polymer in addition to the monomer molecules. Then the equilibrium constant for the system is

$$K_n = \frac{x_n}{x_M^n} \tag{8}$$

where n signifies the polymer containing n molecules. The shift observed is then given by

$$\delta = \frac{x_M \delta_M + n x_M^n K_n \delta_n}{x_M + n x_M^n K_n}, \tag{9}$$

where δ_n is the shift characteristic of the nth polymer. This equation is merely Eq. (1) expressed in terms of mole fractions and the equilibrium constant. If all the hydroxyl protons in the polymer are involved in equivalent hydrogen bonds then δ_n is the shift for one of these hydrogen-bonded protons. If there are any unbonded protons, however, δ_n is again an "average" shift of all the protons in the polymer.

Saunders and Hyne[13] have used Eq. (9) in an analysis of several alcohol systems by adjusting K_n and δ_n until the calculated shifts fit the experimental shifts. Their approach, however, neglects the monomer-dimer equilibrium which is known to exist and which may impair the usefulness of their conclusions.

It is possible to use the results of the preceding section in the following way. Assume that in addition to the monomer-dimer equilibrium there is an equilibrium involving one larger polymer containing n unit molecules and having a characteristic shift δ_n, and that this equilibrium is expressed by an equilibrium constant (8). In this system the observed shift will be

$$\delta = \frac{x_M \delta_M + 2x_M^2 \ K_2 \ \delta_D + nx_M^n \ K_n \ \delta_n}{x_M + 2x_M^2 K_2 + nx_M^n \ K_n} \ . \qquad (10)$$

Now δ_M is known from the straight-line infinite-dilution extrapolations of the preceding section, and from Liddel and Becker's infrared data we have deduced δ_D and K_2 for ethanol. Thus the only undetermined quantities are K_n and δ_n. By assuming a certain polymer, say a trimer, and adjusting K_n and δ_n to give shifts that fit those experimentally observed, we may obtain information about possible higher polymers in the system.

An analysis of this sort has been attempted for ethanol in carbon tetrachloride at 22° C, both by assuming only monomer-higher-polymer equilibrium and by assuming a monomer-dimer-higher-polymer equilibrium. In the former case it was found that the only satisfactory fit of the data was obtained by assuming a tetramer. The shifts and equilibrium constant giving this fit were $\delta_M = 18$ cps, $\delta_4 = -260$ cps, $K_4 = 1 \times 10^4$. The curve is illustrated in Fig. 8. It can be seen that a fit does not occur in the middle concentration region where the slope should be steeper. This equilibrium constant is larger than that found by Saunders and Hyne for a tetramer model, and the tetramer shielding is farther from the monomer than found by them. This is caused primarily by slightly higher measured shifts in the region x = 0.01 to 0.05 in this study than measured by Becker et al.[14]

Taking into account the dimer equilibrium as expressed in Eq. (10), we found that three higher polymers gave approximate fits, although none of them were really exact fits. The best curves obtained are shown in Fig. 9 and the corresponding parameters listed in Table XXI. Not even approximate fits were found for other polymers. The pentamer and hexamer appear to give the best fits except for the lower concentration region. Higher polymers deviate widely from the measured shifts in this region. The lower polymers will fit the low concentration shifts but not the higher region as seen to some extent for the tetramer.

These results seem to indicate that the polymers present in ethanol-carbon tetrachloride solutions cannot be readily distinguished. Indeed, Becker[53] has pointed out that several polymers are indicated in the behavior of the broad OH band at 3380 cm^{-1}, and the NMR shifts are themselves averages of all the species present. In fact, the rather close fit of the monomer-tetramer curve in Fig. 8 indicates that the presence and extent of the monomer-dimer equilibrium is not necessarily proven by the NMR analysis. The calculated values of Δ_b in Table XVIII, however, are a strong indication of the dimer, or at least of two predominant types of bonding in the system. For many of the alcohols around room temperature, the straight line portions of the δ vs x curves are not long and the limiting slopes may not necessarily be due to the dimer alone. However, at the higher temperatures, long straight portions are observed and the monomer-dimer equilibrium certainly is more predominant. Only the monomer-dimer equilibrium would give a straight-line approach to infinite dilution. It seems likely, therefore, that the dimer species is present.

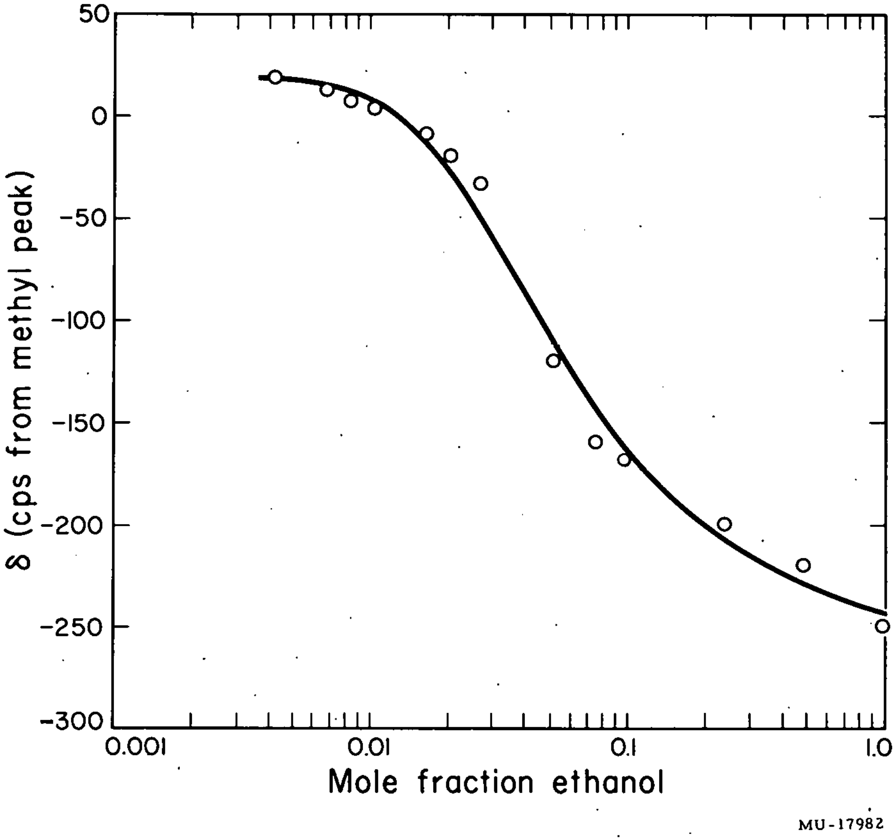


Fig. 8. Approximation of ethanol - CCl_4 system by monomer-tetramer model.

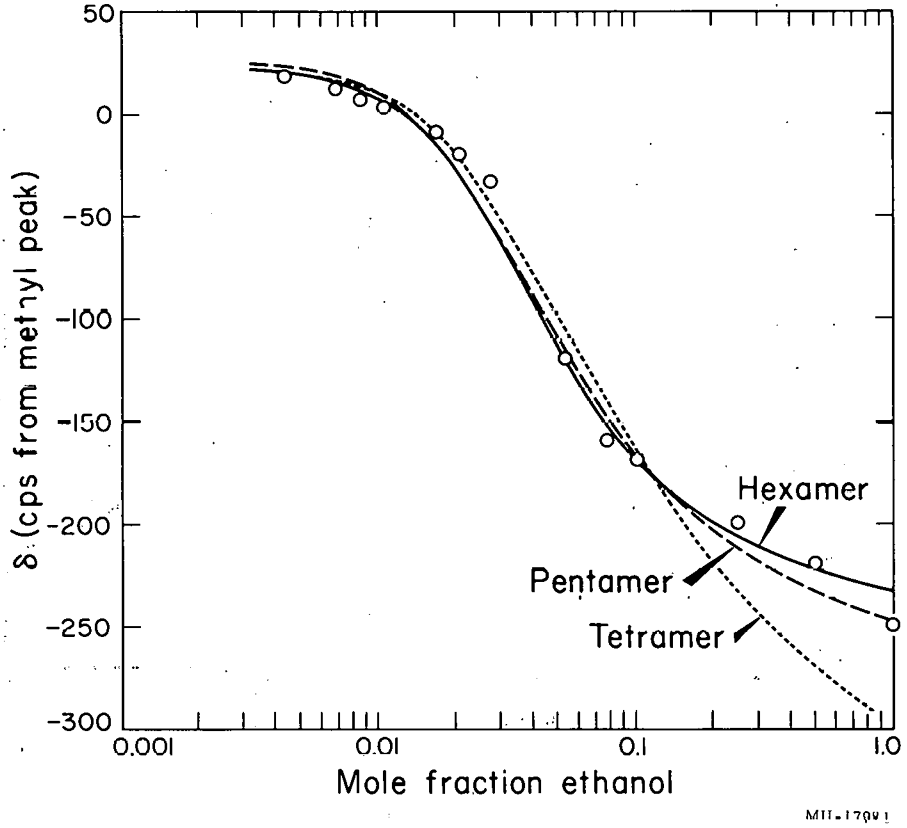


Fig. 9. Approximation of ethanol-CCl_4 system by monomer-dimer-polymer model.

Table XXI

Polymer shieldings and equilibrium constants for ethanol in carbon tetrachloride for a monomer - dimer - polymer model

Polymer	δ_n (cps from methyl peak)	K_n
Monomer	28.5	-
Dimer	-72	11.0
Tetramer	-350	1×10^4
Pentamer	-270	1×10^6
Hexamer	-250	5×10^7

CONCLUSIONS

The measurements and analyses made in this study generally indicate that the stronger the hydrogen bond formed, the greater is the observed shift to lower shielding. However, in the case of the higher polymers of carboxylic acids, there is some indication that a reversal of this trend might occur when the O--O bond distances become very small. Although there is some uncertainty regarding the errors in the calculations, the analysis of the acid-benzene systems indicates an association of the monomer species with the solvent. Apparently the unassociated acid protons are shielded to approximately the same extent as unassociated alcohol protons if not more so.

The shifts observed for both alcohol and acid monomers do not correspond directly to the shieldings that would be expected on the basis of electronegativity effects alone. It is interesting also that steric factors evidently play a part in the heat of dimerization of the alcohols; the higher alcohols were found to have progressively smaller heats of association.

It cannot be shown unambiguously by NMR measurements that there is a monomer-dimer equilibrium at low temperatures in the alcohols although the use of infrared measurements strongly indicates a characteristic dimer shift. At higher temperatures, straight-line approaches to infinite dilution are better evidence for this equilibrium. Further infrared analysis combined with NMR measurements would undoubtedly throw more light on the constancy of Δ_D and on the ΔH of polymerization.

It appears that a monomer-tetramer model will fit the observed shifts for ethanol as will several other models involving the dimer and higher polymers. While these might be useful for describing an average behavior of the ethanol-carbon tetrachloride system, they do not show with certainty what polymers are actually present.

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