[CONTRIBUTION FROM THE MENDENHALL LABORATORY OF PHYSICS, THE OHIO STATE UNIVERSITY]

Infrared Absorption Studies of Hydrogen Bonds between Unlike Molecules

BY WALTER GORDY[1]

The hydrogen bond theory[2] is proving to be of considerable aid in the understanding of liquids and solutions as well as of the structure of certain crystals and organic molecules. There are now available comprehensive reviews[3] of the evidence supporting the theory, which in essence means that a proton under certain conditions is able to form a bridge between two atoms by sharing an electron pair with each. Recently infrared absorption measurements have supplemented older data obtained from measurements of vapor density, boiling points, freezing points, solubilities, etc.

Wulf and his associates,[4] using the absorption spectra method, have found evidence for the existence of intramolecular hydrogen bonds in a number of organic molecules. They worked with compounds containing the OH and NH groups, and noted the effects of neighboring groups on the absorption of these groups.

X-Ray[5] and electron diffraction[6] methods as well as the infrared absorption spectra[7] have been used to confirm the polymerization through hydrogen bonds of the carboxylic acids. The association of alcohol in the liquid state through hydrogen bonding has been verified by several investigators,[8] who observed the effects of the bonding on the infrared absorption of the OH group. Similar evidence favoring intermolecular hydrogen bonds in liquid water[9] and in phenol[10] has been reported.

Molecular weight measurements show that the tendency of certain solvents to dissociate polymerized solutes into their unimolecular form is not in every case dependent upon the dielectric constant of the solvent. In many cases it is no doubt a result of the ability of the solvent to combine with the solute. As Sidgwick has pointed out,[11] the methods of determining molecular weights in solutions, while they indicate the polymerization of the solute, do not reveal the combinations of the solute with the solvent. The spectroscopic method of investigation in many instances may be used to ascertain whether combination of the solute and the solvent takes place, and this method has an additional advantage in that it is sometimes possible from variations in the spectra to determine something of the nature of the linkage. There are, however, serious limitations to the method, among which are: the spectra of complex molecules are only partially understood and classified; the solute and solvent often have overlapping bands which make interpretations difficult or impossible; the extremely thin cells required beyond 2 μ make intensity measurements somewhat uncertain and repetition of results difficult.

In dilute solutions of alcohol in carbon tetrachloride there appears, in addition to the broad intense band at about 2.95 μ, a sharp band at about 2.7 μ.[8] The band at 2.95 μ is commonly attributed to the OH of associated alcohol molecules, while the band at 2.7 μ is thought to be characteristic of the OH of single molecules. Therefore the effect of polymerization is to shift the OH band to the longer wave lengths by approximately 0.25 μ. In solvents possessing a donor and hence able to combine with the alcohol by sharing the proton of the OH group, the OH band appears at a position intermediate[12] between 2.7 and 2.95 μ. This intermediate band may be due, as has been suggested previously,[13] to the alcoholic OH linked by hydrogen bonds to the solvent. Badger and Bauer,[14] working in the photographic infrared, recently have shown that the OH band characteristic of unassociated

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(1) Present address: Mary Hardin-Baylor College, Belton, Texas.

(2) W. M. Latimer and W. H. Rodebush, THIS JOURNAL, **42**, 1419 (1920); N. V. Sidgwick, "The Covalent Link in Chemistry," Cornell University Press, Ithaca, N. Y., 1933.

(3) M. L. Huggins, *J. Org. Chem.*, **1**, 407 (1936); E. N. Lassettre, *Chem. Rev.*, **20**, 259 (1937).

(4) O. R. Wulf and U. Liddel, THIS JOURNAL, **57**, 1464 (1935); O. R. Wulf, U. Liddel and S. B. Hendricks, *ibid.*, **58**, 2287 (1936).

(5) R. W. Morrow, *Phys. Rev.*, **31**, 10 (1928).

(6) Pauling and Brockway, *Proc. Nat. Acad. Sci.*, **20**, 336 (1934).

(7) R. H. Gillette and F. Daniels, THIS JOURNAL, **58**, 1139 (1936).

(8) J. Errera and P. Mollet, *Compt. rend.*, **204**, 259 (1937); J. J. Fox and A. E. Martin, *Nature*, **139**, 507 (1937); E. L. Kinsey and J. W. Ellis, *J. Chem. Phys.*, **5**, 399 (1937); A. M. Buswell, V. Dietz and W. H. Rodebush, *ibid.*, **5**, 501 (1937).

(9) E. L. Kinsey and J. W. Ellis, *Phys. Rev.*, **51**, 1074 (1937); G. B. Bosschieter and J. Errera, *J. Phys. Radium*, **8**, 229 (1937).

(10) J. J. Fox and A. E. Martin, *Proc. Roy. Soc.* (London), **A162**, **419** (1937); W. Gordy and A. H. Nielsen, *J. Chem. Phys.*, **6**, 12 **(1938)**.

(11) N. V. Sidgwick, "The Electronic Theory of Valency," Oxford University Press, 1932, p. 136.

(12) W. Gordy, *Phys. Rev.*, **50**, 115 (1936); **51**, 564 (1937); D. Williams and W. Gordy, THIS JOURNAL, **59**, 817 (1937).

(13) W. Gordy, *J. Chem. Phys.*, **5**, 202 (1937).

(14) R. M. Badger and S. H. Bauer, *ibid.*, **5**, 839 (1937).

molecules of methyl alcohol in carbon tetrachloride solution decreases appreciably when acetone is introduced into the solution.

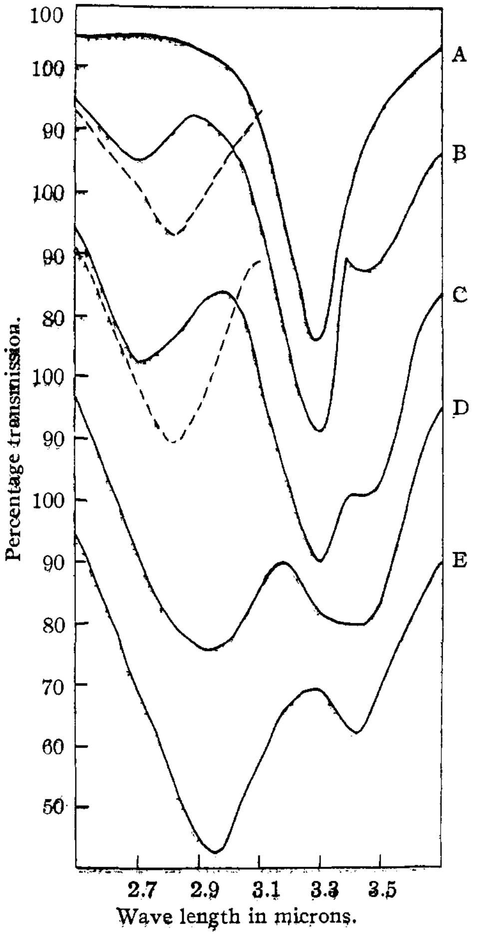
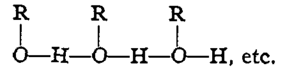


Fig. 1.—Transmission of methyl alcohol in nitrobenzene and in dioxane: A, pure nitrobenzene (thickness 0.01 cm.); B, solid line, 1% (by volume) methyl alcohol in nitrobenzene (thickness 0.01 cm.); broken line, 1% (by volume) methyl alcohol in dioxane (thickness 0.01 cm.); C, solid line, 4% (by volume) methyl alcohol in nitrobenzene (thickness 0.01 cm.); broken line, 4% (by volume) methyl alcohol in dioxane (thickness 0.01 cm.); D, 12% (by volume) methyl alcohol in nitrobenzene (thickness 0.006 cm.); E, pure methyl alcohol (thickness 0.001 cm.).

There may be two reasons why the hydrogen bonds between the alcohol and the solvent do not effect so great a shift to the longer wave lengths in the OH band as do the hydrogen bonds between alcohol molecules. In the first place the bonds between the alcohol and the solvent may be weaker. In the second place if, as is supposed, alcohol polymerizes into chains of more than two molecules as



$$\overset{\displaystyle R}{\overset{|}{O}}\text{—H—}\overset{\displaystyle R}{\overset{|}{O}}\text{—H—}\overset{\displaystyle R}{\overset{|}{O}}\text{—H, etc.}$$

both the O and the H of a single OH group would participate in the bond formation—that is, a single group would furnish both an acceptor and a donor, while, in the case of the association of an alcohol molecule with a molecule of the solvent, the donor would be provided by the solvent. However, if the above chain should contain only two alcohol molecules, no single OH group would be required to contribute both an acceptor and a donor, and thus the resulting longer wave length shift, as in the case of association of solute and solvent, may be less than for longer chains. In fact, Fox and Martin[10] have resolved the association band for some of the alcohols into two components and have suggested that the component nearer to the band of unimolecular OH may be due to double molecules. It may be proposed that the strong OH band which occurs at about 2.8 μ for alcohol in solvents like acetone[12] is due to double molecules of alcohol rather than to a single molecule of alcohol linked to a molecule of the solvent. This explanation, however, would require that a predominance of double alcohol molecules exists in dilute solutions in solvents of this type, an assumption which is not borne out by molecular weight measurements.

Experimental Procedure

For most of the measurements[15] a 60 rock salt prism of 7 cm. face was used, through which the light was made to pass twice in order to increase the dispersion. Further description of the instrument will be omitted, as instruments of this type have been discussed fully by other investigators.[16] Rock salt, mica, and fluorite were employed as cell windows. Mica washers were used to maintain cell thicknesses except in the cases in which the intense absorption prohibited the use of any washers. At each setting of the prism circle, galvanometer deflections were taken with the cell in and with the cell out of the beam, and the percentage transmission was taken as the ratio of the two readings. In all cases certified chemicals were used. Those chemicals which

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(15) The study of the water-methyl cyanide mixtures was made with a Hilger instrument equipped with a fluorite prism.

(16) D. S. McKinney, C. E. Leberknight and J. C. Warner, THIS JOURNAL, 59, 481 (1937); W. Dahlke, *Z. Instrumentenk.*, 57, 18 (1937).

take up water rapidly from the atmosphere were redried immediately before use.

Discussion of Results

The results reported here represent a continuation of the previous studies by the author on hydrogen bonds between unlike molecules.[12]

Although most of the cases of hydrogen bonding which are known are between the electronegative atoms, N, O, and F, the ability of these atoms to share a proton would depend upon their effective negative charges and hence upon the atoms or groups to which they already are attached. Recent infrared data[17] indicate that if phenol forms any hydrogen bonds with nitrobenzene they must be considerably weaker than those between phenol and dioxane. In Fig. 1 are given transmission curves for several different concentrations of methyl alcohol in nitrobenzene in the region of 3 μ. For the most dilute solutions the OH band appears at approximately 2.7 μ, the position of the band of the unassociated OH. For comparison, transmission curves of two concentrations of methyl alcohol in dioxane are given in the same figure. Figure 2 shows how the molal absorption coefficients of the OH band of the two solutions differ from those of the pure methyl alcohol. The absorption coefficient k is here defined as

$$k = \frac{1}{ct} \log \frac{I_0}{I}$$

where t represents the cell thickness in cm., c the concentration of the solution in moles per liter, I_0 the transmission of the pure solvent, and I the transmission of the solution.

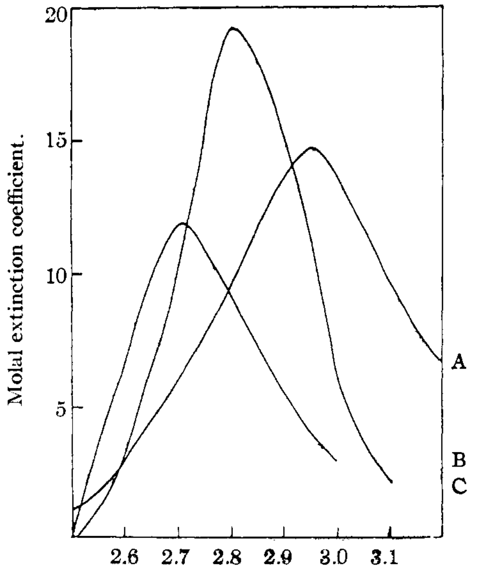

Fig. 2.—Molal extinction coefficients of methyl alcohol solutions: A, pure methyl alcohol; B, 0.98 mole/liter methyl alcohol in dioxane; C, 0.98 mole/liter methyl alcohol in nitrobenzene.

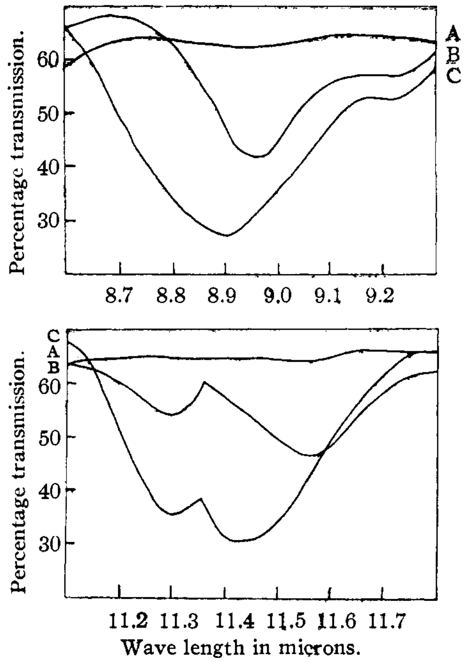

Fig. 3.—A, Transmission of pure water; B, transmission of 20% (by volume) dioxane in water; C, transmission of pure dioxane.

Water vapor has a strong fundamental with its center at 2.67 μ. In carbon disulfide solutions water bands occur at about 2.65 and 2.80 μ.[9] The band at 2.65 μ is probably caused by single or vapor-like molecules in the solution. It is possible that the 2.80 μ band is characteristic of double molecules, the 3 μ band in the pure liquid being indicative of a more highly polymerized form. In dilute solution in dioxane apparently there is only one band in this region, which occurs at about 2.8 μ.[18] Also this seems to be true for water in acetone.[19] Dioxane, like carbon disulfide, is non-polar, though it is different in that it possesses a donor and may form hydrogen bonds with the water. Hydrogen bonds formed with the dioxane oxygen would weaken the C–O bonds and, if the hydrogen bonds are sufficiently strong, should measurably affect the spectrum of the

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(17) W. Gordy and A. H. Nielsen, *J. Chem. Phys.*, in press.

(18) W. Gordy, *ibid.*, **4**, 769 (1936).

(19) D. Williams and E. K. Plyler, *ibid.*, **4**, 157 (1936).

dioxane. In this study the previous work on dioxane–water mixtures has been extended to the longer wave lengths in an effort to observe the effects of water on the dioxane spectrum. It will be evident from Fig. 3 that the strong dioxane bands at 8.9 and 11.43 μ are both shifted appreciably to the longer wave lengths in the dioxane–water mixtures. In these measurements there was some sodium chloride in the solution because of the necessity for using rock salt as cell windows in the longer wave length region.

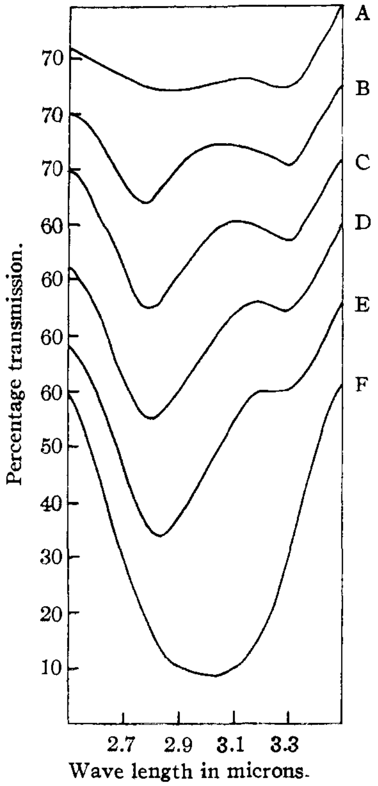

Fig. 4.—Transmission of water–methyl cyanide mixtures: A, pure methyl cyanide; B, 0.5% water (by volume); C, 2% water (by volume); D, 5% water (by volume); E, 10% water (by volume); F, pure water.

Methyl cyanide has a donor and may possibly form weak hydrogen bonds with hydroxyl compounds. This solvent has been found to produce variations in the OH band of methanol similar to those produced by oxygenated solvents like dioxane or acetone. It is one of the few liquids not absorbing appreciably in the region 2.6 to 3 μ which is miscible in all proportions with water. For this reason a study was made of the 3 μ water band for different concentrations of water in this solvent.[20] The results obtained are given in Fig. 4. The water band is shifted to the shorter wave lengths in the solutions and appears at about 2.78 μ for concentrations below 10 per cent. It will be noted that this limiting position of 2.78 μ appears at wave lengths longer than does the band for single molecules of water vapor, a fact which may indicate the formation of weak hydrogen bonds between the water and methyl cyanide. It may, however, be entirely a result of the rather high dielectric constant of methyl cyanide. Because of the overlapping of the broad 4.7 μ water band, a study of the effects of water on the CN vibrational band of methyl cyanide, which appears at 4.38 μ, was not found practical. If hydrogen bonds are formed with the water, as CH_3CN–HOH, the CN band should be shifted slightly to the longer wave lengths.

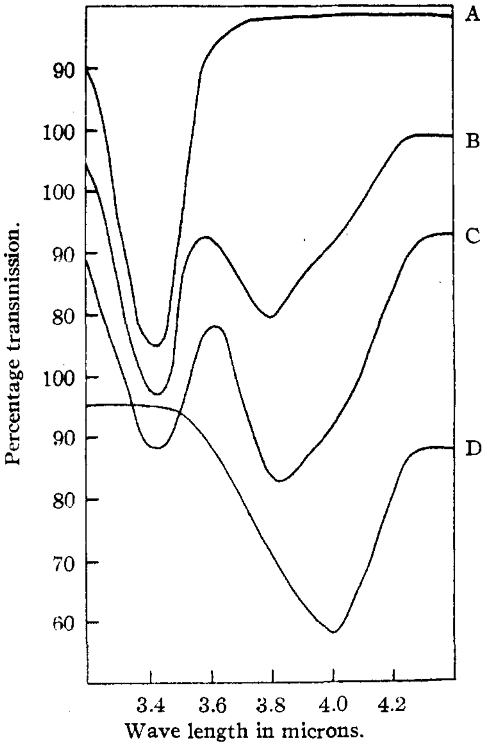

Fig. 5.—Transmission of deuterium oxide–dioxane mixtures: A, pure dioxane; B, 5% deuterium oxide (by volume); C, 20% deuterium oxide (by volume); D, pure deuterium oxide.

Solutions containing heavy water are of interest in this study because deuterium bonds are

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(20) The measurements on water–methyl cyanide mixtures were made in the Physics Laboratory of the University of North Carolina, and the writer is indebted to Dr. E. K. Plyler for the use of his laboratory facilities.

supposedly stronger than those of ordinary hydrogen.[21] Also measurements on heavy water solutions provide a partial check on the results obtained for solutions of ordinary water. The band of deuterium oxide corresponding to the 3 μ band of ordinary water appears at 4.0 μ.[22] Neither dioxane nor acetone absorbs appreciably in this region, and it is therefore possible to make a reasonably accurate study of the variations in the position of the 4 μ band in these solvents. However, because of the great intensity of the deuterium oxide band, which prevented the use of washers in making the cells, it was not possible to make a comparison of intensities. Results for this region are given in Figs. 5 and 6. The band which appears at 4 μ in the curve for pure deuterium oxide is shifted to about 3.8 μ in both of the solvents. While the shift here is to the shorter wave lengths, the maximum of absorption in these solutions appears at wave lengths longer by about 0.21 μ than does the fundamental of deuterium oxide vapor in this region, the center of which appears at 5.59 μ.[23]

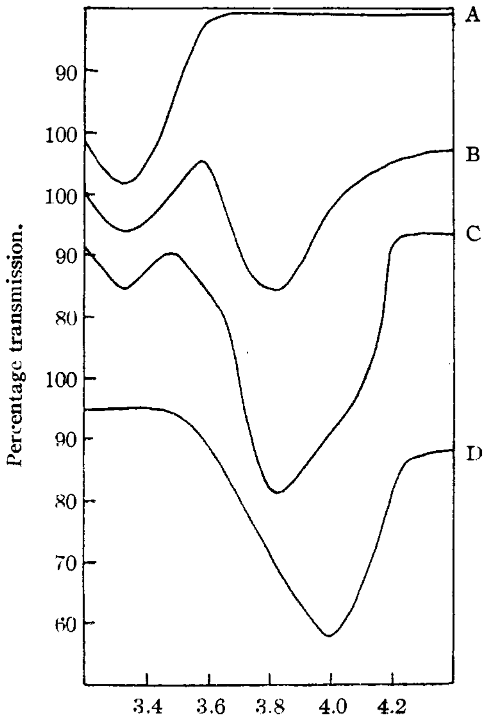

Fig. 6.—Transmission of deuterium oxide–acetone mixtures: A, pure acetone; B, 5% deuterium oxide (by volume); C, 20% deuterium oxide (by volume); D, pure deuterium oxide.

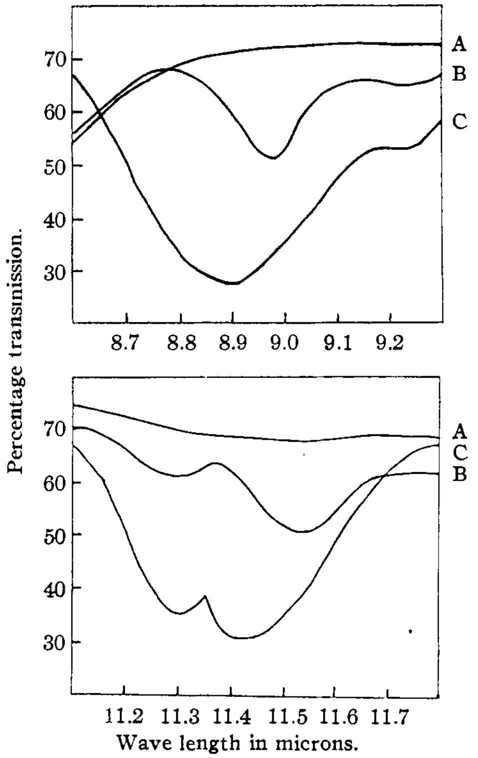

Fig. 7.—A, Transmission of pure deuterium oxide; B, transmission of 20% (by volume) dioxane in deuterium oxide; C, transmission of pure dioxane.

The effects of deuterium oxide on the two dioxane bands at 8.9 and 11.43 μ were found to be about the same as those of ordinary water (compare Figs. 7 and 3). Deuterium oxide produces an appreciable shift to the longer wave lengths of the C=O band of acetone, Fig. 8. Because of

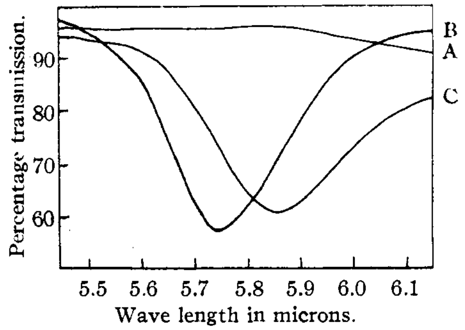

Fig. 8.—A, Transmission of pure deuterium oxide; B, transmission of pure acetone; C, transmission of 30% (by volume) of acetone in deuterium oxide.

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[21] G. N. Lewis and P. W. Schutz, THIS JOURNAL, **56**, 493 (1934).

[22] J. W. Ellis and B. W. Sorge, *J. Chem. Phys.*, **2**, 559 (1934).

[23] E. F. Barker and W. W. Slater, *ibid.*, **2**, 660 (1935).

the proximity of the 6.18 μ water band it was impossible to obtain reliable measurements on acetone–water mixtures in this region.

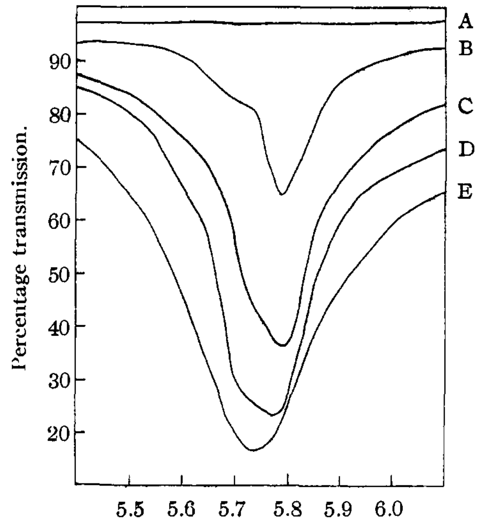

Fig. 9.—Transmission of chloroform–acetone mixtures: A, pure chloroform; B, 2.5% acetone (by volume); C, 10% acetone (by volume); D, 50% acetone (by volume); E, pure acetone.

The shift of the 4 μ band of liquid deuterium oxide to the shorter wave lengths in mixtures of heavy water with dioxane and with acetone, probably indicates the breaking of deuterium bonds between molecules of heavy water. The fact that the band occurs at wave lengths appreciably longer than the corresponding band of deuterium oxide vapor may be a result of the formation of deuterium bonds with the solvent. This interpretation would also account for the effects of the solute on the solvent, and is in accord with the results obtained for ordinary water and for alcohol in these solvents. If these are merely induction effects due to the internal field of the solvent, it is not clear why two solvents like dioxane and acetone should produce so nearly the same shifts in the OH band. Also it would seem that nitrobenzene, with its much greater dipole moment, would produce a greater diminution in the OH frequency than does dioxane. Actually the measurements on methyl alcohol in these two solvents indicate that the reverse is true.

Measurements[24] of vapor pressures, viscosities and dielectric constants show that mixtures of chloroform with liquids such as acetone or ether behave abnormally. Glasstone has shown that it is possible to explain these abnormalities by assuming that hydrogen bonds are formed, to some extent, between the CH hydrogen of the chloroform and the oxygen of the second liquid. An attempt has been made to obtain infrared data which may throw additional light on this problem. If hydrogen bonds are formed between the chloroform and solvent, the vibrational band of the chloroform CH would be shifted to the longer wave lengths. However, because of the strong overlapping CH bands of the solvents, measurements on this band would be uncertain. For this reason, the study was confined to the influence of chloroform upon the spectrum of the solvents. It was made upon mixtures of chloroform with acetone, ethyl acetate, ethyl ether, and dioxane. In the case of hydrogen bonds between chloroform and acetone, the most pronounced effects on the spectrum of the acetone should be those upon the C=O band which appears at 5.74 μ. Fortunately chloroform has no bands in this region, and hence it is possible to study the C=O band for dilute solutions of acetone in chloroform. The results which were obtained are given in Fig. 9. In the curves for the mixtures, the maximum of absorption appears at wave lengths longer by about 0.05 μ than it does in the curve for the pure acetone. The curves for the mixtures ap-

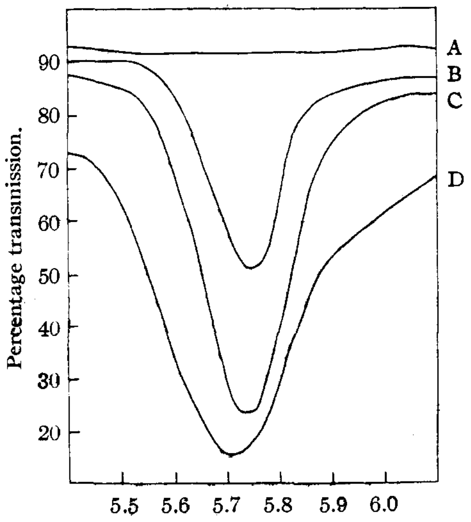

Fig. 10.—Transmission of chloroform–ethyl acetate mixtures: A, pure chloroform; B, 2.5% ethyl acetate (by volume); C, 10% ethyl acetate (by volume); D, pure ethyl acetate.

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[24] Macleod and Wilson, *Trans. Faraday Soc.*, **31**, 596 (1935); S. Glasstone, *ibid.*, **33**, 200 (1936).

pear to be double with one component unshifted. Chloroform also produces a longer wave length shift in the C=O band of ethyl acetate, Fig. 10. The shift, however, seems to be very slight, only about one-half that of the acetone band.

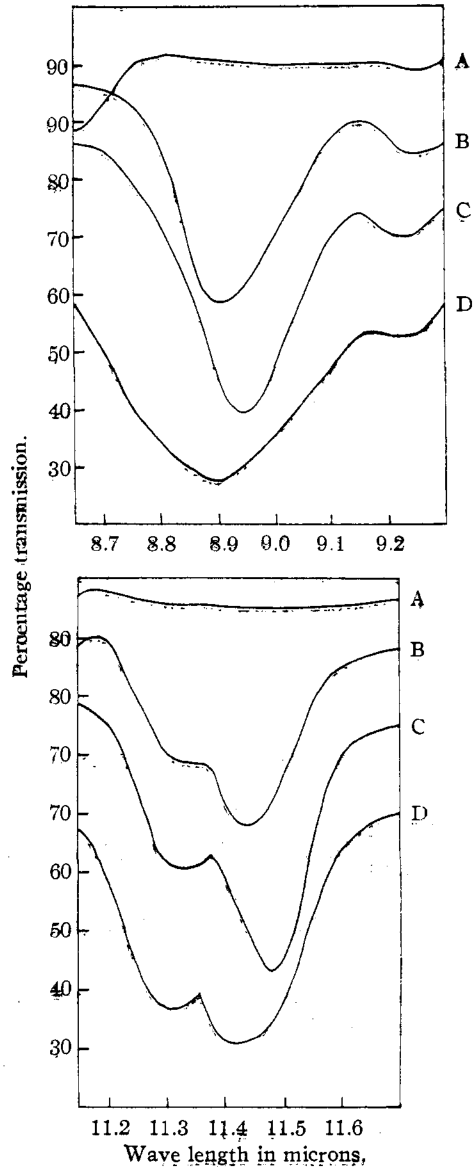

Fig. 11.—A, Transmission of pure chloroform; B, transmission of 20% (by volume) dioxane in carbon tetrachloride; C, transmission of 20% (by volume) dioxane in chloroform; D, transmission of pure dioxane.

Figure 11 shows the effects of chloroform upon the dioxane bands at 8.9 and 11.43 μ. Both of the bands are definitely shifted to the longer wave lengths in the chloroform solution. For purposes of comparison, in the same figure are given transmission curves for dioxane in carbon tetrachloride solution which show that carbon tetrachloride produces very little, if any shift in the dioxane bands.

The C–O band of liquid diethyl ether appears at 8.93 μ, bottom curve, Fig. 12. For 20% ether in chloroform the center of the band is shifted to 9.03 μ approximately, while for diethyl ether in carbon tetrachloride, its position remains very near that for the pure liquid ether.

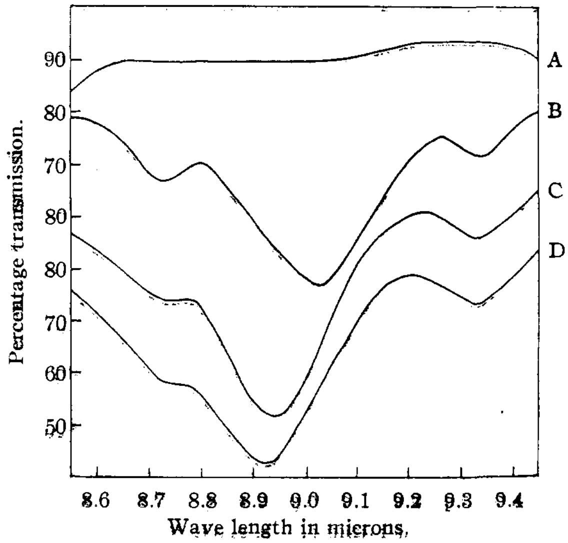

Fig. 12.—A, Transmission of pure chloroform; B, transmission of 20% (by volume) ethyl ether in chloroform; C, transmission of 20% (by volume) ethyl ether in carbon tetrachloride; D, transmission of pure ethyl ether.

Raman spectra studies have been made of equal mixtures of chloroform with acetone, ethyl acetate, and with ethyl ether. Effects similar to those reported here were found.[25]

Although these results alone do not prove that hydrogen bonds are formed between chloroform and these solvents, it is possible to account for them on that assumption. The shift produced in the C=O band of ethyl acetate is small and may be due wholly to the influence of the dielectric constant of chloroform. The more pronounced effects upon the spectrum of acetone and ether suggest the formation of definite bonds. A study of $CDCl_3$ in these solvents should be interesting; measurements could be made of the variations in the CD band, as it would not be overlapped by the CH bands of the solvents.

The writer is grateful to Dr. H. H. Nielsen for

(25) Dadieu and Kohlrausch, *Physik. Z.*, **31**, 514 (1930).

the use of his laboratory facilities and for his helpful suggestions, and to Dr. Alpheus W. Smith for his support of this work.

Summary

Transmission curves for several different concentrations of methyl alcohol in nitrobenzene are given for the region 2.5 to 3.7 μ, and the effects of nitrobenzene on the OH band are compared with those of other solvents. The effects of hydrogen bonding on the OH band are discussed.

A study has been made of mixtures of water with methyl cyanide, and previous work on dioxane–water mixtures has been extended to longer wave lengths.

Evidence for the formation of deuterium bonds between deuterium oxide and acetone and between deuterium oxide and dioxane has been obtained from observations of the spectra of mixtures of these liquids.

Chloroform has been found to produce shifts to lower frequencies of certain bands of acetone, ethyl acetate, ethyl ether and dioxane. The possibility of the formation of hydrogen bonds between chloroform and these liquids is discussed.

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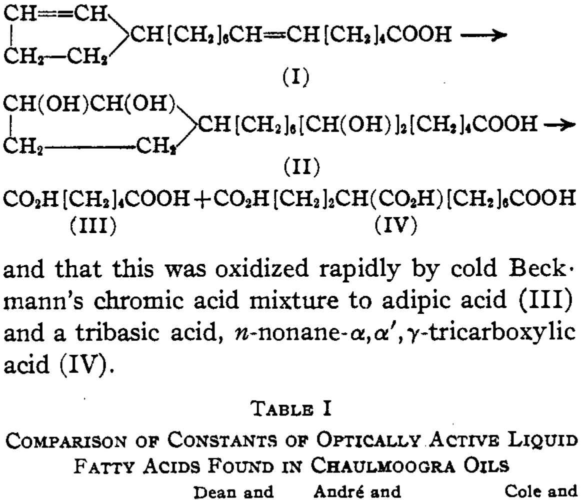
[CONTRIBUTION FROM THE INTERNATIONAL LEPROSY CENTER, RIO DE JANEIRO]

Isolation and Properties of Gorlic Acid, an Optically Active Liquid Fatty Acid

BY HOWARD IRVING COLE AND HUMBERTO T. CARDOSO

In the course of analyzing chaulmoogra oils, several investigators have mentioned a liquid fatty acid fraction apparently containing an optically active fatty acid with a high iodine number, indicating the presence of two double bonds. Thus Dean and Wrenshall[1] obtained from a "chaulmoogra oil" a liquid acid having the constants shown in Table I. It gave no solid bromide and yielded dihydrochaulmoogric acid upon hydrogenation. They concluded that an acid $C_{18}H_{30}O_2$, corresponding to chaulmoogric acid but with a second double bond located in the side chain, was present. In 1928 André and Jouatte[2] reported the presence of an acid with similar characteristics in *Oncoba echinata* oil (Table I) and although they were unable to purify it completely they named it gorlic acid after the native name for *O. echinata* oil, "Gorli" oil. Recently Paget[3] found in *Carpotroche brasiliensis* (sapucainha) oil a liquid fatty acid which he named dehydrochaulmoogric acid and which he showed was similar to that obtained by Dean and Wrenshall. He makes no reference to the gorlic acid of André and Jouatte. Although he also did not obtain it pure (Table I) he was able to characterize it definitely by means of its hydrogenation and oxidation products as an acid corresponding to chaulmoogric acid with one extra double bond located in the side chain between the fifth and sixth carbon atoms (formula I). Its relation to chaulmoogric acid was proved by the fact that dihydrochaulmoogric acid was obtained upon hydrogenation. The position of the second double bond in the side chain was shown by the fact that oxidation with permanganate yielded a tetrahydroxydihydrochaulmoogric acid (II)



$$\begin{matrix}CH{=}CH \\ | \\ CH_2{-}CH_2\end{matrix}\!\!>CH[CH_2]_6CH{=}CH[CH_2]_4COOH \longrightarrow$$

(I)

$$\begin{matrix}CH(OH)CH(OH) \\ | \\ CH_2{-\!\!-\!\!-\!\!-}CH_2\end{matrix}\!\!>CH[CH_2]_6[CH(OH)]_2[CH_2]_4COOH \rightarrow$$

(II)

$$\underset{\text{(III)}}{CO_2H[CH_2]_4COOH} + \underset{\text{(IV)}}{CO_2H[CH_2]_2CH(CO_2H)[CH_2]_6COOH}$$

and that this was oxidized rapidly by cold Beckmann's chromic acid mixture to adipic acid (III) and a tribasic acid, *n*-nonane-α,α',γ-tricarboxylic acid (IV).

TABLE I

COMPARISON OF CONSTANTS OF OPTICALLY ACTIVE LIQUID FATTY ACIDS FOUND IN CHAULMOOGRA OILS

	Dean and Wrenshall	André and Jouatte	Paget	Cole and Cardoso
Source of oil	Commercial chaulmoogra	*Oncoba echinata*	*C. brasiliensis*	*C. brasil.* and *O. echinata*
Sp. gr. 25/25	0.9322	0.9364^{15}	...	0.9436
Ref. index, $n^{25}D$	1.4745	1.4783	...	1.4782
Sp. rotation, $[\alpha]^{25}D$	+53.1	+50.3	+45	+60.7
B. p. (10 mm.), °C.	....	....	...	232.5
M. p., °C.	....	....	Below 5	6
Acid value	201.2	....	198	201.8
Mol. wt.	278.9	....	...	277.8
Iodine no. (Hanus)	180.4 (Hubl)	169.6	138	179.7

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(1) Dean and Wrenshall, THIS JOURNAL, **42**, 2626 (1920); *U. S. Pub. Health Reports, Bull.*, **141**, 15 (1924).

(2) André and Jouatte, *Bull. soc. chim.*, **43**, 347 (1928).

(3) Paget, *J. Chem. Soc.*, 955 (1937).