

The Infrared Absorption of Alcohol-Acetone Mixtures

WALTER GORDY,* *Department of Physics, University of North Carolina, Chapel Hill, North Carolina*

(Received October 12, 1936)

Several mixtures of methyl alcohol and acetone have been studied in the region 2.5μ to 8.5μ . The acetone was found to shift the OH vibrational band of alcohol to the shorter wave-lengths and to increase appreciably its intensity; the effects of the alcohol on acetone were to increase the intensity of the vibrational band of the CO group and to shift it to the longer wave-lengths. No other bands were measurably affected. The results indicate association of the alcohol and acetone through interaction of the OH and CO groups. The possibility of the formation of proton bonds is suggested.

INFRARED absorption studies¹ of aqueous and alcoholic solutions of inorganic acids, hydroxides and salts have revealed bands which indicate molecular association between the solvent and the solute molecules. More recently infrared studies² have been made of mixtures of water and some organic liquids. The present work on alcohol-acetone mixtures was undertaken to ascertain the influence of each liquid on the spectrum of the other in various mixtures of alcohol and acetone.

A Hilger infrared spectrometer with a fluorite prism was used as a resolving instrument throughout the investigation. Cell windows were of fluorite, and the absorbing layer was maintained at a constant thickness of 0.002 cm by mica washers. The chemicals were Baker's analyzed. The methyl alcohol was dried for several hours over CaO, and the acetone over CaCl₂ as an additional precaution against the presence of water in the samples.

A study was made of the 2.9μ alcohol band and of the acetone bands appearing at 5.73μ and at 8.17μ for several methyl alcohol-acetone mixtures. Fig. 1 shows the transmission curves for methyl alcohol and acetone and for four methyl alcohol-acetone mixtures in the region 2.5μ to 3.15μ . The broad band appearing in the region of 2.9μ in the methyl alcohol curve is characteristic of all alcohols, and arises from changes in

the vibrational energy of the OH group. For alcohol concentration of 12 percent and below, this band appears at 2.75μ , having been shifted to the shorter wave-lengths by 0.15μ . In addition to the shift to higher frequencies, the intensity of the OH band is increased appreciably. That is, the intensity of the band does not decrease in proportion to the decrease in the number of absorbers. As the alcohol concentration is increased to 25 percent and to 50 percent, the band approaches that for pure alcohol. It may be that the bands for these concentrations are made up of two components with maximum of absorption at 2.75μ and 2.9μ . However, the bands are very broad, and it was not found possible to resolve them into two components. Fig. 2 shows the effects of alcohol on the vibrational band of the CO group of acetone. In contrast to the shift to the shorter wave-lengths of the OH alcohol band, the effect of the alcohol on the acetone is to shift the CO band to the longer wave-lengths. This shift is accompanied by an increase in intensity, as was the case of the OH alcohol band.

To show that the above mentioned variations of the OH and CO bands are not merely apparent effects due to the superposition of alcohol and acetone absorption, theoretical curves have been computed for mechanical mixtures in which no interaction occurs. In Figs. 3 and 4 these curves are shown in comparison with the experimental curves for the same mixtures. We have assumed that the transmission of the mixture for a given frequency is

$$T = e^{-f_1 m_1 - f_2 m_2},$$

where f_1 and f_2 are the fractional parts of alcohol

* Now at Mary Hardin-Baylor College.

¹ E. K. Plyler and W. Gordy, *J. Chem. Phys.* **2**, 470 (1934); E. K. Plyler and E. S. Barr, *J. Chem. Phys.* **2**, 306 (1934); E. K. Plyler and F. D. Williams, *J. Chem. Phys.* **2**, 565 (1934).

² D. Williams and E. K. Plyler, *J. Chem. Phys.* **4**, 154 (1936); D. Williams, R. D. Weatherford and E. K. Plyler, *J. Opt. Soc. Am.* **26**, 149 (1936).

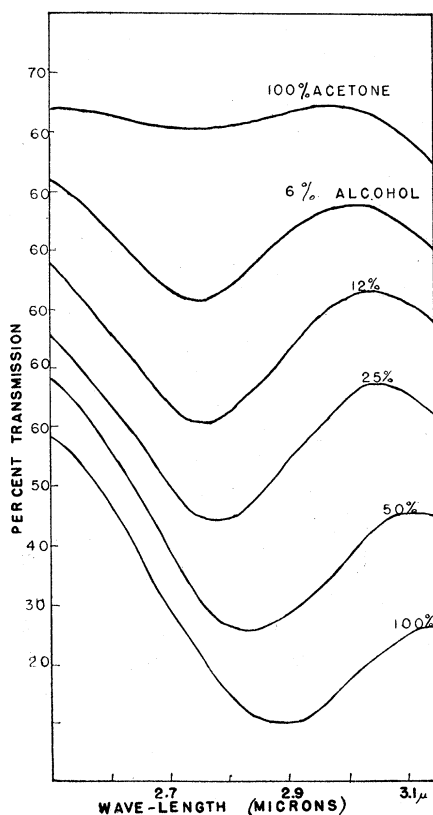


FIG. 1. The percent transmission of alcohol and acetone and alcohol-acetone mixtures in the region 2.5μ to 3.15μ .

and acetone, respectively, and where m_1 and m_2 are defined by

$$T_1 = e^{-m_1}, \quad T_2 = e^{-m_2},$$

T_1 and T_2 being the transmission of pure alcohol and pure acetone, respectively, for the given wave-lengths. It should be remembered that the cell thickness was the same in all cases.

From Fig. 5, which gives the absorption of several alcohol-acetone mixtures in the region 7.85μ to 8.45μ , it will be seen that the strong acetone band appearing at about 8.17μ , bottom curve, apparently is not shifted in position for any of the mixtures, nor is its intensity appreciably increased as was the case of the CO acetone band and the OH alcohol band. A curve was obtained for 6 percent acetone in alcohol which is not included in the figure. The intensity of the band was so low that the position of maximum absorption could not be ascertained.

An attempt was made to study other bands in the region 2.5μ to 9μ , but because of the overlapping of alcohol and acetone bands no definite results could be obtained. A study was made of the effects of benzene on the CO acetone band for concentrations of acetone in benzene varying from 50 percent to 6 percent. There appeared to be no shift in the CO band for any of the concentrations. A similar study was made of the effects of benzene on the OH band of alcohol. Likewise, no measurable shift was observed in the OH band, although there appeared for low alcohol concentrations a slight depression on the short wave-length side of the band, which may indicate the presence of vapor-like molecules of alcohol. Evidence for vapor-like molecules of alcohol in carbon tetrachloride solutions has been reported by Kinsey and Ellis.³

The pronounced changes in the electric moments of the CO and OH groups of acetone and alcohol indicate dipole interaction. It may be

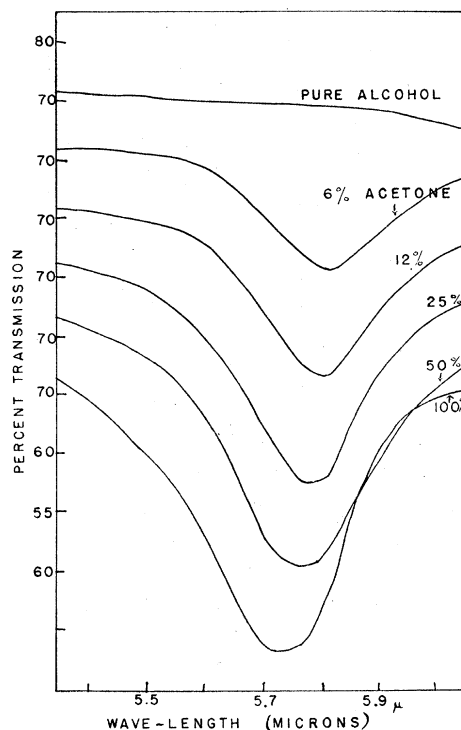


FIG. 2. The percent transmission of alcohol and acetone and alcohol-acetone mixtures in the region 5.35μ to 6.05μ .

³ E. L. Kinsey and J. W. Ellis, Phys. Rev. **49**, 105 (1936).

that we have here the formation of proton bonds, the hydrogen of the OH group being shared between the oxygen of the two groups. This

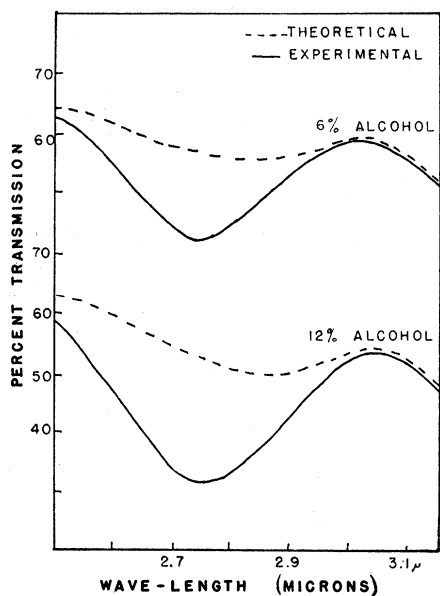


FIG. 3. Theoretical and experimental transmission of alcohol-acetone mixtures in the region 2.5μ to 3.15μ .

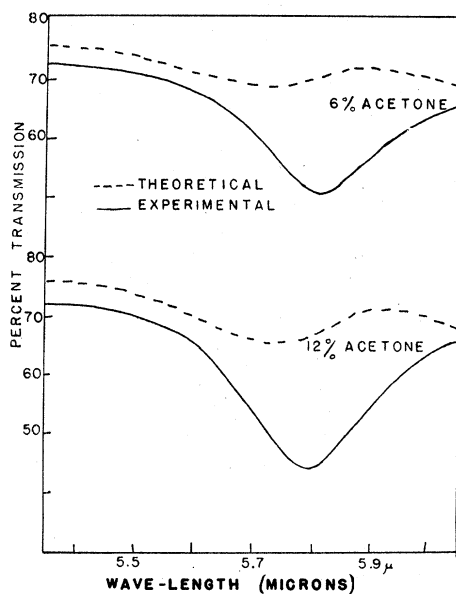


FIG. 4. Theoretical and experimental transmission of alcohol-acetone mixtures in the region 5.35μ to 6.05μ .

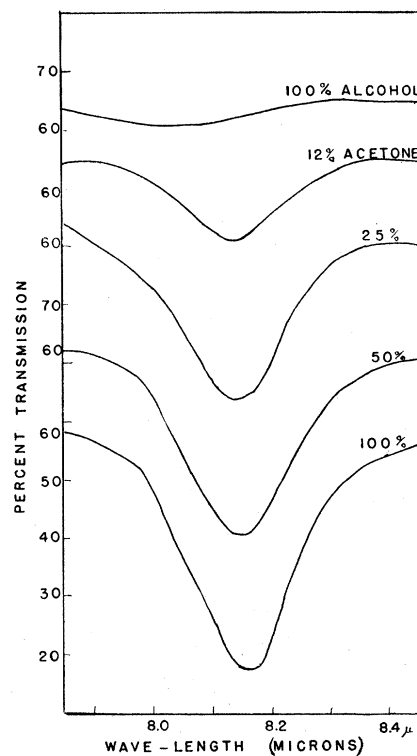


FIG. 5. The percent transmission of alcohol-acetone mixtures in the region 7.85μ to 8.45μ .

would account for the extreme changes in the polarization of these groups. Similar results⁴ indicating dipole interaction in dioxane-water, methyl cyanide water, acetone-water mixtures and in mixtures of aniline with several other organic liquids may be explained by the proton bond theory. This theory has received other emphasis recently.⁵ Abnormal results obtained in dielectric constant measurements of liquid mixtures are likely due to similar changes in the electric moments of certain groups which may be observable by infrared absorption measurements. The work is being continued.

The writer wishes to thank Dr. E. K. Plyler for the use of his instrument and Dr. J. A. Wheeler for suggesting a convenient method of making the theoretical computations.

⁴ Unpublished data obtained by the author.

⁵ L. Pauling, *J. Amer. Chem. Soc.* **57**, 2680 (1935); **58**, 94 (1936); L. Onsager, *J. Am. Chem. Soc.* **58**, 1486 (1936).