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# The Infrared Absorption of Various Solutions of Acetic Acid

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The characteristic vibrational band associated with the C=O group of acetic acid has been studied as a function of concentration of acetic acid in benzene, in carbon tetrachloride, and in isopropyl ether. The effects of benzene and carbon tetrachloride on the band were approximately the same. In both solvents the band became sharper, its intensity was increased, and its center was shifted to the longer wave-lengths. For concentrations of acetic acid as low as 6 percent the shift amounted to 0.15μ. Although in isopropyl ether solution there was a measurable shift of the band to the longer wave-lengths, the shift was small compared to that observed for benzene and carbon tetrachloride solutions. It is suggested that the changes in the C=O acetic acid band are likely due to variations in the polymerization of the acetic acid as the concentration is varied. However, the position of the band does not approach that for the vapor state in any of these solvents. Ethyl acetate was also studied in benzene and in isopropyl ether; no shifts could be detected in the C=O band.

CHEMICAL data[1] indicate that acetic acid in dilute solutions in benzene has a molecular weight equal approximately to that which it would have if polymerized into double molecules. In ether solution, however, acetic acid is thought to exist as double and as single molecules. Latimer and Rodebush[2] were the first to suggest that the association of acetic acid is due to the formation of hydrogen bonds. This theory has more recently been confirmed by other workers.[3] X-ray studies[4] support the theory that the acetic acid molecules are joined end to end through their carboxyl groups. It is thought that two molecules of the acid are joined by a pair of hydrogen bonds to form the monoplaner ring

$$CH_3-C \begin{matrix} O-H-O \\ \diagup \quad \diagdown \\ \diagdown \quad \diagup \\ O-H-O \end{matrix} C-CH_3.$$
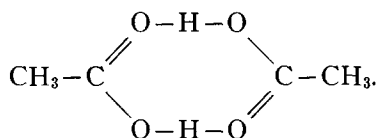
If the acetic acid molecules are joined in this manner by hydrogen bonds, the infrared band associated with the C=O group would be affected and it should be possible to detect any changes in the association of the acid through measurements of this band.

In the present work a study has been made of the vibrational band of the C=O group of acetic acid as the concentration is varied in benzene, carbon tetrachloride, and isopropyl ether. For purposes of comparison a similar study was made of the C=O group of ethyl acetate for the same concentrations of ethyl acetate in benzene and in isopropyl ether. Transmission curves of pure acetic acid, of pure benzene, and of several solutions of different concentrations of acetic acid in benzene are shown in Fig. 1. The center of the C=O band in the pure acetic acid curve appears at 5.75μ. In benzene solution the band is slightly sharpened and is shifted to the longer wave-lengths. In the curve for 3 percent acetic acid the center of the band appears at 5.9μ. In addition, the intensity of the band is in-
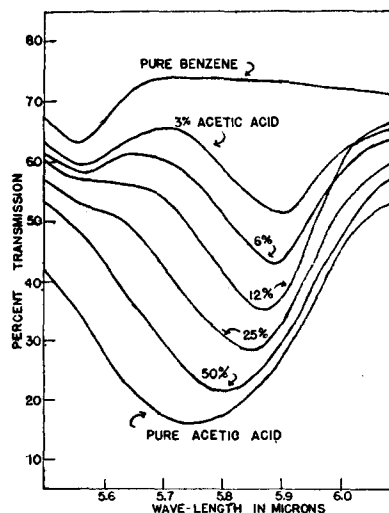
* Now at Mary Hardin-Baylor College.
[1] C. P. Smith, *Dielectric Constant and Molecular Structure* (Chemical Catalog Company, New York, 1931) p. 173.
[2] W. M. Latimer and W. H. Rodebush, J. Am. Chem. Soc. 42, 1419 (1920).
[3] Pauling and Brockway, Proc. Nat. Acad. Sci. 20, 336 (1934).
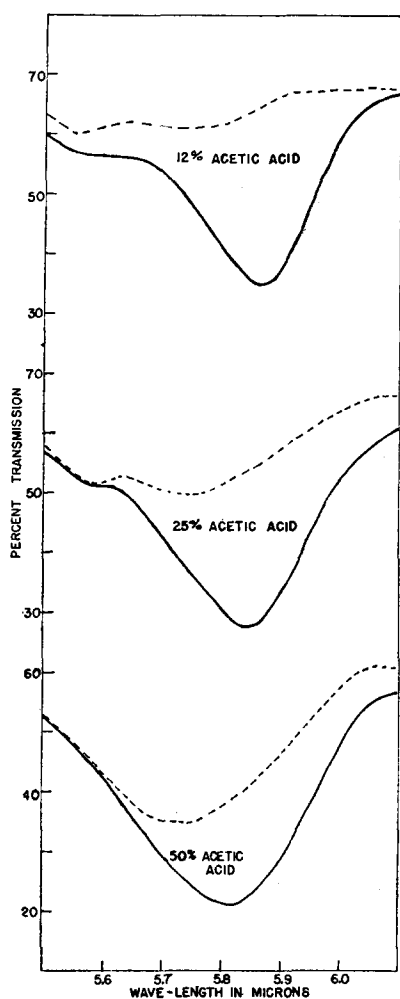[4] R. M. Morrow, Phys. Rev. 31, 10 (1928).



Fig. 1. Percentage transmission of acetic acid, of benzene, and of some acetic acid-benzene mixtures.

FIG. 2. Theoretical (dotted line) and experimental (solid line) transmission of acetic acid-benzene mixtures.
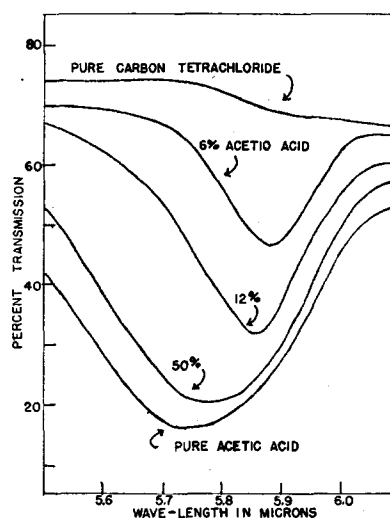


FIG. 3. Percentage transmission of acetic acid, of carbon tetrachloride, and of some acetic acid-carbon tetrachloride mixtures.



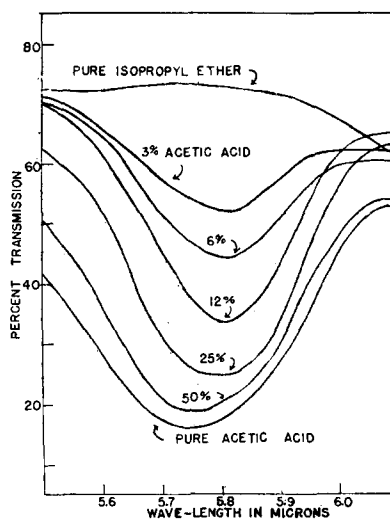FIG. 4. Percentage transmission of acetic acid, of isopropyl ether, and of some acetic acid-isopropyl ether mixtures.

creased. It is advantageous to compare the transmission observed for some of these mixtures with that which would be expected if no chemical change should take place in either of the liquids and if neither component should influence in any way the spectrum of the other. Theoretical curves have been computed on the assumption that the absorption coefficient for the mixture at a given frequency is equal to a suitably weighed mean of the absorption coefficients of pure benzene and of pure acetic acid for the same frequency. These are compared with the experimental curves in Fig. 2. The method used in computing the theoretical curves has been given in a previous paper.[5] It is interesting to note

[5] Walter Gordy, Phys. Rev. **50**, 1151 (1936).

that the variations in the $C=O$ band are very much the same when the solvent is carbon tetrachloride as when the acid is dissolved in benzene. This will be made evident by a comparison of the transmission curves for the same concentrations of acetic acid in these two solvents, Figs. 1 and 3.

If, as is generally believed,[1] acetic acid in ether solution exists in both dimeric and monomeric forms, one would expect the variations in the $C=O$ band when the acetic acid is dissolved in ether to differ markedly from the variations of
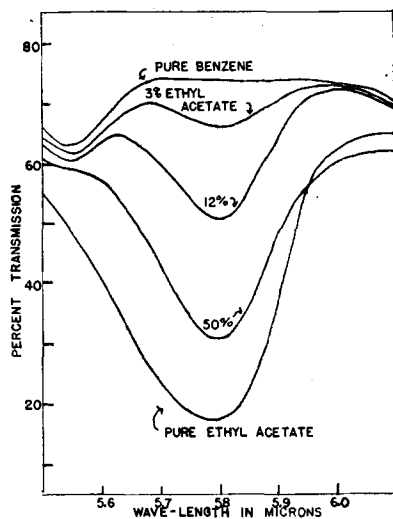
Fig. 5. Percentage transmission of ethyl acetate, of benzene, and of some ethyl acetate-benzene mixtures.



Fig. 6. Percentage transmission of ethyl acetate, of isopropyl ether, and of some ethyl acetate-isopropyl ether mixtures.

this band when the solvent is benzene, since in benzene, even in very dilute solutions, the acetic acid molecules are thought to be dimeric. Fig. 4 shows the effects of the isopropyl ether on the C=O acetic acid band. Although there is a shift to the longer wave-lengths, the shift is not as great as is the shift for acetic acid in benzene and in carbon tetrachloride. Furthermore, the band is broader for the lower concentrations in ether solution.

The shifts and marked intensity changes observed in the vibrational band of the carbonyl group of acetic acid when the acid is dissolved in benzene and in isopropyl ether apparently are not produced by these solvents upon the carbonyl band of ethyl acetate. There appears to be, nevertheless, a slight increase in the intensity of the band. Transmission curves showing the C=O ethyl acetate band and the effects of benzene and isopropyl ether on this band are given in Figs. 5 and 6. In Fig. 7 is given a comparison of the observed curves for two different ethyl acetate-benzene mixtures with the theoretical curves for the same mixtures.

The hydroxyl group not being present in ethyl acetate, it would not be possible for this substance to be polymerized through the formation of hydrogen bonds, as is acetic acid. Since the shifts of the C=O band in solutions of acetic acid were not observed for solutions of ethyl acetate, it seems likely that the shifts in the
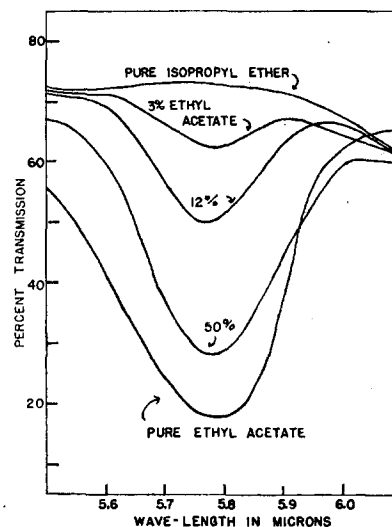
acetic acid band are due to variations in the association process. The shifts, being to the longer wave-lengths, do not indicate the formation of vapor-like molecules as has been reported for water and alcohol in nonpolar solvents.[6] Gillette and Daniels[7] obtained a shift of the C=O acetic acid band to the shorter wave-lengths as the acid was made to approach the vapor state
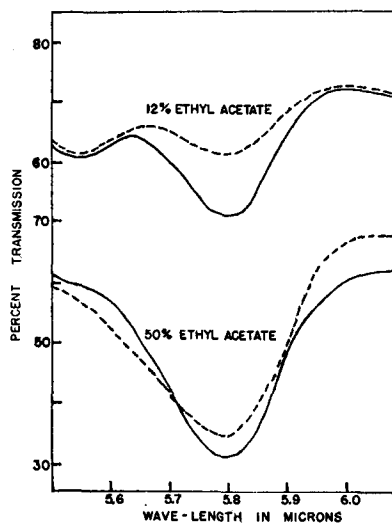


Fig. 7. Theoretical (dotted line) and experimental (solid line) transmission of ethyl acetate-benzene mixtures.

[6] E. L. Kinsey and J. W. Ellis, Phys. Rev. 49, 105 (1936).
[7] R. H. Gillette and F. Daniels, J. Am. Chem. Soc. 58, 1139 (1936).

through an increase of temperature. At a temperature of 172°C, at which, under the conditions of their experiment, the molecules were thought to exist principally as monomers, these observers reported the frequency of the band to be 1786 cm⁻¹. This frequency corresponds to a wavelength of 5.6μ. In the present work, it will be recalled, the position of the band was found to be 5.75μ for the pure liquid and 5.9μ for dilute solutions of the acid in benzene and in carbon tetrachloride. If, as is generally believed, the molecules exist principally as dimers in the dilute solutions, the difference in position and appearance of the band in the more concentrated solutions and in the pure liquid acid may indicate the presence of a more complex form.

The writer wishes to express his gratitude to Dr. E. K. Plyler for the use of his laboratory facilities and to Dr. B. G. Carson for his helpful suggestions.

# The Raman Spectra of Deuteroparaldehyde and Paraldehyde

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RAMAN spectra of deuteroparaldehyde were obtained with material prepared by Professor E. Zanetti of Columbia University. A little over 1 cc was available sealed in a quartz tube furnished with a ground and polished window. As it seemed advisable to have spectra of ordinary paraldehyde made with the same instrumental equipment, a very pure sample was prepared and distilled into a tube of Pyrex glass of the same type. This was of some importance, as there is not complete agreement between the values obtained by Petrikaln and Hochberg, Venkateswaran and Bhagavantam and others.

The technique which I now employ in making spectrograms of the Raman effect differs from that which I have previously described, and is very superior in many ways. The same apparatus can be used for large or very small quantities of fluid, requires no auxiliary cooling devices, and enables one to excite the radiation either by the total light of the quartz mercury arc, or by 4358 or 4046 alone. A Hanovia mercury arc in its metal housing is turned on its trunnions into the vertical position, and a glass tube, 5 cm in diameter and 50 cm high (closed at the bottom) is mounted about 6 cm in front of the vertical aperture through which the light of the arc emerges. This tube is half-filled with water or an absorbing solution, and serves both as a cylindrical lens and ray filter. It is closed at the top with a cork to prevent evaporation, the vapor condensing on the wall and running down. The liquid under observation is contained in a tube of the form which I have previously described in numerous papers, shown in Fig. 1.

This is mounted in such a position that the mercury arc is focused along its axis, and a concave cylindrical mirror of thin and highly polished aluminum (now obtainable commercially) is attached to the rear wall as shown. The light emerging from the window at the bottom is reflected by a right angle prism and focused on the slit of the spectrograph by an achromatic lens of about 20 cm focus mounted at a distance of 2 meters from the prism. This arrangement insures that all parts of the illuminated column of liquid are in good focus, and no light scattered by the wall of the tube enters the spectrograph. The reflecting prism is held between two stiff brass clips, and can be rocked in the vertical plane or rotated on a vertical axis into such a position that the reflected image of the illuminated fluid column is exactly horizontal and in line with the axis of the collimator of the spectrograph. In some cases a flat tube filled with a strong solution of praeseodymium is inserted between the large tube and the irradiation tube. A certain brand of tooth brush is supplied in a