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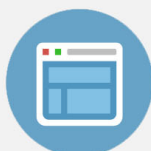
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## The Infrared Absorption Spectra of Mixtures of Acetone and Water

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A study of the infrared absorption spectra of acetone containing water revealed an associational band in the region  $2.7\mu$ . This band was studied for concentrations of water varying from 0.5 percent to 70 percent by weight. The intensity of the associational band increased with the

water content of the mixture. When the water content was large, the  $3\mu$  water band overlapped the associational band. Absorption spectra were obtained for ten mixtures. It was found that concentrations of water as low as 0.1 percent could be detected by the presence of this band.

IN previous infrared absorption studies<sup>1</sup> of aqueous solutions of several acids and bases, certain bands were observed which were not characteristic of either the pure solvent or solute. These bands were interpreted as arising from hydration effects in the solutions. The absorption spectra of alcoholic solutions of hydroxides were found to contain similar bands.<sup>2</sup> The presence of these solvation bands in the spectra of these two types of solutions suggested the possible existence of associational bands in still other types of solutions and mixtures.

Fajans<sup>3</sup> has applied the first law of thermodynamics to the problem of thermal effects in the formation of solutions. His work shows that in aqueous solutions the heat of hydration of the ions makes up the greater part of the total heat of solution. In the case of nonionizing solvents, the heat of solution is probably due to solvation effects. These results indicate that substances generating heat on mixing should have absorption bands arising from their associational energies. If these energies are of sufficient magnitude, the resulting absorption would be expected to occur in the near infrared.

In tests on several mixtures it was found that the addition of a small amount of water to acetone resulted in a rise of temperature of several degrees. The absorption spectra of various mixtures of acetone and water were investigated and the results are discussed below. The methods of measurement have been previously described.<sup>4</sup>

The absorption of a sample of Baker's absolute acetone was studied in the region from  $1.0\mu$  to  $6.5\mu$ . Intense bands were observed at  $3.3\mu$  and  $5.8\mu$ , and weaker bands at  $1.4\mu$ ,  $2.1\mu$ ,  $2.7\mu$ , and  $4.7\mu$ . This absorption curve is shown in Fig. 1. The second curve of Fig. 1 shows the absorption of a mixture of nine parts of acetone to four parts of water. The small band at  $2.7\mu$  in the first curve appears with greatly increased intensity in the second curve. The water bands at  $4.7\mu$  and  $6.2\mu$  were also observed in the mixture. It should be noted that the intense absorption in the region of  $2.9\mu$  in the second curve is due in part to the  $3\mu$  water band.

These radical changes in the spectra indicated that the absorption at  $2.7\mu$  was possibly due to an associational effect in mixtures of acetone and water. In order to examine the absorption in this region in a more detailed manner, it was decided to measure this absorption with various known concentrations of water in acetone. In order to obtain water-free acetone for use in this investigation a sample of Baker's chemically pure acetone was dried for three days over  $\text{CaCl}_2$  and then distilled in a system with drying tubes. Several concentrations varying from 0.5 percent to 70 percent by weight of water were prepared and sealed in dry bottles until needed. The fluorite windows used for the cells were kept in a desiccator with  $\text{P}_2\text{O}_5$  for several hours before being used.

In Fig. 2 are shown the results obtained in the region from  $2.3\mu$  to  $3.5\mu$ . The concentrations of water in the mixtures used for these curves vary from zero percent to 70 percent. The first curve, which represents the transmission of the supposedly absolute acetone, shows a slight absorption at  $2.7\mu$ , indicating the presence of a small amount of water, which was probably

<sup>1</sup> E. K. Plyler and E. S. Barr, *J. Chem. Phys.* **2**, 306 (1934). E. K. Plyler and W. Gordy, *J. Chem. Phys.* **2**, 470 (1934).

<sup>2</sup> E. K. Plyler and F. D. Williams, *J. Chem. Phys.* **2**, 565 (1934).

<sup>3</sup> H. S. Taylor, *Treatise on Physical Chemistry* (D. Van Nostrand Co., 1930), p. 334.

<sup>4</sup> W. Gordy and D. Williams, *J. Chem. Phys.* **3**, 664 (1935).

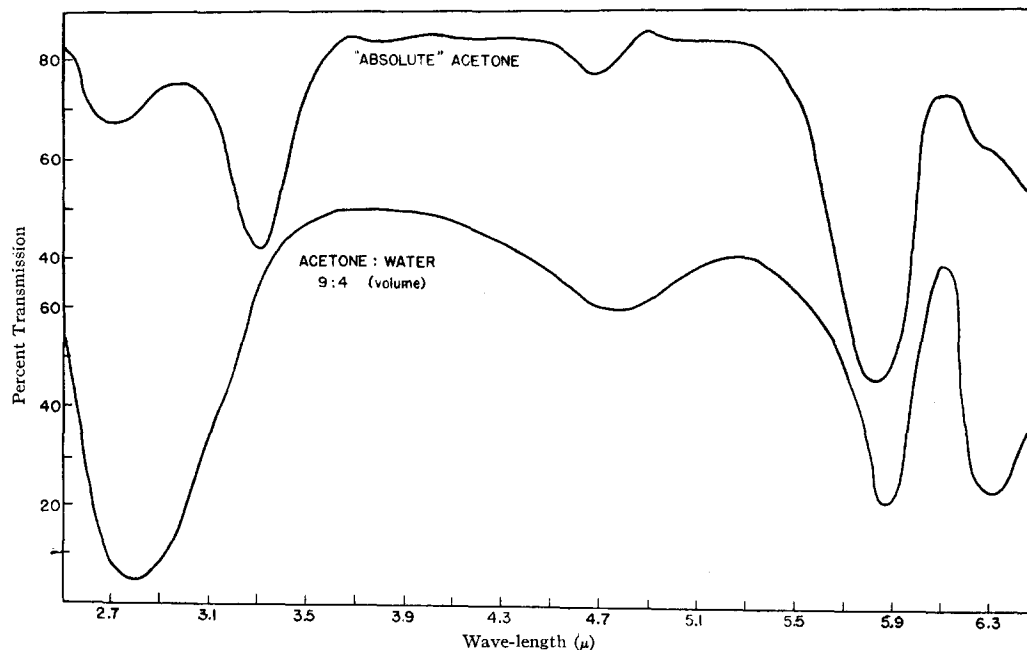


FIG. 1. The transmission of "absolute" acetone and a water-acetone mixture from  $2.5\mu$  to  $6.5\mu$ . Cell thickness: 0.03 mm.

absorbed from the air while the cell was being prepared. The curves for 5 percent and 10 percent water show clearly the associational band at  $2.7\mu$  and also the acetone band at  $3.3\mu$ . The absorption curves for the higher concentrations of water do not show two distinct bands on account of the absorption of water at  $3\mu$ . This water band is predominant for the 50 and 70 percent solutions of water. At these concentrations the band actually observed is broad and intense, extending from  $2.5\mu$  to  $3.4\mu$ , and arises from the combined absorption of the water, the acetone, and the associated molecules.

In Fig. 2 the absorption curve for the 5 percent concentration of water shows that the intensity of the  $2.7\mu$  associational band is greater than that of the  $3.3\mu$  acetone band. This suggested the possibility of using this associational band for detecting the presence of small amounts of water in acetone. In Fig. 3 are shown the transmission curves for low concentrations of water in acetone. A freshly prepared sample of absolute acetone was used for comparison, and no appreciable absorption was observed in the region of  $2.7\mu$ . At a concentration of 0.5 percent water, a strong associational band appeared, and the intensity of this band increased with increasing

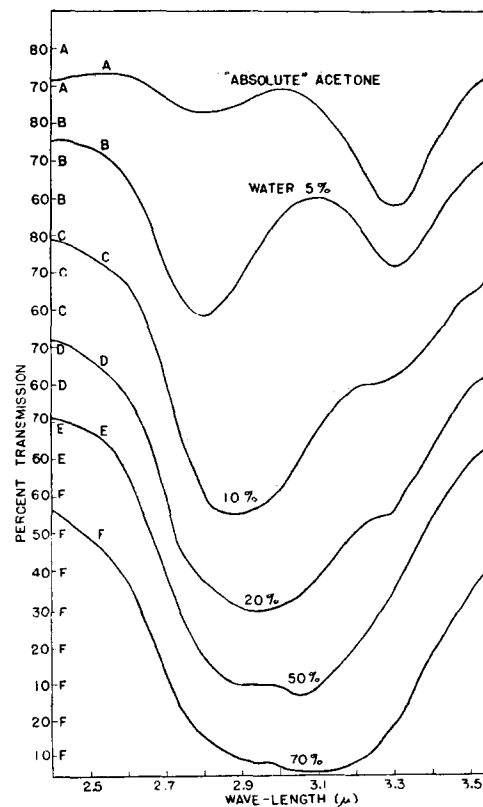


FIG. 2. The transmission of several water-acetone mixtures from  $2.3\mu$  to  $3.5\mu$ . Cell thickness: 0.03 mm.

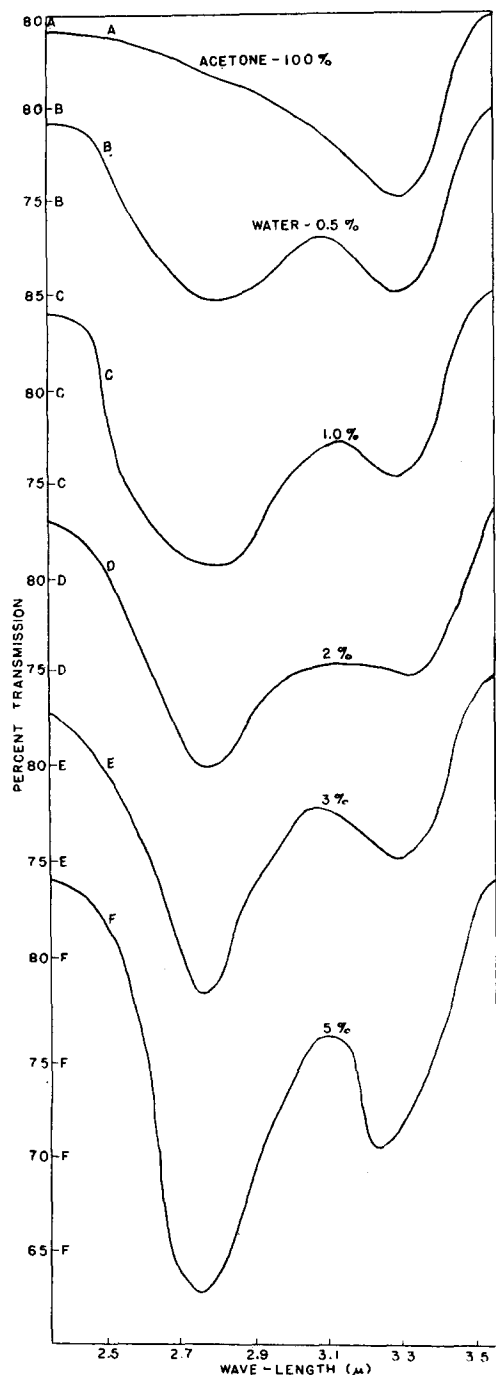


FIG. 3. The transmission of low concentrations of water in acetone from  $2.3\mu$  to  $3.5\mu$ . Cell thickness: 0.01 mm.

concentrations of water. The bands appearing in Fig. 3 are sharper than those shown in Fig. 2 as a result of the use of thinner absorbing layers.

As it has been stated above, the absorption at

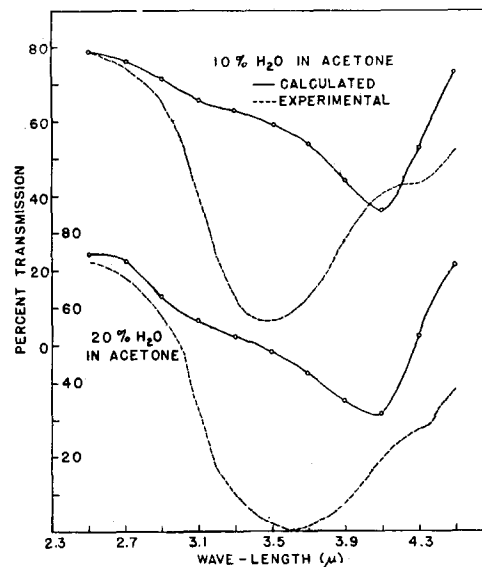


FIG. 4. The theoretical and experimental transmission of the water-acetone mixtures. Cell thickness: 0.03 mm.

$2.7\mu$  is attributed to an associational effect. In order to show that this band is not merely an apparent effect arising from the superposition of water and acetone absorptions, theoretical transmission curves have been plotted showing the absorption to be expected in a purely mechanical mixture of the two liquids, in which there is no association. These curves are shown in Fig. 4 and are developed on the assumption that the coefficient of absorption at any wave-length is equal to a suitably weighted mean of the absorption coefficients at the same wave-length; i.e.,

$$\alpha_{12}x = \alpha_1 n_1 x + \alpha_2 n_2 x. \quad (1)$$

where  $\alpha_{12}$ ,  $\alpha_1$ , and  $\alpha_2$  are the coefficients of absorption of the mixture, the water, and the acetone, respectively, and  $x$  is the cell thickness. Here  $n_1$  is the ratio of the number of water molecules in the cell to the total number of water molecules in a cell of equal thickness when only water is present;  $n_2$  is the same ratio for acetone. As is evident from the figure the sharp absorption band actually observed at  $2.7\mu$  is not present in the theoretical curves.

There are two different types of association which would give rise to the  $2.7\mu$  band. First, the band may arise from a modified vibration of the water molecule. Second, the band may be

produced by the molecules of an association compound. Although it is impossible from the observation of only one absorption band to determine definitely the nature of the mechanism producing it, the authors are inclined toward a belief in the existence of an association compound, since the absorption coefficient at  $2.7\mu$  for an acetone-water mixture is several times greater than the absorption of water at the  $3\mu$  water band.

By comparison with the set of absorption curves in Fig. 3, small amounts of water in

acetone can be determined in a quantitative manner. For example, the absorption curve for the sample of supposedly absolute acetone used for Fig. 2 shows a band which by comparison with the curves of Fig. 3 indicates the presence of approximately 0.3 percent water. Concentrations of water as low as 0.1 percent give rise to appreciable absorption bands in the  $2.7\mu$  region. As a test for the presence of water in acetone this method is more rapid and more accurate than the usual tests involving anhydrous copper sulphate.

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## The Infrared Absorption Spectra of Deuterioxide Solutions in Deuterium Oxide

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The infrared absorption spectra of deuterium oxide and deuterioxide solutions in D<sub>2</sub>O have been measured in the region from  $2.5\mu$  to  $9\mu$ . Also solutions of Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> in D<sub>2</sub>O have been studied in the same region. The spectra of deuterium oxide possess strong bands at  $4.0\mu$  and  $8.2\mu$  and the results agree with those of other workers. The absorption at  $4.0\mu$  is probably composed of several overlapping bands. Intense bands were observed in the NaOD solutions at  $3.1\mu$ ,  $4.95\mu$  and  $7.1\mu$ . The hydrolyzing salts in

D<sub>2</sub>O gave rise to bands in these regions, but with some shifts in wave-length. The changes in the spectra were probably caused by the absorption of the CO<sub>3</sub> ion and D<sub>2</sub>CO<sub>3</sub> which was formed in the solution. The relation of the absorption of NaOD in D<sub>2</sub>O to the absorption of NaOH in H<sub>2</sub>O is discussed. It is concluded that the OD ion has an absorption band at  $3.1\mu$  and that the bands at  $4.95\mu$  and  $7.1\mu$  are produced by hydration.

THE infrared absorption spectra of several hydroxides in aqueous solutions have already been measured.<sup>1</sup> Absorption bands were found at  $3.65\mu$  and  $5.2\mu$ . Grantham<sup>2</sup> had previously found a band at  $2.3\mu$  which was characteristic of all hydroxide solutions. He concluded that this band was due to the absorption of the OH ion. By studying the intensity of the  $2.3\mu$  band in solutions of hydrolyzing salts it has been shown<sup>1</sup> that this band is due to the OH ion. The bands produced by alcoholic solutions of hydroxides have also been measured.<sup>3</sup> There is little difference in the absorption spectra of the hydroxides in solutions of water or alcohol except for the shift of the band at  $3.65\mu$  in

aqueous solutions to  $3.8\mu$  for the alcoholic solutions.

The present work was undertaken to find the change in these bands due to the substitution of deuterium for hydrogen in the aqueous solutions. On account of the increase in mass there should be an appreciable shift to the longer wavelengths of the vibrational frequencies which were observed for the ordinary aqueous solutions. Deuterium oxide, marked 99.5 percent, was obtained from the California Isotope Company, Berkeley, California, and also a solution of NaOD in deuterium oxide. A large type Hilger infrared spectrometer with a fluorite prism was used in the region from  $2.5\mu$  to  $6.9\mu$  and a rocksalt prism from  $6\mu$  to  $9\mu$ . In order to observe the band in the  $7\mu$  region with a single prism the observations with the rocksalt prism were started at  $6\mu$ . The effective slit width at  $4\mu$  was

<sup>1</sup> E. K. Plyler and Walter Gordy, J. Chem. Phys. **2**, 470 (1934).

<sup>2</sup> G. E. Grantham, Phys. Rev. **18**, 339 (1921).

<sup>3</sup> E. K. Plyler and Dudley Williams, J. Chem. Phys. **2**, 566 (1934).