

## The Infrared Absorption Spectra of Dioxane-Water Mixtures

Walter Gordy

Citation: *J. Chem. Phys.* **4**, 769 (1936); doi: 10.1063/1.1749789

View online: <http://dx.doi.org/10.1063/1.1749789>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v4/i12>

Published by the AIP Publishing LLC.

---

### Additional information on J. Chem. Phys.

Journal Homepage: <http://jcp.aip.org/>

Journal Information: [http://jcp.aip.org/about/about\\_the\\_journal](http://jcp.aip.org/about/about_the_journal)

Top downloads: [http://jcp.aip.org/features/most\\_downloaded](http://jcp.aip.org/features/most_downloaded)

Information for Authors: <http://jcp.aip.org/authors>

## ADVERTISEMENT



Explore the **Most Cited**  
Collection in Applied Physics

AIP  
Publishing

## The Infrared Absorption Spectra of Dioxane-Water Mixtures

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

(Received August 10, 1936)

The absorption spectra of various dioxane-water mixtures have been studied in the region  $2.5\mu$  to  $6.5\mu$ . Dioxane was found to produce marked changes in the water spectrum. The observed variations are more pronounced for low water concentrations. Association of the water and dioxane molecules is suggested as a possible explanation of the observed effects.

THE fact that dioxane is completely miscible with water and the additional fact that dioxane has a very low dielectric constant as compared to water, makes dioxane-water mixtures very advantageous in chemical investigations.<sup>1</sup> These properties suggest the study of variations in the electric moment, as evidenced by changes in the infrared absorption spectra, of the water molecules when mixed in various proportions with dioxane. Since dioxane is almost, if not completely, nonpolar, the electric moment of the water dissolved in dioxane may be expected to approach that of the vapor-like state as the water concentration is lowered. Spectroscopic evidence for the existence of vapor-like molecules of water dissolved in carbon disulfide has been given by Kinsey and Ellis.<sup>2</sup> Their work has been reported only for the region  $1.0\mu$  to  $2.5\mu$ . On the other hand, there may be a linkage between the dioxane and water molecules, resulting in changes of the electric moment and hence variations in the absorption spectra of the water. In addition, associational bands may appear. Infrared absorption evidence of associational effects in acetone-water mixtures<sup>3</sup> and in alcohol-water mixtures<sup>4</sup> has been reported. Akerlof and Short<sup>1</sup> have measured the dielectric constant of mixtures of dioxane and water and have computed the polarization of each for various concentrations. They found the apparent polarization of the water to increase linearly as the dioxane content in the solution was increased.

The experimental method has been previously

described.<sup>5</sup> A fluorite prism was used for the entire region studied. Cell windows were of fluorite and were sealed with paraffin. The absorbing layer was maintained at a constant thickness of 0.002 cm. The dioxane was dried for four days over sodium. Cell windows were dried over  $P_2O_5$ .

A careful study has been made of the water bands in the  $3\mu$ ,  $4.7\mu$ , and the  $6.18\mu$  regions for various dioxane-water mixtures. Results for the  $3\mu$  region are given in Fig. 1. The bottom curve represents the transmission of pure water. The center of the water band appears at approximately  $3\mu$ . It will be seen from the next curve, which represents the transmission of a dioxane-water mixture of 50 percent water, that the  $3\mu$  water band has been shifted to the shorter wave-lengths. As the water concentration is decreased to 13 percent, to 7 percent and to 4 percent, the position of maximum absorption continues to shift to the shorter wave-lengths. For 4 percent water solution the band appears at  $2.8\mu$ , having been shifted approximately  $0.2\mu$ . Results obtained for 2 percent and 0.5 percent concentrations are not given in the figure. For concentrations below 4 percent the shift apparently remains constant. The band, however, is still strong for concentrations as low as 0.5 percent. This suggests the possibility of using this band for purposes of detecting small traces of water in samples of dioxane. In addition to the shift in position there is an increase in intensity of the  $3\mu$  band as the water content in the mixture is decreased. The intensity of the band does not decrease in proportion to the decrease in the number of absorbers. The curve for the supposedly anhydrous dioxane shows a small band in the  $2.8\mu$  region. It is likely that

\* Now at Mary Hardin-Baylor College.

<sup>1</sup> C. A. Kraus and R. M. Fuoss, *J. Am. Chem. Soc.* **55**, 21 (1933); G. Akerlof and O. A. Short, *J. Am. Chem. Soc.* **58**, 1241 (1936).

<sup>2</sup> E. L. Kinsey and J. W. Ellis, *Phys. Rev.* **49**, 105 (1936).

<sup>3</sup> D. Williams and E. K. Plyler, *J. Chem. Phys.* **4**, 157 (1936).

<sup>4</sup> D. Williams, R. D. Weatherford and E. K. Plyler, *J. Opt. Soc. Am.* **26**, 149 (1936).

<sup>5</sup> W. Gordy and D. Williams, *J. Chem. Phys.* **3**, 664 (1935).

this absorption is due to traces of water that could not be removed or that was taken in from the air as the cell was being made. The strong band at  $3.38\mu$  in dioxane spectrum appears to remain constant in position as the dioxane concentration is varied. Because of the intense absorption of water it was not possible to study this band for low dioxane concentrations.

The  $4.7\mu$  water band is of particular interest in this study because there is no corresponding band in the vapor state. Its origin has been attributed to association between the water molecules.<sup>6</sup> This band could not be observed in dioxane-water mixtures for water concentrations as low as 7 percent. It definitely appears, however, in the 13 percent mixtures. The absorption curves for the region  $4.4\mu$  to  $5.2\mu$  for 7 and 13

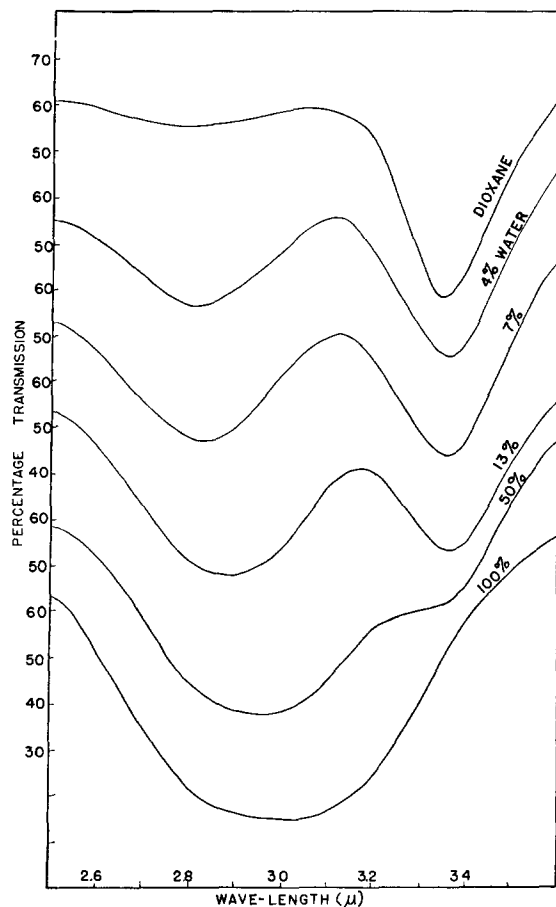


FIG. 1. The percentage transmission of dioxane and water and dioxane-water mixtures in the region  $2.5\mu$  to  $3.6\mu$ . The mixtures are given in percentage by volume.

<sup>6</sup> J. W. Ellis, Phys. Rev. **38**, 693 (1931).

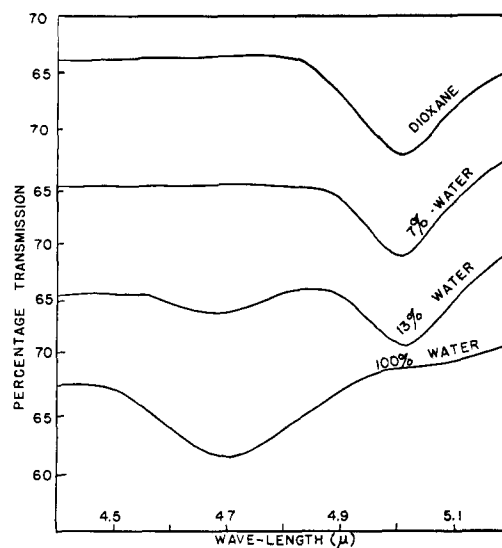


FIG. 2. The percentage transmission of dioxane and water and dioxane-water mixtures in the region  $4.4\mu$  to  $5.2\mu$ . The mixtures are given in percentage by volume.

percent mixtures with those of pure water are given in Fig. 2. The band appearing at  $5.05\mu$ , characteristic of the dioxane, was not measurably affected by the water for the concentrations studied.

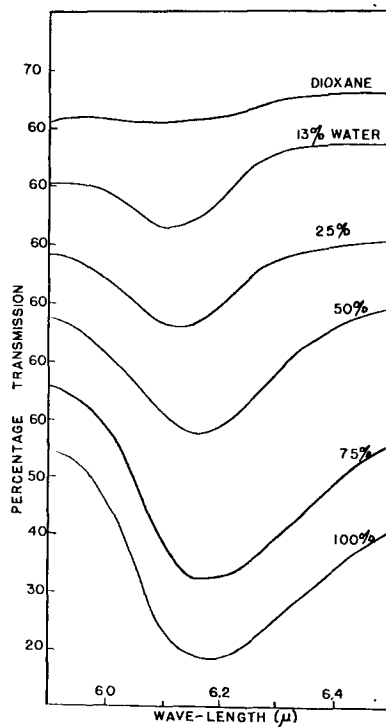


FIG. 3. The percentage transmission of dioxane and water and dioxane-water mixtures in the region  $5.9\mu$  to  $6.5\mu$ . The mixtures are given in percentage by volume.

In Fig. 3 are given the results obtained for the region  $5.9\mu$  to  $6.5\mu$ . The mixtures vary in concentration of water from 13 to 75 percent. It is obvious from the figure that the water band is shifted to the shorter wave-lengths as the dioxane content is increased. The intensity of the band is not increased appreciably as was the case of the  $3\mu$  band. The magnitude of the shift is about half that of the  $3\mu$  band.

Theoretical curves were developed for the  $3\mu$  and  $6\mu$  regions on the assumption that the absorption coefficient of the mixture at any wave-length is equal to the mean of the absorption coefficients of the two components at the same wave-lengths. The method of computation has been explained by Williams and Plyler.<sup>3</sup> In Figs. 4 and 5 these curves are shown in comparison with the experimental curves for the same mixtures. The marked differences in the experimental and theoretical transmission in these regions show clearly that the effects observed cannot be due to the supposition of water and dioxane bands.

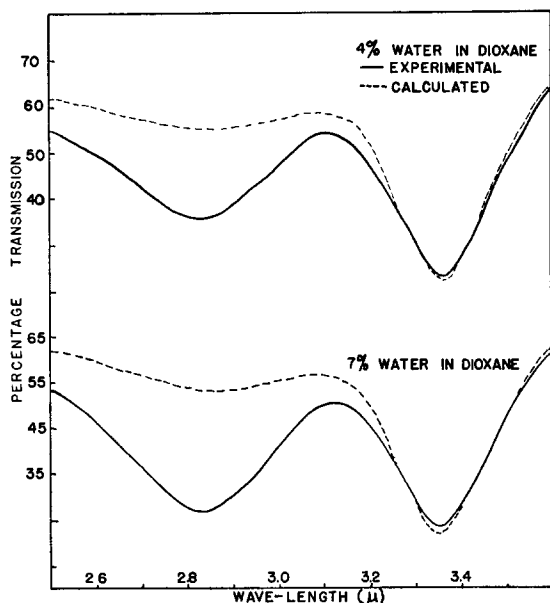


FIG. 4. The theoretical and experimental transmission of the dioxane-water mixtures in the region  $2.5\mu$  to  $3.6\mu$ .

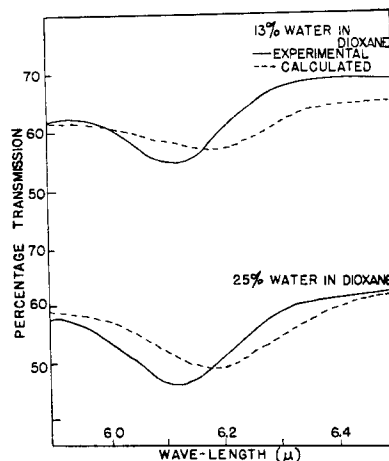


FIG. 5. The theoretical and experimental transmission of the dioxane-water mixtures in the region  $5.9\mu$  to  $6.5\mu$ .

Water vapor has strong absorption bands at  $2.66\mu$  and at  $2.74\mu$ . One might interpret the shift observed in the  $3\mu$  water band as a transition of the water absorption to vapor-like absorption. The disappearance of the  $4.7\mu$  water band for low concentrations supports this hypothesis. The changes observed in the  $6\mu$  region, however, fail to support the assumption that the effects observed are due to vapor-like molecules in the solution. From the behavior of the  $4.7\mu$  band, it seems likely that there is a separation of the associated molecules as the water concentration is decreased. The changes in the  $3\mu$  and  $6.18\mu$  water bands are probably due to association between the water and dioxane molecules. A possible explanation of the association would be the "proton bond" theory.<sup>7</sup> If the dioxane and water molecules are linked through a hydrogen bond, we should expect the electric moment of the group which carries the hydrogen to be increased. This would account for the pronounced changes observed in the water spectrum.

The writer is grateful to Dr. E. K. Plyler for the use of his instrument.

<sup>7</sup> W. M. Latimer and W. H. Rodebush, *J. Am. Chem. Soc.* **42**, 1419 (1920); L. Pauling, *J. Am. Chem. Soc.* **57**, 2680 (1935); *ibid.* **58**, 94 (1936).