35° for an acid strength of 54–55% nitric acid. The results expressed in the form of the constant $K_1 = (P_{NO})/(P_{NO_2})^3$ agree well with the data of Abel, Schmid and Stein, deviating considerably from those of Burdick and Freed.

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[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS, UNIVERSITY OF NORTH CAROLINA]

The Infra-red Absorption of Heavy Acid Solutions

BY DUDLEY WILLIAMS AND E. K. PLYLER

A previous study[1] has revealed the presence of intense absorption bands at 2.4 μ and near 5.5 μ in the spectra of aqueous solutions of a number of acids. These bands were attributed to the effects of hydration. As the position of the band near 5.5 μ varied slightly with the solute, this absorption was identified with a characteristic frequency of an associational group containing undissociated acid molecules, while the 2.40 μ band was attributed to a hydrate in which the H^+ ion is involved. An investigation of the spectra of solutions of hydrolyzing salts gave additional support to this conclusion.[2]

The present work was undertaken in order to determine the changes in the positions of these bands caused by the substitution of deuterium for the hydrogen in the aqueous solutions. The deuterium oxide used as a solvent was a Norwegian product containing only a trace of ordinary water. The DCl solution was obtained from the California Isotope Company of Berkeley and contained about 0.5% H_2O. The D_2SO_4 and D_3PO_4 solutions were prepared by dissolving known amounts of the anhydrides in deuterium oxide. The sulfur trioxide used in this process was obtained by heating fuming sulfuric acid and the gas was allowed to pass through two drying tubes containing phosphorus pentoxide before entering the solvent. From specific gravity determinations it is estimated that the D_2SO_4 solution was approximately four normal and a D_3PO_4 solution of equal concentration was prepared. The spectroscopic methods have been described in a previous paper.[3] A rock-salt prism was used in the region from 2.5 to 12.0 μ, additional measurements being made in the 2.0–3.8 μ region with a fluorite prism. The absorbing layers used in the region of longer wave lengths were 0.02 mm. in thickness, while the layers in the 2.0–3.8 μ region were 0.05 mm. thick.

The infra-red absorption of deuterium oxide has been studied previously by Ellis and Sorge,[4] by Casselman,[5] and by the authors.[3] Intense bands have been observed at 2.85, 4.00, 6.80 and 8.20 μ. Although the broad band at 4.00 μ has three maxima, it was impossible to resolve this band into its components with the rock-salt prism used in the present work. The results obtained with deuterium oxide in the present study are given by the upper curve of Fig. 1. In addition to the bands shown in the figure, another band appeared at 10.4 μ. This band probably corresponds to the band recently observed at 8.6 μ in the spectrum of ordinary water.[6]

The transmission of the DCl solution is shown in the lower curves of Fig. 1. It will be noted that there is a marked increase in absorption near 5.5 μ. The dotted curve shows the transmission of a more concentrated solution of DCl in this region. There is also a slight increase in absorption near 3.4 μ, and this absorption may be seen more clearly when thicker absorbing layers are used. The results obtained in the 3 μ region with thicker cells are shown in another figure. With the exception of the increased absorption in the 3.4 and 5.5 μ regions of the solution spectrum, the transmission curve for the DCl solution bears a close resemblance to the D_2O curve. The curves are practically identical from 9 to 12 μ, and for this reason the transmission curves obtained in this region are omitted from the figure. The results obtained with the D_2SO_4 and D_3PO_4 solutions are the same as those obtained with the DCl except for the appearance of bands near 9 and 4.8 μ which are characteristic of the sulfate and phosphate

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[1] E. K. Plyler and E. S. Barr, *J. Chem. Phys.*, **2**, 306 (1934).

[2] E. K. Plyler and W. Gordy, *ibid.*, **2**, 470 (1934). Recent unpublished work, however, seems to indicate that the hydrated H^+ ion absorbs also in the region of 5.4 μ and the hydrated acid molecules absorb at slightly longer wave lengths.

[3] E. K. Plyler and D. Williams, *ibid.*, **4**, 157 (1936).

[4] J. W. Ellis and B. W. Sorge, *ibid.*, **2**, 559 (1934).

[5] A. L. Casselman, *Phys. Rev.*, **45**, 221 (1934).

[6] D. Williams, *ibid.*, **49**, 869 (1936).

groups. The spectra of compounds containing these groups have been studied extensively by reflection,[7] and regions of intense absorption appear at 9.0 μ in the sulfates and at 9.5 μ in the phosphates. These bands maintain their normal spectral positions even when the compounds are in solution.

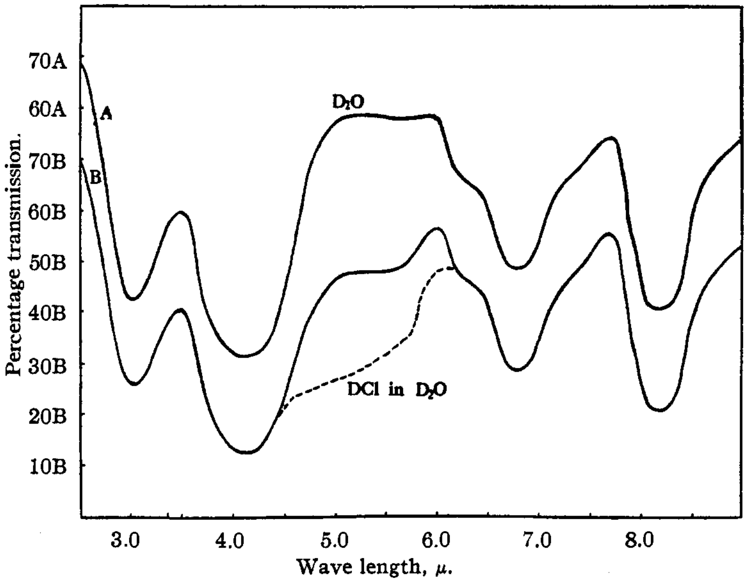

Fig. 1.—The percentage transmission of deuterium oxide and solutions of DCl: region, 2.5 to 9.0 μ.

In order to determine the positions of maximum absorption of the various solutions, curves were plotted showing the ratio of the solution transmission to the solvent transmission. The ratio curves for the 4.5–6.5 μ regions are shown in Fig. 2. As may be seen readily, all the solutions are strongly absorbing near 5.5 μ, the position of maximum absorption varying with the solution. The first two curves are plotted to the same scale and show the results obtained with two concentrations of DCl. It will be noted that increasing the DCl concentration causes additional absorption in the 4.9 μ region, where the absorption maximum of gaseous DCl appears, and it is possible that the absorption observed at this position may be caused by undissociated DCl molecules. However, the corresponding HCl band at 3.46 μ has never been observed in aqueous solution, and it would be surprising to find DCl molecules giving rise to a band of this type. The absorption of D_2SO_4 at 4.6 μ is the first harmonic of the SO_4 band at 9 μ mentioned above, and the D_3PO_4 band at 4.8 μ has a similar relation to the PO_4 maximum at 9.5 μ.

In Fig. 3 are given the results obtained between 2.0 μ and 3.8 μ with 0.05 mm. absorbing layers. The transmission determinations used in plotting the curves shown in this figure were made with a fluorite prism. The DCl curve given here was obtained with a sample of the less concentrated solution. The transmission curve shows intense absorption in the region of 3.4 μ. Increasing the concentration of DCl caused an increase in the intensity of this band, but a shift in position was not observed as in the case of the 5.5 μ region of absorption. The D_2SO_4 and D_3PO_4 solutions are also strongly absorbing in the 3.4 μ region, and additional absorption appears in the 2.2 μ region in the spectra of these latter solutions. The absorption in the 3.4 μ region is so intense that the plotting of ratio curves to aid in locat-

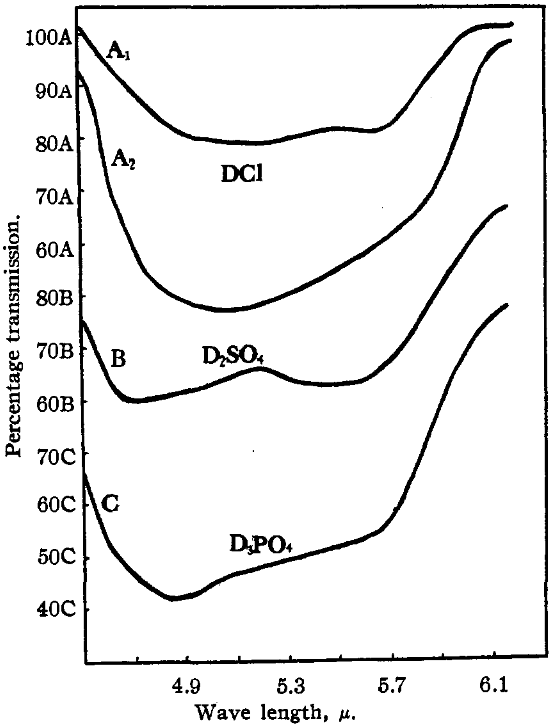

Fig. 2.—The ratio of the transmissions of acid solutions to deuterium oxide transmission: region, 4.5 to 5.8 μ; concentrations, DCl A_1, 3 *N*; DCl A_2, 5 *N*; D_2SO_4, 4 *N*; D_3PO_4, 4 *N*.

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(7) C. Schaefer and F. Matossi, "Das Ultrarote Spektrum," Verlag von Julius Springer, Berlin, 1930, p. 333.

ing the absorption bands is not deemed necessary.

It is interesting to note that the spectra of deuterium oxide solutions of the hydrolyzing salts potassium carbonate and sodium carbonate studied in a previous investigation[3] contain bands near 5.5 μ. Since similar bands appear in the spectra of the heavy acid solutions used in the present work, it is probable that the bands at 5.5 μ in the spectra of the salt solutions are caused by heavy carbonic acid formed on hydrolysis of the salts. In solutions of hydrolyzing salts of this type one would expect D_2CO_3 molecules to be much more numerous than D^+ ions, and hence it is possible that the 5.5 μ bands arise from the hydration of undissociated acid molecules. Other evidence in favor of this hypothesis lies in the slight variations in position of these bands in the different solutions, an effect to be expected if different negative radicals are present in the complex. The exact numbers and natures of the units entering into these associational groups cannot be determined from the data obtained in this study. It will be noted, however, that the position of the associational band produced by heavy acid molecules in deuterium oxide solutions is the same as that of the corresponding band produced by ordinary acids in aqueous solution. This seems to indicate that large groups are involved, since the replacement of hydrogen by deuterium does not produce an appreciable shift. Since the bands observed at 3.4 μ do not change their positions in the different acid solutions, it is probable that they are caused by the hydration of the D^+ ions. The corresponding bands in aqueous solutions of ordinary acids appear at 2.40 μ. Thus, the shift in the position of this absorption is what would be expected if the H in a simple R-H oscillator were replaced by deuterium to form R-D, where the mass of the accompanying group R is large as compared with H and D. The exact nature of the group R is at present unknown.

The experimental results obtained in this study indicate that the 2.4 μ band appearing in aqueous solutions of acids is shifted to 3.4 μ when the hydrogen is replaced by deuterium, while the bands in the 5.5 μ region are common to both types of solution.

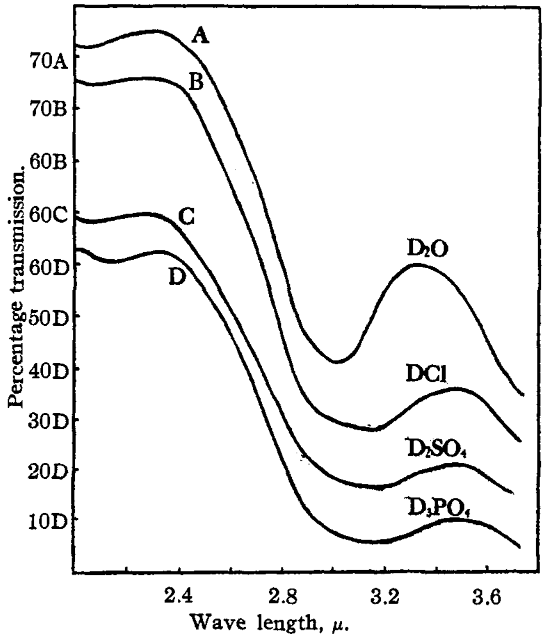

Fig. 3.—The transmission of deuterium oxide and three heavy acid solutions: region, 2.0 to 3.5 μ.

Abstract

The infra-red absorption of deuterium oxide and of DCl, D_2SO_4 and D_3PO_4 solutions has been measured in the region between 2 μ and 12 μ. In addition to the bands at 2.9, 4.0, 6.8 and 8.2 μ, a band at 10.4 μ has been found in the spectrum of deuterium oxide. In the spectra of all the heavy acid solutions studied intense absorption bands appear at 3.4 μ and near 5.5 μ in addition to the bands characteristic of the solvent. The solutions of D_2SO_4 and D_3PO_4 also give rise to characteristic SO_4 and PO_4 absorption, respectively. The intense bands at 3.4 and 5.5 μ are attributed to hydration effects.

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