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A Further Study of the Absorption of Aqueous Solutions at 4.72μ

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By the use of a grating spectrometer, the infra-red absorption spectra of aqueous solutions of five inorganic materials (KI, CuBr_2 , ZnBr_2 , $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$, and NaOH) and six organic materials (acetone, CH_3COONa , $\text{CH}_3\text{COONH}_4$, cane sugar, $\text{C}_6\text{H}_5\text{OH}$, and $\text{C}_2\text{H}_5\text{OH}$) were observed in the region of the water band at 4.72μ . The organic materials investigated caused a displacement of the position of maximum absorption to shorter wave-lengths; the inorganic materials apparently caused a shift to longer wave-lengths, but the actual effect on the water band may be masked by other absorption bands in the same region. The concentration-shift relationship was investigated for some of the materials. Size of the solute molecule and the positive ion seemed to be of comparatively little importance.

IN a previous paper¹ on which one of us collaborated, a report was made on an investigation of the effect of dissolved halogen salts on the 4.72μ water band, using a prism spectrometer. This band is well suited for a study of the effects due to solutes since it arises from association of the water molecules. It was desired to supplement this work with additional investigations of the infra-red spectra of more complex inorganic materials and of certain typical organic materials.

In order to work with more favorable dispersion, in case other bands should be found in the immediate vicinity of the 4.72μ band, the present work was done on the grating spectrometer built under the direction of Dr. E. K. Plyler at the University of North Carolina.² This spectrometer is of the usual type, employing a fore prism of rocksalt to separate the orders, and supplied with a five-inch echelette grating, ruled 4800 lines to the inch. The effective slit width used was approximately 2 cm^{-1} . The wave-length of the radiation falling on the thermocouple for any setting of the grating could be calculated from the circle reading by using the reflection grating formula, $n\lambda = K \sin \theta$, where n is unity and K has the value 10.566μ . The central image corresponded to a circle reading of $81^\circ 20'$. Observations were taken at intervals varying from approximately 0.01μ to 0.05μ . The absorption cells were prepared as in the previous study.

In Fig. 1 are shown transmission curves for water (A), and solutions of potassium iodide (B) and acetone (C, D). The curve for water is included at the top of each figure for comparison, and a line is drawn through the point of maximum absorption so that the displacements of the band of the solutions may be noted readily. In order to determine whether the band observed previously for the potassium iodide solution with the prism instrument was single or composed of two or more neighboring bands, readings were taken at intervals of approximately 0.01μ . Curve 1 B was obtained in this manner and gives no indication of secondary structure. This indicates that the observed displacement is not caused by the presence of a side band, but by a shifting of the water band as a whole. The position of maximum absorption for this $4 M$ solution occurs at 4.90μ (erroneously given as 5.85μ in the reference cited). Curves 1 C and 1 D show the variation in the amount of displacement with concentration in the case of acetone. It is seen that both the 25 percent solution and the 50 percent solution cause a displacement of the band toward shorter wave-lengths, the more concentrated solution producing the greater shift. Because of the broadness of the band, no attempt has been made at this time to make a quantitative study of the relationship between concentration and amount of displacement. It is also seen from Fig. 1 that the introduction of different solutes may cause a displacement of the water band toward either longer or shorter wave-lengths.

Transmission curves for solutions of two acetic

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¹ Plyler and Barr, *J. Chem. Phys.* **6**, 316 (1938).

² Shearin and Plyler, *J. Opt. Soc. Am.* **28**, 61 (1938).

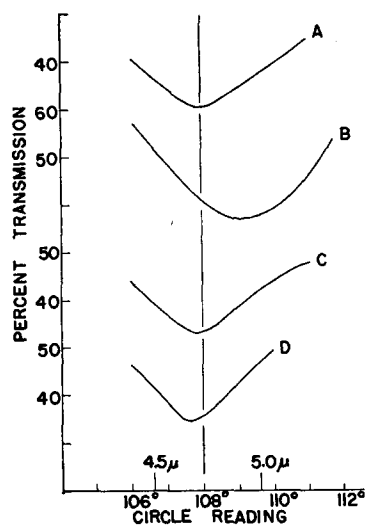


FIG. 1. The transmission of water (A) and aqueous solutions of (B) 4 *M* KI, (C) 25 percent by volume acetone, and (D) 50 percent by volume acetone.

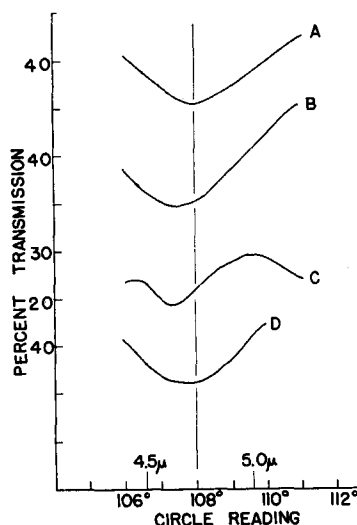


FIG. 2. The transmission of water (A) and aqueous solutions of (B) 3 *M* CH_3COONa , (C) 7 *M* $\text{CH}_3\text{COONH}_4$, and (D) 10 percent by weight cane sugar.

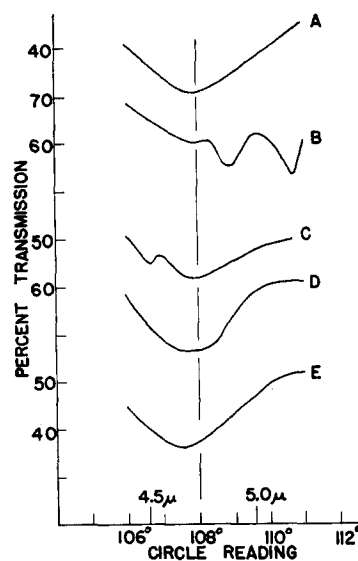


FIG. 3. The transmission of water (A) and aqueous solutions of (B) phenol, concentrated, (C) phenol, dilute, (D) 50 percent by volume $\text{C}_2\text{H}_5\text{OH}$, and (E) 25 percent by volume $\text{C}_2\text{H}_5\text{OH}$.

acid salts, sodium acetate (B) and ammonium acetate (C), are shown in Fig. 2. There is an apparent shift to shorter wave-lengths in the case of both of these salts, but this may be caused by the overlapping of other bands corresponding to materials formed through hydrolysis.³ It is also possible that certain groups of atoms in these molecules could produce overlapping bands; for example, the ammonium group is known to absorb in the region of 4.5μ .

In order to determine whether the size of the solute molecules was an important factor in producing the shift, the spectrum of a 10 percent solution of cane sugar was obtained. This material was selected also because of its lack of ionization in solution. As is seen from Fig. 2 (D), this large molecule produces no marked change in the position of the water band; there is, however, some broadening of the band. This indicates that while the sugar molecules form no strong linkages with the water molecules, they serve to separate them to some extent.

As is well known, at room temperature aqueous solutions of phenol exist in two ranges of concentration, one dilute and the other quite concentrated. The two solutions used were prepared

at room temperature by adding phenol to water until saturation for the dilute solution, and adding water to phenol for the concentrated solution. The estimated concentrations were 8 percent and 72 percent phenol, respectively. The absorption spectra of these solutions were obtained and the results are shown in Fig. 3 (B, C). Since in the concentrated solution there is a preponderance of phenol, the bands caused by the solute itself which are found in this region prevent the observation of any possible change in the position of the water band. There is a slight shift to shorter wave-length found for the dilute solution, and it is interesting to notice that a new band has appeared in the neighborhood of 4.5μ . This may be due to the linking of OH groups with water molecules, since this band is observed in all solutions containing OH ions.

The curves D and E in Fig. 3 show the observed transmission for 50 percent and 25 percent solutions of ethyl alcohol. A shift to shorter wave-lengths is seen for both solutions, the more dilute solution giving the greater shift of the water band. No band was observed in the region of 4.5μ , as in the case of the dilute phenol solution, but, since alcohol does not ionize

³ Plyler and Gordy, J. Chem. Phys. 2, 470 (1934).

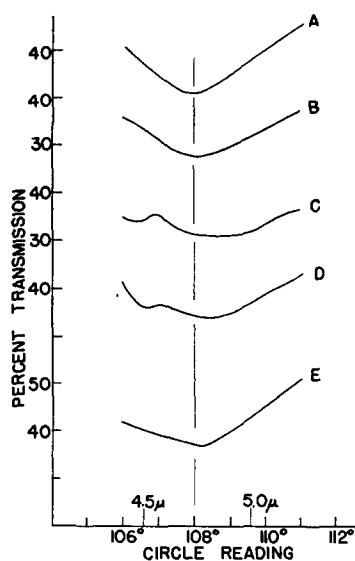


FIG. 4. The transmission of water (A) and aqueous solutions of (B) 1.25 M CuBr_2 , (C) 4 M ZnBr_2 , (D) 4 M $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$, and (E) 1 M NaOH .

appreciably in water, this difference was to be expected.

As the previous work on the halogen salts was confined to comparatively light, univalent positive ions, the spectra of three inorganic materials containing, respectively, copper, zinc and cadmium were observed and the results are shown in Fig. 4. In each case there is a shift of the water band to longer wave-lengths. The bands at about 4.5μ in curves C and D are attributed to hydrolysis products, since hydrated OH ions give rise to a band in this region. The investigation of solutions of halogen salts with heavy positive ions was not carried further because of the interference of these bands, and because of the impossibility of obtaining suitably concentrated solutions. For the comparatively dilute NaOH solution it is seen that the intense absorption of the hydroxide has distorted the water band on the short wave side. A slight shift to longer wave-lengths of the maximum absorption of water is seen, despite the presence of the distortion.

Solutions of 7 M ZnCl_2 and 5 M $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ were also investigated, but any effect of the solute on the water band was masked by the strong general absorption throughout the region studied.

It seems quite probable that, in addition to the displacements commented upon above, the

presence of the solutes may cause a change in the intensity of the water band, as has been observed in other cases.⁴ This possibility was not examined in the present work, however, since the construction of equivalent water cells was not feasible, because of the fact that the absorption cells used were necessarily limited in thickness to about 0.02 mm because of the large coefficient of absorption of water in this region.

From an examination of the foregoing transmission curves it seems that there is no direct correlation between the observed shift in the position of the water band and (1) size of molecule of solute, (2) size of positive ion and (3) valency of positive ion. There has not been found any simple relationship as was found in the previous work on the simpler and lighter halogen salts. Because of the hydrolyzation which takes place in the case of the salts selected, with accompanying production of bands in the region of study, any regular shift due to size and valency of the positive ions may have been masked. However, if such an effect does exist, its magnitude is not comparable with that produced by the halogen ions, since otherwise the shifts could have been seen superimposed on the bands due to hydrolysis.

The change in the absorption of water at 4.72μ caused by organic solutes seems to be influenced more by the nature of the molecule than by its size. Thus we find that in the case of ethyl alcohol a 25 percent solution shows more shift than the 50 percent solution, while the acetone solutions showed the reverse effect.

In no instance where a shift was found did it seem to be caused by the formation of another band in addition to the 4.72μ band, and it is therefore concluded that the shift is always the result of a displacement of the band as a whole. These results indicate that a considerable change may be produced in the associational water band at 4.72μ by the presence of solutes, but from the information obtained so far it cannot be predicted which way the position of maximum absorption would be shifted for a given solute.

The writers wish to express their appreciation of the constructive criticism and helpful suggestions of Dr. E. K. Plyler of the University of North Carolina.

⁴ Grantham, *Phys. Rev.* 18, 339 (1921).