The Infrared Absorption of Solutions of Hydroxides and Hydrolyzing Salts

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Absorption bands have been found at 3.65μ and 5.2μ in aqueous solutions of NaOH, KOH and LiOH. Solutions of $ZnCl_2$, $ZnBr_2$, $NH_4C_2H_3O_2$, Na_2CO_3, $NaC_2H_3O_2$, $Na_2B_4O_7$, Na_2SiO_3 and $Al_2(SO_4)_3$ were studied in the region from 2.8μ to 6μ and bands were observed at about 3.45μ, 4.5μ, 5.2μ and 5.6μ. The solutions which are acid in reaction had intense bands at 3.6μ and 5.2μ, while the basic solutions gave a strong band at 5.6μ. This variation in intensity indicates that the absorption bands are due to undissociated molecules bound to water molecules. The band at 4.5μ is probably due to water which has been modified by the ions. The hydroxides showed the absorption bands at 3.6μ and 5.2μ when 0.1N solution was used.

GRANTHAM[1] measured the absorption of several hydroxides in aqueous solutions from 1μ to 3μ and found an intense band at 2.29μ for all the solutions except NH_4OH which had the maximum of absorption at 2.20μ. tions and found that the intensity of the water absorption was changed. Small bands occurred at 0.96μ, 1.10μ, and 1.27μ for all the hydroxides in alcoholic solutions and these bands were thought to be due to the OH ion.
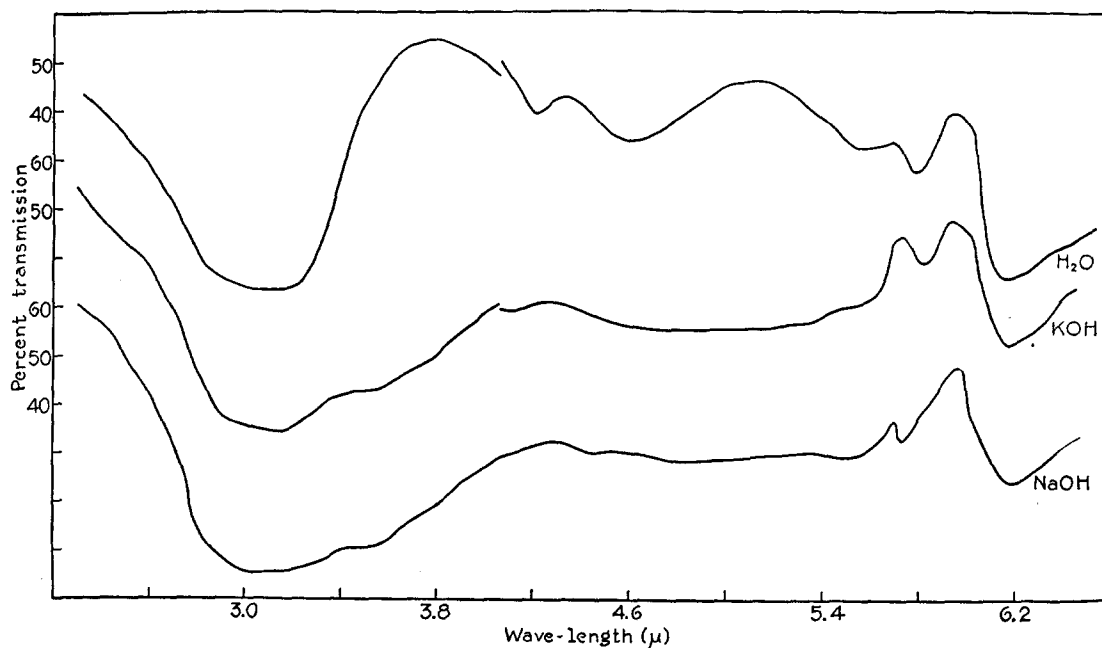

FIG. 1. The percent transmission of water and of NaOH and KOH solutions from 2.8μ to 6.6μ.

Because the absorption bands had the same wave-length Grantham concluded that the absorption was due to the OH ions. Collins[2] also measured the absorption of hydroxides in solu-

These bands appear to be part of a harmonic series which has a fundamental in the long wavelength region. The present work was undertaken to look for such bands and the region from 2.8μ to 6.5μ was studied. The measurement of the absorption bands was done in a way similar to

[1] G. E. Grantham, Phys. Rev. **18**, 339 (1921).

[2] J. R. Collins, Phys. Rev. **20**, 486 (1922).

that employed by Plyler and Barr.[3] In Fig. 1 is shown the percent transmission of H_2O and 7.5N NaOH and 7.5N KOH solutions. In the region of 4.2μ the spectrometer slits were changed and this caused breaks in some of the curves. The cell thickness was approximately 0.01 mm for each solution. The transmission is less than is found for water. In Fig. 2 the ratio of the percent transmission of the solutions to that of water is plotted. Intense bands are shown in the regions of 5.20μ and 3.65μ.

A 5N solution of LiOH also gives the same bands. In the region of 3.65μ the bands appear to be double with a less intense component on the long wave-length side. On account of the rapid change in the coefficient of absorption of water, it was difficult to determine the true shape or position of this band. The small band in the region of 4.2μ was not found in all determinations and may be due to observational

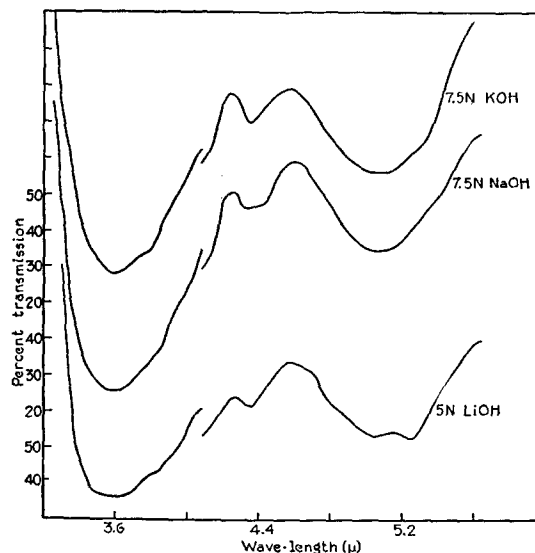

FIG. 2. The ratio of the transmission of solutions of KOH, NaOH, and LiOH as compared to water.

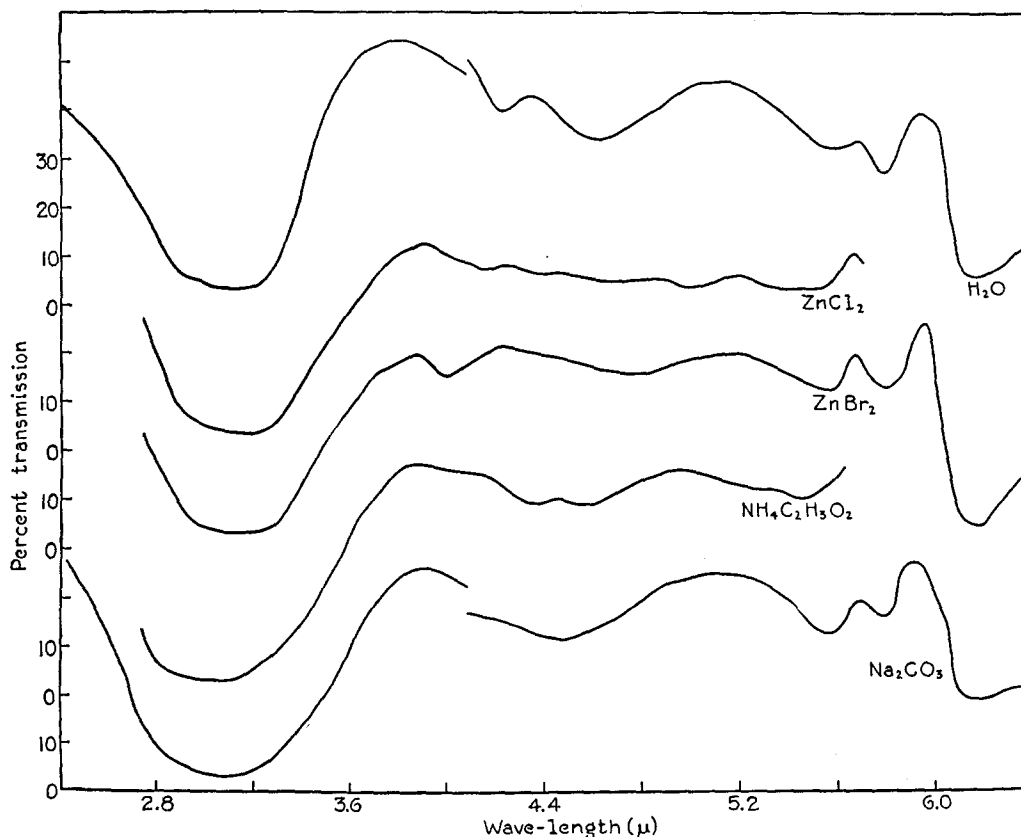[3] E. K. Plyler and E. S. Barr, J. Chem. Phys. (in press).

FIG. 3. The percent transmission of some hydrolyzing salts from 2.8μ to 6.6μ.
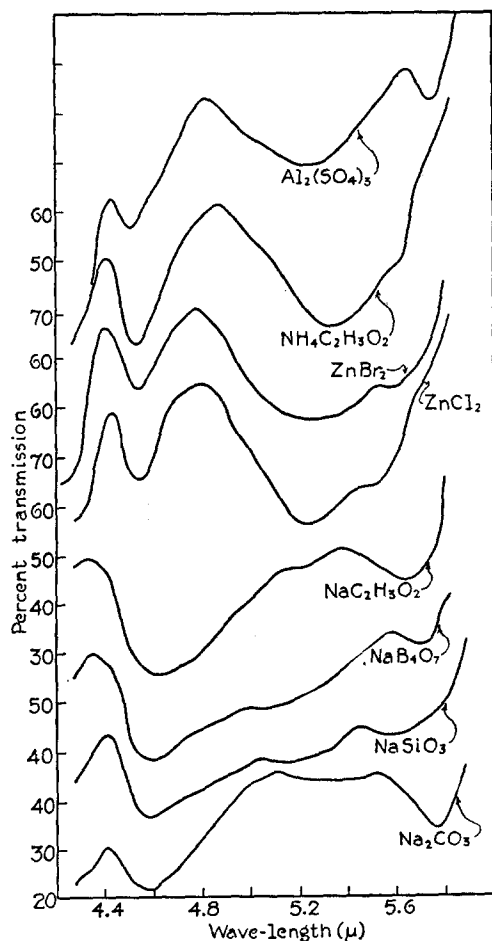
FIG. 4. The percent transmission of some hydrolyzing salts compared with water from 4.2μ to 6.0μ. (The curve labelled NaB$_4$O$_7$ should be Na$_2$B$_4$O$_7$; the curve NaSiO$_3$ should be Na$_2$SiO$_3$.)

errors. There is a strong band in this region due to CO$_2$ in the atmosphere and the deflections of the galvanometer are greatly reduced.

The bands reported by Collins[2] agree in position with harmonics of these bands. If the 3.65μ band is called ν_1, and the 5.2μ band ν_2, then $3\nu_1$ corresponds to 1.27μ and $4\nu_1$ to 0.95μ and $5\nu_2$ corresponds to 1.05μ. The combination of $\nu_1+\nu_2$ corresponds to a band at 2.3μ. This agreement is not very satisfactory as the observed band occurs at 2.2μ. By a study of hydrolyzing salts in this region it has been found that the 2.2μ band is a fundamental frequency and not a combination band.

A study of hydrolyzing salts was next made to see if the hydroxides formed in this way had bands at 3.65μ and 5.2μ. Solutions of 10N ZnCl$_2$,

10N ZnBr$_2$, 10N NH$_4$C$_2$H$_3$O$_2$ and 2.5N Na$_2$CO$_3$ were measured from 2.8μ to 6.6μ and the results are shown in Fig. 3. The percent transmission in this region is much less than that of water. The acid solutions have less transmission at 3.45μ and 5.2μ than the basic solutions but the basic solutions have less transmission at 5.6μ. This variation in intensity is readily seen when the ratio of the percent transmission of the solution compared to water is plotted. The results for the region from 4μ to 6μ are shown in Fig. 4. The first curves are for acid solutions and the band at about 5.6μ, which is characteristic for all acid solutions,[3] is very weak. The band at 5.2μ, which has been found for all hydroxides, is intense. As an acid solution of a hydrolyzing salt indicates more H ions than OH ions, the 5.6μ acid band must be due to the
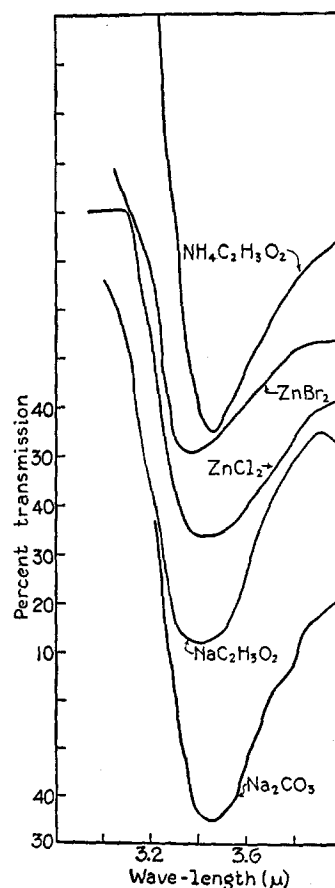

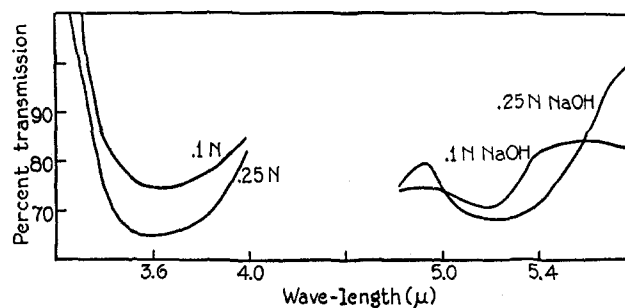FIG. 5. The percent transmission of some hydrolyzing salts compared with water from 2.8μ to 4μ.

FIG. 6. Intensity of the hydroxide bands at 3.65μ and 5.2μ as affected by concentrations.

undissociated acid molecule attached to one or more water molecules and the 5.2μ band due to the undissociated hydroxide molecule attached to one or more water molecules. The four lower curves in Fig. 4 show the percent transmission of 7N $NaC_2H_3O_2$, 0.5N $Na_2B_4O_7$, 5N Na_2SiO_3, 2.5N Na_2CO_3 which are basic. The 5.6μ acid band is intense and the 5.2μ hydroxide band is weak. This result also shows that these bands are due to the undissociated molecule. Because of the strong hydroxide band at 5.2μ, the bands produced by the acids at 5.6μ are somewhat distorted. The $NH_4C_2H_3O_2$ solution acts similarly to acid solutions but this result may be produced by the absorption due to the NH_4 ion in the region of 5.2μ.

Intense bands were found for all the hydrolyzing salts in the region of 4.5μ. These bands are not present in the solutions of acids or hydroxides and are to be attributed to energy levels characteristic of hydrolyzing salts. A strong absorption band is found in this region in all crystals having water of crystallization and it is possible that some of the water molecules of the solution are bound between the ions in a similar way to water in crystals. In Fig. 5 are shown the results for solutions of $NH_4C_2H_3O_2$, $ZnBr_2$, $ZnCl_2$, $NaC_2H_3O_2$ and Na_2CO_3 in the region from 2.8μ to 4μ. On account of the low transmission of water in this region, the position of the band could not be found so accurately. However, it was readily found that this region had an intense band at about 3.45μ.

The hydroxide bands at 3.65μ and 5.2μ have been found to arise in energy changes between the undissociated hydroxide molecule and one or more water molecules. Measurements were made on concentrations from 10N to 0.1N to see if the bands decreased rapidly in intensity as the concentration decreased. The intensity appeared to vary directly as the concentration and the bands were still present with 0.1N solutions. Curves for 0.1N and 0.25N solutions of NaOH are shown in Fig. 6.

The hydroxide solutions have been studied[4] by means of the Raman spectra and shifts have been found which correspond to a band with a frequency of 3600 cm^{-1}. Neither of the bands at 3.65μ or 5.2μ was observed.

The intensity of the bands at 3.45μ, 5.2μ and 5.6μ is a measure of the hydration for the given concentration. Because of the thin cells it is difficult to obtain quantitative results. However, the harmonics of these bands, which occur in the region of 2μ, could be used to determine the degree of hydration. A study of this type has been made by Krishnamurti[5] by the use of the Raman effect. He did not find any shifts which correspond to the bands observed in this work.

[4] L. A. Woodward, Phys. Zeits. 32, 261 (1931).

C. C. Hatley and Dixon Callihan, Phys. Rev. 38, 909 (1931).

[5] P. Krishnamurti, Ind. J. Phys. 6, 345 (1931).