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The Infrared Absorption of Alcoholic Solutions of Hydroxides

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Bands have been observed at 0.76μ, 0.95μ, 1.05μ, 1.27μ, 1.30μ, 1.73μ, 1.89μ, 2.30μ, 2.60μ, 3.80μ and 5.20μ in alcoholic solutions of hydroxides. Solutions of NaOH and KOH gave the same positions for the bands. It was found that if the bands at 3.80μ and 5.20μ were considered as fundamentals, the remaining bands could be classified as harmonics. The similarity of the observed bands of the alcoholic solutions to the bands of aqueous solutions is mentioned.

A RECENT study[1] of the infrared absorption bands of aqueous solutions of certain hydroxides has shown that intense bands exist at 3.65μ and 5.2μ. These bands were found to be due to changes in energy levels of the hydroxide molecule when attached to water molecules. Collins[2] had previously found that different hydroxides in alcoholic solutions had similar bands in the regions of 0.96μ, 1.10μ and 1.26μ. He concluded that the absorption was due to the OH ion. The present work was undertaken to see if any bands existed at the longer wave-lengths in alcoholic solutions of the hydroxides which were related to the bands observed by Collins. The region studied was from 0.8μ to 7μ. The infrared absorption spectra of the alcohols have been studied by several workers[3] but the work has been repeated in order that the absorption for the same cell thickness of alcohols and the solutions would be available.

The experimental method was the same as has been previously described.[4] The absorption spectra of solutions of NaOH and KOH in both methyl and ethyl alcohol were measured. All the solutions were saturated at 22°C. Since these hydroxides are very soluble in water, it was necessary to have alcohols free from water. Absolute alcohols were obtained and tested for the presence of water with anhydrous copper sulphate and also by density measurements. These tests indicated that the alcohols were free from water in any appreciable amount. An additional proof that water was not present in any appreciable amount became apparent when the strong absorption bands due to water failed to appear at all.

In Fig. 1 are shown the results obtained in the region from 3μ to 5.4μ. No absorption which

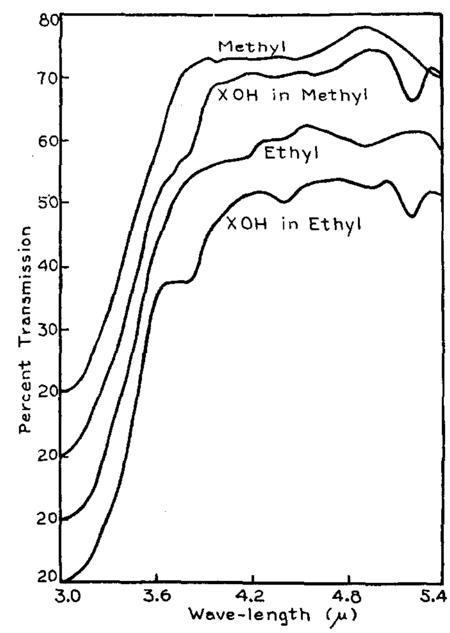

FIG. 1. Bands at 3.8μ and 5.2μ produced by hydroxides in alcoholic solutions. The cells were about 0.1 mm thick.

might be attributed to hydroxides was found in the region from 5.4μ to 7μ and this part of the spectrum was omitted from the figure. Two bands which were not observed in the pure alcohols were found in the solutions at 3.8μ and 5.2μ. These bands occurred in the same region for NaOH and KOH solutions and at approximately the same wave-length when the solvent was methyl or ethyl alcohol. The region from 4μ to 5.4μ transmits about 80 percent of the radiation

[1] E. K. Plyler and W. Gordy, J. Chem. Phys. **2**, 470 (1934).
[2] J. R. Collins, Phys. Rev. **20**, 486 (1922).
[3] W. Weniger, Phys. Rev. **31**, 388 (1910); J. W. Sappenfield, Phys. Rev. **33**, 37 (1929); E. K. Plyler and T. Burdine, Phys. Rev. **35**, 605 (1930).
[4] E. K. Plyler and E. S. Barr, J. Chem. Phys. **2**, 307 (1934).

and the percent transmission would have been greater if corrections had been made for the reflection of the fluorite windows in this region.

The band at 5.2μ is the most intense of all the bands observed. It is found at approximately the same position in aqueous solutions of the hydroxides. The band at 3.8μ occurs at a longer wave-length than the corresponding band in aqueous solutions. Since these bands are characteristic of different hydroxides in solution, they are designated as XOH in the figure.

The results obtained in the region from 0.8μ to 2.0μ are shown in Fig. 2. There are many small

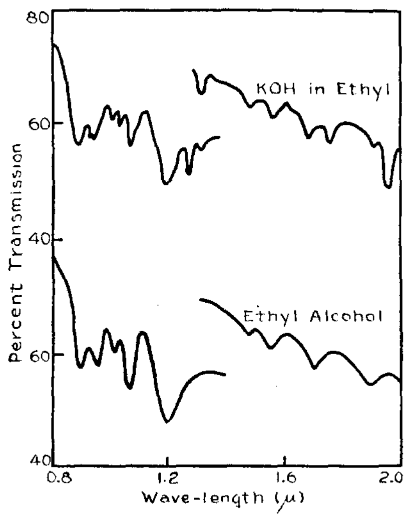

FIG. 2. Small bands produced in the region from 0.8μ to 2μ by hydroxide solutions. The cells were 1 cm thick.

bands in this region due to the alcohols and the additional bands are not so easily detected. Small bands were located at 0.96μ, 1.05μ, 1.27μ, 1.30μ, 1.73μ and 1.89μ.

Also a small band was located at 0.76μ but it is not shown in the figure. The region from 2.0μ to 2.8μ was studied with thinner cells and the results are shown in Fig. 3. Two bands with greater intensity were found at 2.30μ and 2.60μ. The observed bands have been classified as given in Table I. The bands at 3.8μ and 5.2μ are considered as fundamentals and called ν_2 and ν_1, respectively. All the other observed bands except the band at 2.30μ are found to be harmonics of these bands. The calculated band for the combination $\nu_1+\nu_2$ does not check closely with the observed band at 2.30μ and this band may be

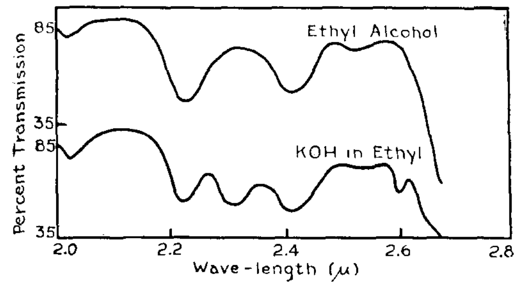

FIG. 3. The bands at 2.3μ and 2.6μ produced by hydroxides in alcoholic solutions. The cells were about 1 mm thick.

a fundamental. No correction term was introduced in the calculation of harmonic frequencies but the check is very good. The intensity of the harmonic bands does not decrease rapidly. The fourth harmonic of each fundamental was observed.

Except for the shift of the band at 3.65μ in aqueous solutions of the hydroxides to 3.8μ for the alcoholic solutions, there appears to be little change in the absorption of the hydroxides in solutions of water or alcohol. It has already been shown that the two fundamental bands of the hydroxide solutions are due to the energy levels between the undissociated hydroxide molecule and water molecules. The present work shows that the energy levels between hydroxide molecules and the alcohol molecules are very similar

TABLE I. *Classification of observed bands.*

Term	Frequency in cm^{-1} Calc.	Obs.	Wave-length in microns Calc.	Obs.
ν_1	1923*	1923	5.20*	5.20
ν_2	2632*	2632	3.80*	3.80
$2\nu_1$	3846	3846	2.60	2.60
$\nu_1+\nu_2$	4554	4348	2.20	2.30
$2\nu_2$	5264	5291	1.90	1.89
$3\nu_1$	5769	5780	1.73	1.73
$4\nu_1$	7692	7692	1.30	1.30
$3\nu_2$	7896	7874	1.26	1.27
$5\nu_1$	9615	9524	1.04	1.05
$4\nu_2$	10528	10526	0.95	0.95
$5\nu_2$	13160	13158	0.76	0.76

* Observed values taken as calculated values.

to the energy levels where water is the solvent. This result is in agreement with the general observation that aqueous and alcoholic solutions of the same substance usually give rise to the same color.