All the compounds used for the determination of absorption spectra were purified carefully, until they had the correct melting points. The one optically active isomer isolated (d-methylethyl-β-naphthylamine oxide) was tested also for agreement with Meisenheimer's value for the specific rotation for the sodium line.

Summary

1. Curves and table record the absorption spectra data for dimethylaniline oxide, the hydrochlorides of dimethylaniline oxide and of methylethylaniline oxide, methylethyl-β-naphthylamine and its oxide, all in solution in absolute alcohol.

2. Curve and table and equation are given for the rotatory dispersion of d-methylethyl-β-naphthylamine oxide into (but not through) the region of absorption.

3. Detailed directions are given for the oxidation of methylethyl-β-naphthylamine and the isolation of the oxide.

4. Conclusions are tentatively drawn concerning the non-homogeneity of the absorption band of the amine oxide group, and its relation to the carbonyl group.

Infrared Studies. III. Absorption Bands of Hydrogels between 2.5 and 3.5 μ

BY A. M. BUSWELL, KARL KREBS AND W. H. RODEBUSH

The use of the infrared spectrograph for studying the state of water in various compounds especially where the valence was obscure was first suggested by Coblentz in 1911.[1] He found that the water of hydration of certain minerals showed absorption peaks at the approximate wave lengths of 1.5, 2, 3, 4.75 and 6 μ. He also noted similar absorption especially at 3 μ for gelatin which contained some moisture. This he interpreted as indicating some sort of combination between the water and the gelatin.

Little progress was made in the clarification of many such situations until the development of our modern theory of valence a decade later. One of the corollaries to this theory of valence was put forward in the paper by Latimer and Rodebush[2] which proposed the hydrogen bond as an explanation of the valence in certain compounds (e. g., ammonium hydroxide, $H_3N:H:OH$). This suggestion appeared to offer a plausible explanation of the way in which many substances combine with water to form gels since such substances (gelatin, agar, starch, silica, etc.) have oxygen or nitrogen atoms with free electron pairs which could share one of the hydrogens of water.[3]

About two years ago we undertook investigation of the water in gels by means of the infrared spectrograph to determine whether water was in fact held by means of this hydrogen bond. Previous

papers from this Laboratory[4] reported data which showed that compounds of the formula ROH in dilute solution had strong absorption at 2.75 μ, an absorption which is considered to be due to —OH. Where opportunity for hydrogen bonding existed as in more concentrated solutions of alcohols (intermolecular) or in compounds like o-nitrophenol (intramolecular) the absorption shifted to a longer wave length (2.95 to 3 μ). One difficulty encountered in extending this work to the study of water in gels is that the gels are rather opaque in this region and must be examined in very thin films. Quantitative data for correlating the absorption with water content will require micro-analytical apparatus not yet available to us. The present paper reports a study of gel films under various conditions of moisture to determine qualitatively whether the moisture content would affect the absorption where —OH and O:H:O are known to be active. The substances studied were, β-amylose, gelatin, agar and a clay montmorillonite.

Experimental Method

Films of the materials to be studied were prepared on microscope cover slips floating on mercury. The spectrometer used was described in the previous paper.[4] The initial curve was made in most cases on a film dried in a vacuum vessel attached to a water pump. Subsequent absorption curves were made by dehydrating the film in an oven set at various temperatures.

Preparation of Specimens. β-Amylose.—Two cubic centimeters of a 3% solution of this carbohydrate pre-

(1) W. W. Coblentz, J. Franklin Inst., **172**, 309 (1911).

(2) W. M. Latimer and W. H. Rodebush, THIS JOURNAL, **42**, 1419 (1920).

(3) A. M. Buswell, A. C. S. Monograph No. 38, 1929, pp. 53 and 60.

(4) A. M. Buswell, Victor Dietz and W. H. Rodebush, J. Chem. Phys., **5**, 84, 501 (1937).

pared by the method of Taylor and Keresztesy[5] from air-dried corn starch, was evaporated on a 24–40 mm. glass cover slip. The film was then mounted in a suitable holder.
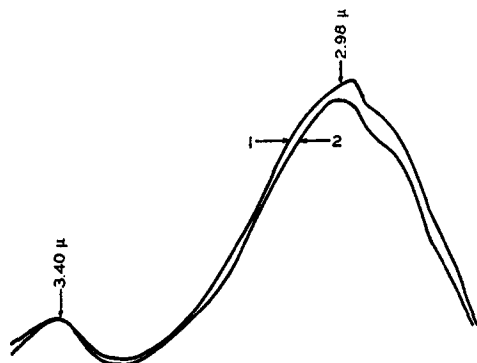

Fig. 1.—Amylose: curve 1, after removal of excess water by the water pump; curve 2, after drying in oven at 67° for eighteen hours.

The montmorillonite was obtained from R. H. Bray, Assistant Chief, Soil Survey, Agricultural Experiment Station, University of Illinois, who furnished the following description: "The clay was a sample of montmorillonite, which occurs as practically the whole constituent of the Wyoming bentonite deposits and the superfine fraction, composed of particles less than 0.06 micron, would repre-

sent a very pure sample of this mineral. The water of ignition for this particular sample was 14.55% based on the air-dried sample." A 1% suspension was allowed to settle for twelve hours, and a 2-cc. sample from the upper portion of the tube was pipetted out and dried on a cover slip as above.

Agar and Gelatin.—Two cc. of a 3% solution of Difco Bacto-agar, and a 5% solution of Eastman ash-free gelatin were used in making the other films, respectively.

Discussion

The β-amylose films show two characteristic absorption peaks (Fig. 1), one at about 3.4 μ, characteristic of C–H, and one at 3 μ characteristic of the hydrogen bond (O:H:O). On drying the film at 67° the 3.4 μ band remains constant but the 3 μ band is decreased.

Fig. 3.—Gelatine: curve 1, film dried with water pump; curve 2, film dried at 65° for one and one-half hours; curve 3, film dried at 62° for fourteen hours; curve 4, film dried at 105° for two hours; curve 5, film dried at 122° for fourteen hours.
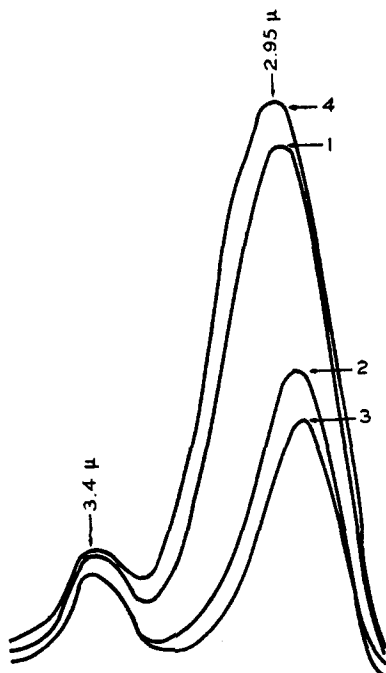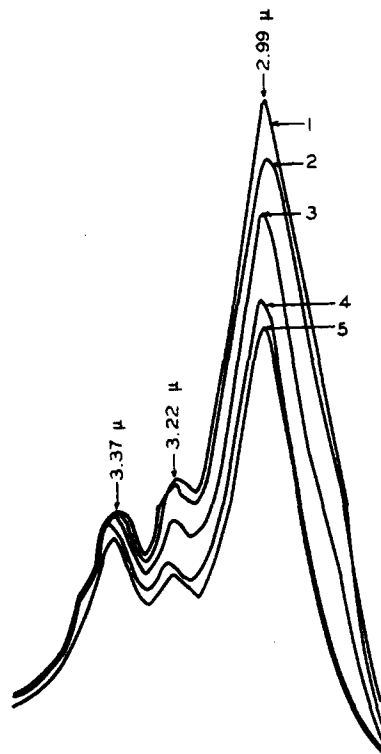

Fig. 2.—Agar: curve 1, film dried by water pump; curve 2, film dried at 105° for five hours; curve 3, film dried at 138° for eleven hours; curve 4, film exposed to saturated water vapor at room temperature for ninety-six hours.

The agar films (Fig. 2) show the same type of absorption as do the starch films. The 3 μ band seems a bit sharper and is shifted slightly to shorter wave lengths on drying. It seems particularly significant that there is no OH absorption (2.75 μ) in either of these carbohydrates even

(5) Taylor and Keresztesy Ind. Eng. Chem., 28, 502 (1936).

in the most dehydrated conditions obtained. A film of dry glucose melted between quartz plates and allowed to solidify also showed absorption at 3 μ but none at 2.75 μ.

Gelatin (Fig. 3) in addition to peaks at 3.4 and 3 μ, shows a third absorption peak at 3.2 μ which may be related to the water content of the film since it decreases as the film is dehydrated. This band possibly may be due to an O:H:N or N:H:N bond. We have been unable to find an analogous absorption peak in other organic nitrogen compounds. The height of the 3 μ band again depends upon the water content. This hydration was found to be reversible since the absorption curve of the film dried at 65° and rehydrated by exposure to a water saturated air superposed curve 1. There is no indication of an OH band at 2.75 μ.

The curves for montmorillonite (Fig. 4) indicate the presence of both free OH (2.75 μ) and the hydrogen bond (3 μ). X-Ray investigations[6-9] have indicated two types of water combination in this material one of which was supposed to result in the formation of OH groups. The present data agree with the X-ray indications and identify the second water linkage as occurring through hydrogen bonds. As would be expected, drying has a much greater effect on the absorption at 3 μ than on that at 2.75 μ.

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(6) U. Hofmann, K. Endell, and D. Wilm, *Z. Krist.*, **86**, 340–348 (1933).

(7) G. Nagelschmidt, *ibid.*, **93**, 481–488 (1936).

(8) U. Hofmann and W. Bilke, *Kolloid Z.*, **77**, 238–251 (1936).

(9) W. F. Bradley, R. E. Grim, and G. L. Clark, *Z. Krist.*, **A97**, 216–222 (1937).
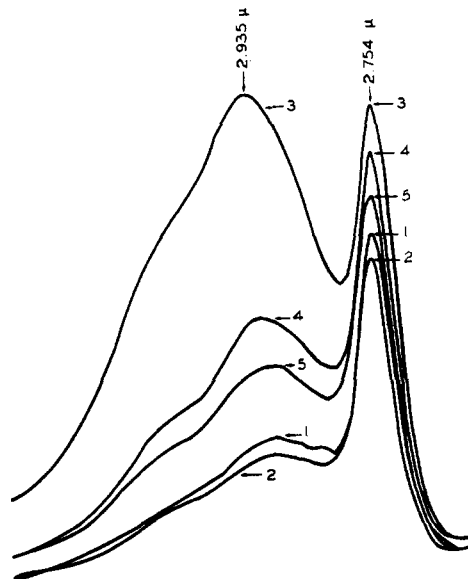
Fig. 4.—Montmorillonite: curve 1, film dried at 100° for thirty-six hours; curve 2, film dried at 100° for additional six hours; curve 3, air saturated with water vapor at 26° passed through cell for five hours; curve 4, film dried at 110° for six hours; curve 5, film dried at 110° for additional twenty-four hours.

Summary

1. Certain gels show absorption at 3 μ which appears to be proportional to their water content.

2. Three carbohydrates examined show no absorption at 2.75 μ.

3. A clay montmorillonite shows absorption at 2.75 and 3 μ. The height of the 3 μ band is much more strongly affected by water content than is the 2.75 μ band.

4. A study correlating the absorption with quantitative data on water content is under way.

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