

their solubility curve for lithium nitrate in water. I have been unable to obtain the transition point dilatometrically and, if the solubility figures of Donnan and Burt are plotted, there seems no reason to give the curve the shape drawn by them; their figures are better represented by a smooth curve: in any case, their determinations are too far apart to settle the matter definitely. I conclude that the existence of the hydrate,  $\text{LiNO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ , is doubtful.

### Summary

1. The system  $\text{LiNO}_3\text{-NH}_4\text{NO}_3$  has been investigated by thermal analysis. The results of Perman and Harrison are confirmed and extended.
2. The system  $\text{LiNO}_3\text{-NH}_4\text{NO}_3\text{-H}_2\text{O}$  has been investigated at 90, 60, 31 and 25° by the usual solubility technique.

3. No compound occurs, under any of the above conditions; neither is solid ammonium nitrate soluble in solid lithium nitrate (up to 90°), nor lithium nitrate in any of the four crystalline modifications of ammonium nitrate.

4. Lithium nitrate exists in but one crystalline form between room temperature and its melting point, in accordance with Perman and Harrison.

5. The hydrate,  $\text{LiNO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ , described by Donnan and Burt, nowhere exists as stable solid phase. A direct investigation of transition point with the dilatometer failed to reveal the transition:  $\text{LiNO}_3 \cdot \frac{1}{2}\text{H}_2\text{O} \rightleftharpoons \text{LiNO}_3 + \frac{1}{2}\text{H}_2\text{O}$ , which is said to occur at 61.1°. The existence of this hydrate is doubtful.

WINNIPEG, CANADA

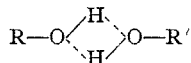
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[CONTRIBUTION FROM THE DEPARTMENTS OF PHYSICS AND CHEMISTRY OF THE UNIVERSITY OF FLORIDA]

## Spectroscopic Evidence of Intermolecular Transfer of Protons

BY DUDLEY WILLIAMS<sup>1</sup> AND W. DAVID STALLCUP<sup>2</sup>

The high degree of association exhibited by pure liquids and by liquid mixtures in which the molecules contain hydrogen atoms attached to atoms of the electronegative elements fluorine, oxygen or nitrogen has been explained, qualitatively at least, in terms of proton bonds or hydrogen bridges formed between neighboring molecules. According to the proton-bond theory, protons are "shared" between adjacent molecules in somewhat the following manner



In the case of water and other liquids having especially strong proton bonds, the proton can be transferred from one molecule to another when the molecules are separated. Whether actual intermolecular transfer of protons can occur in all liquid mixtures having association of the type indicated above is not entirely clear. The purpose of the present paper is to report a method for detecting intermolecular transfer and to give the results for a single binary mixture.

The method is rather simple: the hydrogen in one liquid is replaced by deuterium. Then the

two liquids are mixed. After mixing, the liquids are separated by distillation and the liquid originally containing no deuterium is tested for the presence of deuterium. The changes in physical constants produced by the presence of deuterium are, in most cases, so slight that it was decided to use the infrared absorption of the liquids as a test for the presence of deuterium. The separation of OH and OD bands in alcohols is approximately 830  $\text{cm}^{-1}$ ; the OH and OD absorption bands appear at 3.0  $\mu$  and 4.0  $\mu$ , respectively. The two liquids chosen for study were methanol and heavy butanol.

### Experimental Results

Anhydrous methanol was prepared by treating a suspension of magnesium methylate in methanol with freshly distilled methanol and then separating the methanol from this mixture of magnesium oxide and magnesium methylate by distillation. The methanol thus prepared had the following physical constants: b. p. 64.5°,  $n_{25}^D$  1.3268, and  $d_{25}^4$  0.7896.

The deuterium butoxide was prepared by adding deuterium oxide to *n*-butyl borate. After standing a few hours, the precipitated boric acid was removed by filtration. The filtrate was then fractionated in order to separate the deuterium

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butoxide from unreacted butyl borate. The deuterium butoxide fraction was then re-fractionated through a thirty-plate column and the material distilling at 119.0–119.5° was collected. The physical constants of this material were:  $n_D^{25}$  1.3974 and  $d_4^{25}$  0.8131.

The transmission of samples of the methanol and the deuterium butoxide was then measured in the region between 2 and 5  $\mu$ . The absorption cells used were approximately 0.03 mm. in thickness. The spectrometer was a Littrow instrument equipped with a rock salt prism. The results obtained are shown in Fig. 1. Curve A is the transmission curve for methanol and exhibits only two absorption bands; the band at 3.0  $\mu$  arises from an OH vibration and the band at 3.4  $\mu$  from a CH vibration. Curve B represents the transmission of the deuterium butoxide prepared in the manner described above. In this curve strong bands are found near 3.4  $\mu$  and 4.0  $\mu$ , arising from CH and OD vibrations, respectively; a rather weak band is also observed at 3.0  $\mu$ , indicating that some OH groups are also present in the heavy butanol.

After the spectra of the original liquids had been studied, equimolecular amounts of the liquids were mixed and heated for two hours. At the end of this time, the methanol and butanol were separated by fractionation through a forty-plate column. The first fraction was collected at the end of ninety minutes and, after discarding intermediate fractions, the final butanol fraction was collected three hours later. The recovered alcohols had the following physical constants

Methanol: b. p. 65.5°  $n_D^{25}$  1.3270  $d_4^{25}$  0.7913

Butanol: b. p. 119°  $n_D^{25}$  1.3970  $d_4^{25}$  0.8103

The spectra obtained for a sample of the recovered methanol is shown in Curve C of Fig. 1. Three absorption bands will be noted; these are produced by OH, CH, and OD vibrations. The OH band is weaker than in the spectrum of the original methanol and an OD band can now be observed near 4.0  $\mu$ . Curve D represents the transmission of a sample of the recovered butanol and also indicates absorption arising from OH, CH, and OD groups. The OH band is much stronger

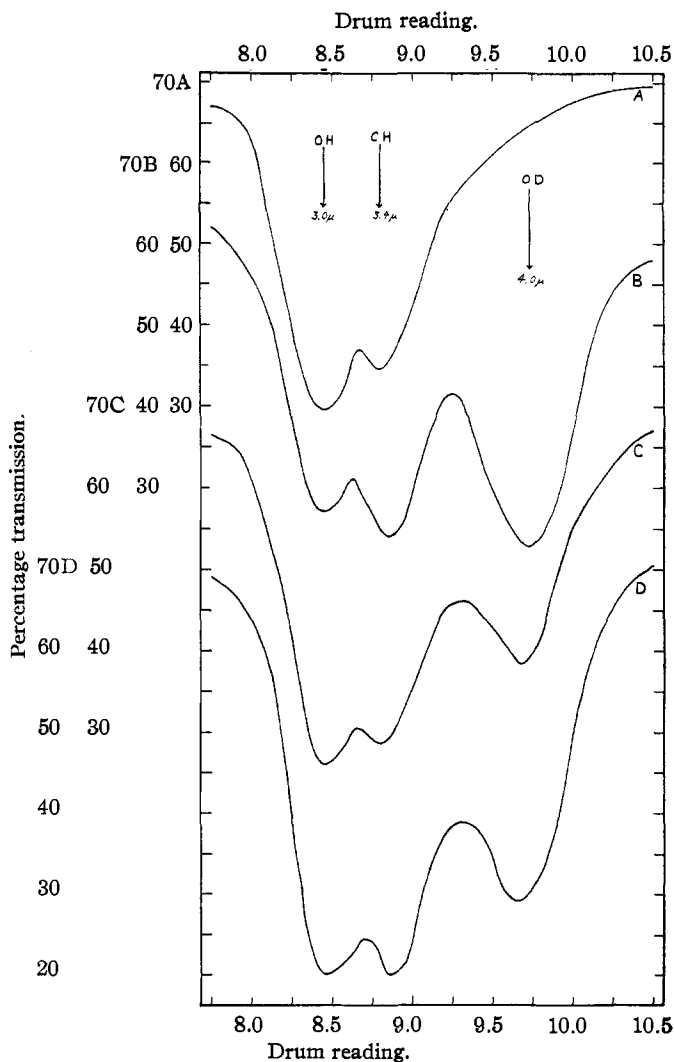


Fig. 1.—The infrared transmission of methanol and butanol: Curve A, original methanol; Curve B, original butanol (containing deuterium); Curve C, recovered methanol; Curve D, recovered butanol.

than in the original butanol, while the OD band is correspondingly weaker.

### Discussion

The spectroscopic results indicated in Fig. 1 can be interpreted on the basis of the actual transfer of hydrogen atoms from methanol to butanol and the transfer of deuterium atoms from butanol to methanol. There are obvious extensions of the method developed in the present study to the study of other mixtures whose components can be separated by distillation. It was originally hoped to extend the present investigation to include the study of proton transfers between other alcohol molecules, between amine molecules, and be-

tween alcohols and amines. Numerous other applications of the method suggest themselves, but the pressure of other work will prevent pursuing the problem further at present.

### Summary

When a mixture of MeOH and BuOD is fractionated, it is found that MeOH and MeOD are

both present in the recovered methanol and that BuOH and BuOD are both present in the recovered butanol. It is concluded that the intermolecular hydrogen bonds involve the actual transfer of protons between molecules. Extension of the present study to include other compounds is suggested.

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## The Structures of Dimethyl Boron Fluoride and Methyl Boron Difluoride

BY S. H. BAUER AND J. M. HASTINGS

The structures of boron trifluoride and boron trimethyl as determined by Lévy and Brockway<sup>1</sup> were among the first items of information to suggest that rather artificial explanations may be necessary in some cases to make the observed interatomic distances harmonize with the Pauling and Huggins<sup>2</sup> table of covalent radii and with the postulate of the dependence of bond order on the distances between the atoms in a molecule.<sup>3</sup> The suggestion of Schomaker and Stevenson<sup>4</sup> that as a next best approximation the electronegativity difference between the atoms be considered in computing the separation for normal covalent bonding was a welcomed one since it permitted a reasonable interpretation of data otherwise not readily accounted for; it removed the necessity for the artificial postulates applied to various boron compounds.<sup>5</sup> The structures of the methyl boron fluorides discussed in this paper furnish critical tests for the applicability of the table of atomic radii as revised by them and of the use of their equation

$$r_{ab} = r_a + r_b - 0.09 |x_a - x_b| \quad (1)$$

Both the methyl boron difluoride and the dimethyl boron fluoride were furnished by Dr. Anton B. Burg.<sup>6</sup> We wish to acknowledge his coöperation and to thank him sincerely for this and other compounds he gave us.

### The Apparatus and Photographs

The present electron diffraction apparatus re-

(1) H. A. Lévy and L. O. Brockway, *THIS JOURNAL*, **59**, 2085 (1937).

(2) L. Pauling and M. L. Huggins, *Z. Krist.*, **A87**, 205 (1934).

(3) For references, L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., Chapter V, 1940.

(4) V. Schomaker and D. P. Stevenson, *THIS JOURNAL*, **63**, 37 (1941).

(5) S. H. Bauer and J. Y. Beach, *ibid.*, **63**, 1394 (1941).

(6) A. B. Burg, *ibid.*, **62**, 2228 (1940).

sembles the latest model constructed by Brockway.<sup>7</sup> A simple but highly effective voltage regulator<sup>8</sup> and voltmeter have been set up so that the net voltage fluctuations have been reduced to a few hundredths of one per cent. The apparatus was designed to be flexible and special provision made for the incorporation of a rotating sector,<sup>9</sup> the assembly of which has now been completed. A more detailed description of this unit will be given in a future paper.

The photographs were taken with electrons having a wave length near 0.06 Å., and with the nozzle-plate distance equal to 13.69 cm. The visual appearance of the photographs is that indicated by curves V, Figs. 2 and 4; the  $s_0 = \left[ \frac{4\pi}{\lambda} \sin \theta_0/2 \right]$  values for the maxima and minima as determined by the usual visual technique, and their relative intensities above or below the estimated backgrounds (lines through curves V) are given in Tables II and III.

### Analysis of the Data

Because of their relative simplicity, considerable information regarding the structures of these molecules can be obtained from their radial distribution curves. These were computed according to the method of Walter and Beach,<sup>10</sup> and are plotted in Fig. 1. The results are summarized in Table I. To facilitate the interpretation of these curves and to show the resolution which might be expected under ideal conditions, "synthetic" radial distribution curves for various

(7) E. H. Eyster, R. H. Gillette and L. O. Brockway, *ibid.*, **62**, 3236 (1940), and private communications.

(8) The voltage stabilizer is of the degenerative type and resembles the one described by L. G. Parratt and J. W. Trischka, *Rev. Sci. Instruments*, **13**, 17 (1942).

(9) P. P. Debye, *Physik. Z.*, **40**, 404 (1939).

(10) J. Walter and J. Y. Beach, *J. Chem. Phys.*, **8**, 601 (1940).