used by Lyons and Riley[5] for their optical measurements. Careful examination was made to assure the same temperature in both series of determinations. The results at the molar concentrations designated are given in Table I. Three of the values obtained by Gouy diffusiometry are recorded in parentheses in this table. In the last column of the table, the diffusion coefficient calculated by equations 1, 2 and 3 are presented. Although the present results are higher than those obtained by Harned and Levy, they are still lower than the theoretical values.

Further Considerations Regarding the Diffusion Coefficients of the Alkaline Earth Chlorides.—In Fig. 1, the experimental diffusion coefficients of the alkaline earth chlorides are plotted against the square root of the molar concentration. The curves at the top and bottom represent the calculated values for barium and magnesium chlorides, respectively.[10] As evidenced by the circles representing the experimental results, the theory is confirmed for these salts. The second and third curves from the top are plots of the theoretical values for calcium and strontium chlorides, respectively. It appears that the strontium chloride diffusion coefficients, represented by crosses, lie near the theoretical curve and that the calcium chloride values, represented by circles, lie below the curve computed theoretically. The three results at the higher concentrations were obtained by Gouy diffusiometry and are seen to be in accord with the conductometric values.

(10) In Table 1, H. S. Harned and F. M. Polestra, This Journal, **76**, 2064 (1953), under $MgCl_2$, the following corrections should be made. At $c = 0.00205$, the observed result should be 1.163 and the calculated value 1.168 and at $c = 0.004$ the observed value should be 1.155 and the calculated 1.150.

New Haven, Conn.

[Contribution from the Metcalf Chemical Laboratories of Brown University]

The Structure of the Aqueous Borate Ion

By John O. Edwards, Glenn C. Morrison,[1] Virginia F. Ross and John W. Schultz

Received July 28, 1954

The Raman spectrum of the borate ion in aqueous solution has been reinvestigated. The number, shapes and positions of the lines indicate that this ion has tetrahedral symmetry and is $B(OH)_4^-$. The infrared spectrum of a synthetic sample of the mineral teepleite, reported to contain this ion, confirms the Raman data. The Raman spectrum of the fluoborate ion has been reinvestigated.

The structure, in aqueous solution, of the conjugate base of boric acid has remained a mystery in spite of attempts to obtain a definitive answer to the problem. One can conceive of three possible structures for a *monomeric* borate ion of single negative charge; the differences between these structures lie primarily in the coördination number of the boron atom.

The first possibility, the metaborate ion BO_2^-, is unlikely on chemical grounds. There are no known compounds in which tripositive boron has a coördination number of two. For example, the anhydrous alkali metaborates contain cyclic triborate ions in which the boron atoms have a coördination number of three.[2] The second possible structure, which is $H_2BO_3^-$, would be the most reasonable possibility if boric acid were a Brönsted-Lowry acid (*i.e.*, a proton donor). On the other hand, if boric acid acts as a Lewis acid (an electron pair acceptor) as does boron trifluoride, then the most reasonable possibility for the structure of the conjugate base is $B(OH)_4^-$. Since some boron-oxygen compounds have a coördination number of three and others of four and since most solid borates contain polymeric anions, the chemical evidence available does not discriminate between the latter two structures.[3]

It is necessary, therefore, to rely on physical measurements which do not alter the equilibrium position in order to study this aqueous system; the Raman effect, it was felt, was most applicable to this problem. Previous work on the Raman spectra of various borate solutions has been done by three groups[5–7]; the results of these studies have been summarized by Hibben.[7] (The work of Ghosh and Das[5] is in complete disagreement with all of the other studies including the present one. As they gave no details on their preparation of "sodium metaborate," their work will not be considered further.) The fact that the borate ion has only one strong Raman line led to the conclusion that it has the metaborate structure; however, this conclusion was later questioned on the discovery of other weaker Raman lines.[6,7]

Recently, it has been found by Fornaseri[8] through X-ray studies on the minerals teepleite (analysis gives $NaBO_2 \cdot NaCl \cdot 2H_2O$) and bandylite (analysis gives $Cu(BO_2)_2 \cdot CuCl_2 \cdot 4H_2O$) that the borate ion in each of these solids has four oxygens situated about each trivalent boron. From the symmetry and the numbers of oxygens and hydrogens present, it was borne out by Fourier analysis that

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(1) Senior Research Assistant, 1953–1954.

(2) W. H. Zachariasen, *J. Chem. Phys.*, **5**, 919 (1937).

(3) This is, in large measure, a result of the rapid rate of replacement reactions involving ligands in the coördination sphere of the borate ion.[4]

(4) J. O. Edwards, This Journal, **75**, 6151 (1953); *J. Chem. Educ.*, **31**, 270 (1954).

(5) J. C. Ghosh and S. K. Das, *J. Phys. Chem.*, **36**, 586 (1932).

(6) (a) J. R. Nielsen and N. E. Ward, *J. Chem. Phys.*, **5**, 201 (1937); (b) J. R. Nielsen, N. E. Ward and H. Dodson, *Phys. Rev.*, **53**, 331 (1938).

(7) (a) J. H. Hibben, *Am. J. Sci.*, **35A**, 113 (1938); (b) J. H. Hibben, "The Raman Effect and its Chemical Applications," Reinhold Publ. Corp., New York, N. Y., 1939, pp. 430–439.

(8) M. Fornaseri, *Periodica mineral, Rome*, **18**, 103 (1949); **19**, 157 (1950); *La Ricerca Scientifica*, **21**, No. 7 (1951).

the structure of the borate ion in these solids is $B(OH)_4^-$. It should be possible, therefore, to compare infrared spectrum data on teepleite with the frequencies found in the Raman spectrum of the aqueous borate ion.

All of the results obtained in this investigation agree with those predicted for the structure $B(OH)_4^-$ and are felt to be convincing proof that this is the structure of the aqueous borate ion.

Experimental

The Raman spectra were obtained on the recording photoelectric instrument built by Busing and Hornig.[9] As Goubeau and Bues,[10] who studied the Raman spectrum of sodium fluoborate solutions, did not give any figures of their photographic plates, it was felt that a comparative spectrum of the fluoborate ion should be obtained on this apparatus to check for similarities and for dissimilarities in the spectra of the two anions.

The potassium borate solutions, usually about ten molar, were made from reagent grade boric acid and potassium hydroxide without further purification. The saturated sodium fluoborate solution was prepared by treating solid ammonium fluoborate with a slight excess of sodium hydroxide in enough water to dissolve the product. The ammonia was volatilized from the solution by warming at reduced pressure.[11] The borate and fluoborate solutions showed some turbidity even after filtration through a fine sintered-glass filter; treatment with decolorizing charcoal and refiltration clarified the solutions to the point where the Raman spectra could be obtained without difficulty.

The synthetic teepleite was prepared by mixing equal volumes of saturated solutions of sodium chloride and sodium borate. After sitting three days at room temperature, large, transparent prismatic crystals were obtained from solution. These were identified as teepleite by the powder X-ray pattern.

Results

Raman.—It was immediately apparent that the strongest Raman line of the aqueous borate ion is only moderately intense; the balance of the lines are decidedly weak, particularly the line of lowest frequency. The observed results for the borate ion are presented in Table I, along with the Raman spectrum of the fluoborate ion and with previous work for comparison. The similarity of these two spectra is striking, not only in respect to the number and positions of the lines but also to the estimated relative intensities.

TABLE I

THE RAMAN FREQUENCIES (IN CM.$^{-1}$) OF THE BORATE AND FLUOBORATE IONS

Assignment	Class	Borate	Fluoborate[e]
ν_1	A_1	754(10)[a] 749[b] 747(6)[c]	786(10)[a] 769(10)[d]
ν_2	E	379(1)[a]	369(2)[a] 353(2)[d]
ν_3	F_2	947(4)[a] 950(1)[b]	1100(4)[a] 984(4)[d]
ν_4	F_2	533(1)[a]	541(3)[a] 524(1)[d]

[a] This study. The ν_1 line in both cases has been given an arbitrary intensity value of ten. [b] Ref. 6 (see also ref. 7). [c] Ref. 7. [d] Ref. 10. [e] Data on the infrared spectra of solid fluoborates are reported in refs. 13 and 14. The results are in general agreement with the Raman data.

The Raman spectrum of the fluoborate ion is closely similar to that of the borate ion. The intensities of three of the lines again are weak while that of ν_1 is again moderately strong. Even the shapes of the lines match fairly well; in both cases, ν_1 is a sharp line[12] and ν_4 is somewhat broadened but has a distinct maximum. All of the other lines are broad; for the borate ion, ν_2 is flat and ν_3 has a rounded maximum, while for the fluoborate ion, ν_3 is flat and ν_2 has a definite maximum.

The Raman data are not in agreement with either the BO_2^- structure or the $H_2BO_3^-$ structure. The metaborate ion would be a linear triatomic particle as it is isoelectronic with CO_2, NO_2^+ and N_3^-. There should be only one Raman line active for this structure, and it presumably would be not far from 1300 cm.$^{-1}$; the above three isoelectronic particles have their Raman lines at 1336, 1400 and 1348 cm.$^{-1}$, respectively.

Assuming the non-existence of oxygen-hydrogen modes and isotope splittings as a first approximation, the structure $H_2BO_3^-$ should have six fundamentals active in the Raman spectrum. Carbonyl fluoride COF_2 shows seven lines (one of which is reported to be an overtone).[15] Urea also has seven lines below 2000 cm.$^{-1}$.[16] The Raman spectra of these two molecules, both of which are isoelectronic with $H_2BO_3^-$, show no apparent similarity to that of the aqueous borate ion.

X-Ray and Infrared.—In order to check the structure of our synthetic teepleite, a powder X-ray pattern was made at the Harvard University Geology Department. The correct lines were obtained and there were no spurious lines traceable to impurities.

The infrared spectrum of a powdered sample of teepleite showed only a band in the region of 900–1000 cm.$^{-1}$; however there was a large amount of scattering. When mulled with Nujol, the teepleite showed the following spectrum: In the NaCl prism region, there is a very strong and broad adsorption band centered near 941 cm.$^{-1}$. There is a weak band at 867 cm.$^{-1}$, and there is also an indication of a teepleite band at 1310 cm.$^{-1}$ although this is not certain since Nujol has a weak band near this frequency. In the KBr prism region, there is a strong and broad adsorption band centered at 598 cm.$^{-1}$ and a weak band at 518 cm.$^{-1}$.

From the selection rules for a tetrahedral structure, there should be infrared bands traceable to the ν_3 and ν_4 vibrations while the ν_1 and ν_2 vibrations should not be active. There also should be, for the borate case, active infrared bands resulting from oxygen-hydrogen vibrations.

The infrared band at 941 cm.$^{-1}$ can be assigned to ν_3, for this frequency is in good agreement with the value of 947 cm.$^{-1}$ from the Raman data. The

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[9] This instrument is partly described by Busing in *J. Opt. Soc. Am.*, **42**, 774 (1952).

[10] J. Goubeau and W. Bues, *Z. anorg. allgem. Chem.*, **268**, 221 (1952).

[11] This preparation was carried out by J. DiPalma.

[12] The position (next to highest frequency) and the shape (moderately strong and sharp) together are another indication of a structure of tetrahedral symmetry. The breathing mode of a tetrahedral structure normally has this position and shape; other modes can be seriously broadened by the environment.

[13] G. L. Coté and H. W. Thompson, *Proc. Royal Soc. (London)*, **210A**, 217 (1951).

[14] T. H. Walnut, Ph.D. dissertation, Brown Univ., 1951.

[15] A. H. Nielsen, T. G. Burke, P. J. H. Woltz and E. A. Jones, *J. Chem. Phys.*, **20**, 596 (1952).

[16] J. T. Edsall, *ibid.*, **4**, 1 (1936).

weak infrared band at 518 cm.$^{-1}$ is assigned to the ν_4 vibration; this value agrees fairly well with the value of 533 cm.$^{-1}$ from the Raman data. The lack of any significant infrared adsorption in the vicinity of 754 cm.$^{-1}$ confirms the assignment of this Raman band as ν_1.

The strong band at 598 cm.$^{-1}$ can be assigned with reasonable assurance to one of the oxygen–hydrogen torsional modes. It is possible that the band at 1310 cm.$^{-1}$ is the other torsional mode, since this is about the frequency which could be expected. It also could result from the overtone $\nu_1 + \nu_4$ although the value of 1310 cm.$^{-1}$ seems somewhat high; such an overtone is not unexpected, however, since it appears in the infrared spectra of the solid fluoborates.[13,14] It does not seem possible at present to give a satisfactory assignment to the weak band at 867 cm.$^{-1}$.

Discussion

As a check on the Raman spectrum of the borate ion, calculations based on the Heath–Linnett[17] potential function for tetrahedral structures were carried out. Using our values for ν_1, ν_3 and ν_4 to evaluate the three constants, the value of ν_2 was then calculated to be 382.7 cm.$^{-1}$. This value is in good agreement with the observed value of 379 cm.$^{-1}$.[18]

In all of the foregoing material, it was assumed that the borate ion is monomeric in aqueous solution. Such is not necessarily the case, but there is no good evidence that polymers do exist in large percentage in aqueous solution. For example, cryoscopic data on sodium borate solutions up to two molar concentration do not show any deviations attributable to polymerization.[19] It is also worth noting that the multiplicity of lines which should occur in the Raman data if polymerization were taking place are certainly not present, and that the ν_1 line is the predominant Raman line in all borate solutions from 0.18 molar up to saturated solutions of the potassium salt. For these reasons, the assumption that the borate ion is monomeric in aqueous solution seems justified.

The combination of results obtained in this investigation plus those from previous studies lead to the conclusion that the structure of the aqueous borate ion has tetrahedral symmetry. In all likelihood, therefore, it is $B(OH)_4^-$.

Acknowledgments.—The authors are indebted to D. F. Hornig and P. N. Schatz for many helpful discussions, and to C. C. Ferriso for carrying out the infrared measurements.

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[17] D. F. Heath and J. W. Linnett, *Trans. Faraday Soc.*, **44**, 878 (1948).

[18] A similar calculation for the fluoborate ion using the values ν_1 = 772 cm.$^{-1}$, ν_3 = 1030 cm.$^{-1}$ and ν_4 = 520 cm.$^{-1}$ from the infrared data[13,14] gave ν_2 = 366 cm.$^{-1}$. This value agrees well with our value of 369 cm.$^{-1}$ and less well with the value of 353 cm.$^{-1}$ of Goubeau and Bues.[10]

[19] H. Menzel and H. Schulz, *Z. anorg. allgem. Chem.*, **251**, 167 (1943).

PROVIDENCE, RHODE ISLAND

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Dielectric Properties and Molecular Structure of Hexamethyldisiloxane[1,2]

BY RUSSELL S. HOLLAND[3] AND CHARLES P. SMYTH

RECEIVED SEPTEMBER 10, 1954

The dielectric constant and loss of hexamethyldisiloxane have been measured over a wide temperature range. From the data, a dipole moment of 0.46 in the pure liquid, and 0.66 in the vapor phase have been calculated; the atomic polarization was determined as 7.9 cc. These values are shown to be consistent with the wide Si–O–Si valence angle and its unusual flexibility. The unusually low critical wave length, about 0.1 cm., calculated from the losses are attributed to the considerable symmetry of the molecule and the low viscosity of the liquid.

Because of the importance of the silicones, the relatively simple molecule of hexamethyldisiloxane has been extensively investigated. From measurements on the pure liquid, Sauer and Mead[4] obtained a dipole moment value 0.74 × 10^{-18} for the molecule, while Baker, Barry and Hunter[5] obtained 0.43. From measurements in benzene solution, Freiser, Eagle and Speier[6] obtained 0.79. Unpublished measurements by Dr. A. Di Giacomo in this Laboratory gave polarization values for the vapor which showed no regular variation with temperature, the observed fluctuations in value being within the possible experimental error. The vapor results indicated zero dipole moment with a large atomic polarization, which could not be determined in the liquid measurements. These apparently discordant results were reconcilable if the dipole moment was actually zero and the atomic polarization, necessarily neglected in the liquid measurements, had a high value of 13 cc. A large atomic polarization seemed entirely reasonable in view of the softness[7,8] of the silicon–oxygen bond, likened to a ball-and-socket joint, indicated by X-ray analysis of octamethylspiro[5.5]pentasiloxane. However, electron diffraction has given 130 ± 10° for the Si–O–Si valence angle,[9] a value consistent with those found for cyclic siloxanes,[10] which, however, could be some-

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[1] This research has been supported in part by the Office of Naval Research. Reproduction, translation, publication, use or disposal in whole or in part by or for the United States Government is permitted.

[2] This paper represents a part of the work submitted by Mr. R. S. Holland to the Graduate School of Princeton University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] Procter and Gamble Fellow in Chemistry, 1953–1954.

[4] R. O. Sauer and D. J. Mead, THIS JOURNAL, **68**, 1794 (1946).

[5] E. B. Baker, A. J. Barry and M. J. Hunter, *Ind. Eng. Chem.*, **38**, 1117 (1946).

[6] H. Freiser, M. V. Eagle and J. Speier, THIS JOURNAL, **75**, 2824 (1953).

[7] W. L. Roth, *ibid.*, **69**, 474 (1947).

[8] E. G. Rochow, "Chemistry of the Silicones," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1951, Chap. 7.

[9] K. Yamasaki, A. Kotera, M. Yokoi and Y. Ueda, *J. Chem. Phys.*, **18**, 1414 (1950).

[10] E. H. Aggarwal and S. H. Bauer, *ibid.*, **18**, 42 (1950).