Conductimetric and Potentiometric Studies of the Stoichiometry and Equilibria of the Boric Acid–Mannitol Complexes

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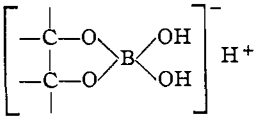
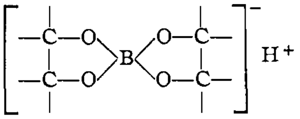
The formation of a complex between boric acid and certain hydroxy compounds has been demonstrated by the increase in mutual solubility, the increase in acidity and the change in the optical rotation. Biot,[1b] as early as 1842, reported that a solution of boric acid became acid to litmus upon the addition of sugars. A large number of these complexes were reported to have been isolated, but few of them were well defined or assigned satisfactory structures. In the early 1900's many workers attempted a systematic study of the stoichiometry of these complexes by physical measurements, but few came to similar conclusions. Thomson[2] found that boric acid could be determined by titration in the presence of various polyhydroxy compounds, using phenolphthalein. Later workers tested a long series of compounds in relation to their ability to raise the conductivity of a boric acid solution.[3,4,5]

Hermans[6] has shown that 1,2- and 1,3-diols of *cis* configuration generally form complexes which are acidic and which may often be isolated. He assigns these complexes two structures. One is a di-ester formed by splitting out two molecules of water between one hydrated borate ion and one molecule of a glycol. The other is formed by splitting out four molecules of water between one hydrated borate ion and two molecules of a glycol. The second type is often of great acidic strength. This "borospiran" structure has a center of asymmetry and thus would be expected to give rise to optical isomers. The fact that some of these isomers have been resolved, supports the proposed structure.





An article by Tung and Chang[7] seems to be the only quantitative study of the boric acid–mannitol complex. They postulated the reaction to be $B^- + nM \rightarrow BM_n^-$, where B^- represents the borate ion, n an integer, M the mannitol and BM_n^- the complex ion. The equilibrium constant for this reaction is K_2. The pH of various solutions was measured by use of a quinhydrone electrode. By graphical solution of an equation derived from the mass action expression, n and K_2 were found to be 2 and 2.75×10^6, respectively. They reported that they were able to isolate this complex.

Neither the constant nor the formulation proposed by these workers is in agreement with the data obtained in this Laboratory. Their interpretation of their data must be questioned in several respects. They used only one concentration of boric acid and only a twenty-three-fold change in mannitol concentration, ranging from about 100 to 4 moles of boric acid per mole of mannitol. On the basis of work performed in this Laboratory, it was found that many formulations led to a constant that was valid over a certain limited range of concentration. Indeed, the formulation proposed by Tung and Chang was found in this Laboratory to be valid in the case of solutions where the mannitol concentration varied several hundred fold, but it did not hold when the boric acid concentration was varied. An examination of the graph from which they determined n and K_2 leaves doubt as to the accuracy of these constants even in this limited range.

Preliminary Experiments.—The reagents used were C. P. boric acid, neutral, boron-free mannitol and conductivity water. Conductivity was measured with a Wheatstone bridge and pH with a Beckman pH meter. Unless otherwise specified, all measurements were made at room temperature (23–25°) in an open beaker. The effect of mannitol upon the conductance of a boric acid solution is shown in Fig. 1. Conductimetric titrations of boric acid and boric acid–mannitol solutions with strong base are shown in Fig. 2.

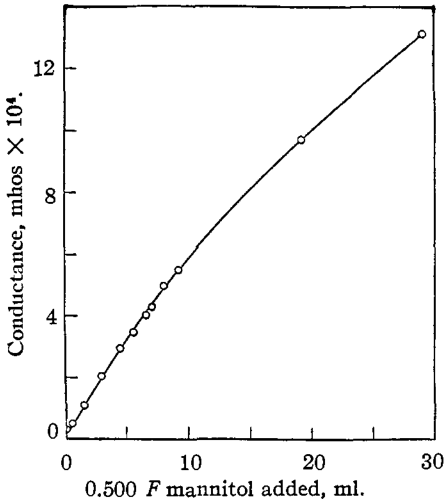


Fig. 1.—Addition of mannitol to 30.0 ml. of 0.0333 F boric acid (corrected for dilution).

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[1b] Biot, *Compt. rend.*, **14**, 49 (1842).

[2] Thomson, *J. Soc. Chem. Ind.*, **12**, 432 (1893).

[3] G. Magnanini, *Z. physik. Chem.*, **6**, 58 (1890).

[4] J. Böeseken and Van Rossen, *Rec. trav. chim.*, **30**, 392 (1912).

[5] J. Böeseken, *et al.*, *ibid.*, **40**, 553 (1921).

[6] P. H. Hermans, *Z. anorg. Chem.*, **142**, 83 (1925).

[7] Jo-Yun Tung and Hok-Ling Chang, *J. Chinese Chem. Soc.*, **9**, 125 (1942).

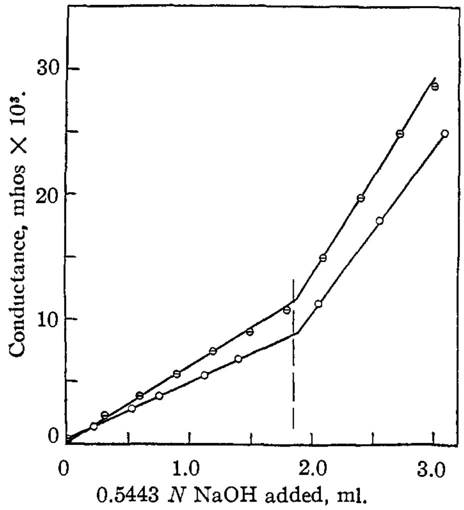

Fig. 2.—Conductimetric titrations of: ○, 40.0 ml. soln. 0.0250 *F* in H_3BO_3 and 0.125 *F* in mannitol; ⊖, 40.0 ml. soln. 0.0250 *F* in H_3BO_3 (corrected for dilution).

It will be seen that the complex is not destroyed in basic solution. The addition of boric acid to a solution maintained saturated with mannitol (about 1.15 *F*) is shown in Figs. 3 and 4. The corresponding experiment, using a saturated boric acid solution, was not attempted because of the anomalous behavior of concentrated boric acid solutions.

Addition of Mannitol to a Large Excess of Boric Acid.—To 50 ml. of a 0.200 *F* boric acid solution, 0.100 *F* mannitol solution was added from a buret. The *p*H was measured after each addition. The data are shown in Table I and Fig. 5.

TABLE I

ADDITION OF MANNITOL TO 50.0 ML. OF 0.200 *F* BORIC ACID

Mannitol, ml.	*p*H	$(H^+) \times 10^6$
0	5.39	4.1
0.050	5.38	4.2
.250	5.33	4.7
.500	5.29	5.1
.750	5.23	5.8
1.000	5.19	6.5
1.500	5.09	8.1
2.000	5.02	9.6
2.500	4.94	11.5
3.500	4.81	15.5
5.000	4.63	23.5

Addition of Mannitol to Boric Acid.—To 26.0 ml. of 0.00770 *F* boric acid there was added in small portions 0.500 *F* mannitol solution, the *p*H being measured as previously (Table II, Fig. 6).

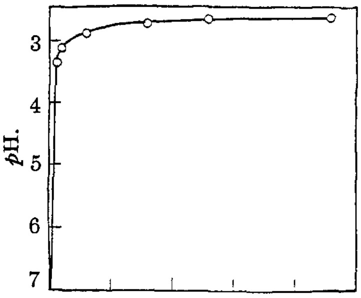

Fig. 3.—Addition of boric acid to 25.0 ml. of soln. maintained saturated with mannitol at 26°.

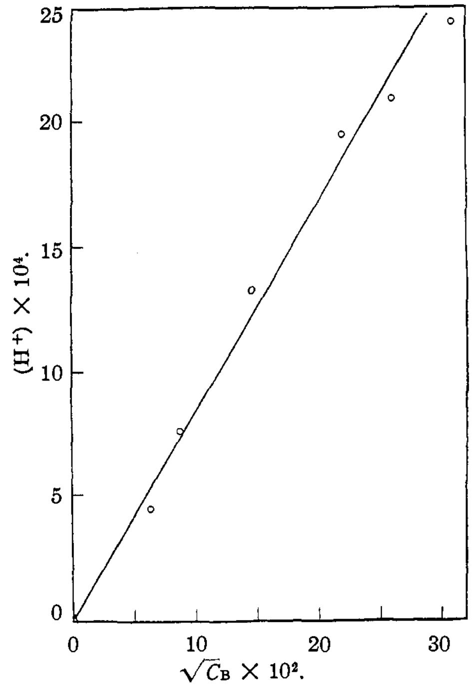

Fig. 4.—Addition of boric acid to soln. maintained saturated with mannitol at 26°.

Discussion

On the basis of the data presented, the following formulations are proposed. Mannitol reacts with borate ion to form two complexes, according to the mechanism

$$HB = H^+ + B^- \qquad (K_B)$$
$$B^- + M = BM^- \qquad (K_1)$$
$$B^- + 2M = BM_2^- \qquad (K_2)$$

where HB represents boric acid, B^- the borate ion, M the mannitol, BM^- and BM_2^- the complexes, and the *K*'s shown at the right of each equation the proposed mass-action constants, the reactions being assumed to proceed from left to right. This "mechanism" is proposed merely because it is the simplest one which satisfies the stoichiometry as deduced from the data obtained in this Laboratory. It is introduced for the purpose of facilitating computations.

Mass-action expressions were written for these reactions. There was some difficulty involved

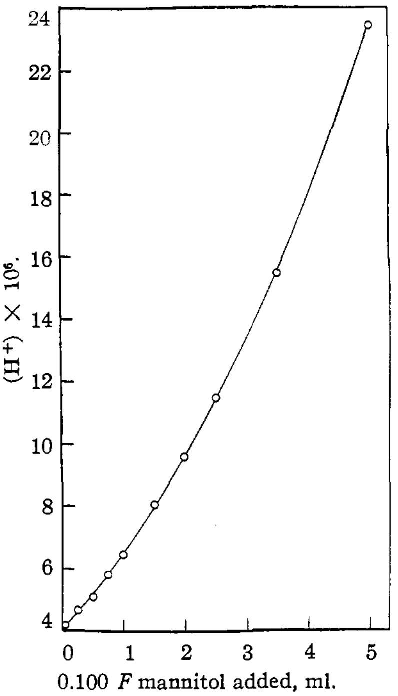

Fig. 5.—Addition of mannitol to 50.0 ml. 0.200 F boric acid.

in choosing a value for K_B due to disagreement in the literature. On the basis of articles by Kolthoff[8] and Thygesen,[9] a value of 6.4×10^{-10} was adopted for all solutions except one, where the concentration of boric acid was 0.20 F, in which case a value of 1.2×10^{-9} was employed since the effective ionization constant of pure boric acid increases in concentrated solution due to polymerization.

TABLE II

ADDITION OF MANNITOL TO 26.0 ML. OF 0.00770 F BORIC ACID

Mannitol, ml.	pH	$(H^+) \times 10^7$
0	6.67	2.14
0.050	6.55	2.82
.100	6.47	3.4
.150	6.37	4.3
.200	6.26	5.5
.250	6.18	6.6
.350	6.01	9.8
.450	5.93	11.7
.600	5.80	15.8
.800	5.61	24.6
1.000	5.50	31.6
1.250	5.38	41.7
1.500	5.24	57.5
2.000	5.13	74.2
2.500	5.00	100
3.000	4.92	120
4.000	4.89	129
6.000	4.68	209
7.000	4.65	224
8.000	4.58	263
10.000	4.48	331

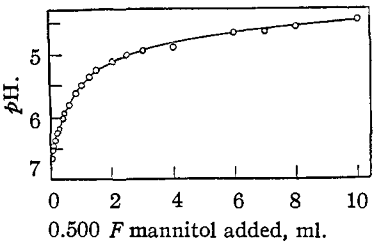

Fig. 6.—Addition of mannitol to 26.0 ml. of 0.00770 F boric acid.

The pH of the pure boric acid solutions were observed to be somewhat higher than values predicted from the dissociation constant. This fact was attributed to the presence of a minute amount of alkali absorbed from the air or present as a contaminant in the conductivity water or the reagents. The concentration of alkali (A) was calculated from the mass-action expression for boric acid and found to be of the order of 10^{-5}.

The assumption was made that in solutions where the ratio of the formal concentrations of boric acid to mannitol (C_B/C_M) was very high, only the first complex (BM^-) would be formed. The validity of this assumption is shown in Fig. 5 where it will be seen that the first few points are substantially linear. It was possible to calculate K_1 from these points in the following manner. Writing T for the total concentration of complex, the mass-action expression for boric acid was written

$$K_B = \frac{(H^+)(B^-)}{(HB)} = \frac{(H^+)[(H^+) - (OH^-) - T + A]}{C_B - [(H^+) - (OH^-) - T + A] - T}$$

Making appropriate simplifications and solving for T

$$T = (H^+) + A - \frac{K_B C_B}{(H^+)}$$

The mass-action expression for the formation of the first complex was written

$$K_1 = \frac{(BM^-)}{(B^-)(M)} = \frac{(BM^-)}{[(H^+) - T + A][C_M + (BM^-) - 2T]}$$

and when the ratio C_B/C_M is very great $[T = (BM^-)]$

$$K_1 = \frac{T}{[(H^+) + A - T][C_M - T]} = \frac{T}{\frac{K_B C_B}{(H^+)}[C_M - T]}$$

Four values of K_1 and the data from which they were calculated are given in Table III. The mean value of K_1 is 3.0×10^2.

From the experimental data obtained in this Laboratory, points were selected to cover a wide range of concentrations. The hydrogen-ion concentration varied 8500-fold, the boric acid 50-fold, the mannitol 1200-fold, and the ratio of

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[8] I. M. Kolthoff, *Rec. trav. chim.*, **46**, 501 (1926).

[9] J. E. Thygesen, *Z. anorg. Chem.*, **237**, 101 (1938).

TABLE III

CALCULATED VALUES OF K_1

$K_1 \times 10^{-2}$	$(H^+) \times 10^6$	$C_M \times 10^3$	$T \times 10^6$
3.14	4.7	0.5	8.0
2.66	5.1	1.0	12.5
3.05	5.8	1.5	18.9
3.25	6.5	2.0	24.0

($A = 5.44 \times 10^{-5}$, $C_B = 0.200$)

C_M/C_B 1900-fold. Using these points, thirty-seven values of K_2 (Table IV) were calculated from a relation derived from the mass-action expression.

$$K_2 = \frac{(BM_2^-)}{(B^-)(M)^2} = \frac{T - (BM^-)}{[(H^+) + A - T][C_M + (BM^-) - 2T]^2} = \frac{T - (BM^-)}{\frac{K_B C_B}{(H^+)}[C_M + (BM^-) - 2T]^2}$$

These values are tabulated in order of increasing magnitude to show that there is no corresponding systematic variation in any of the other calculated or observed quantities. The deviations may be attributed in large part to experimental error and changing temperature. Other uncontrolled factors such as varying concentration of A may have added a small effect. The average value of K_2, taken from the values in Table IV, is 5.1 × 10^4 with a mean deviation from the mean of 39%.

In order to determine the error introduced by making measurements in an open beaker a few experiments were repeated using an apparatus in which the solutions were maintained under an inert atmosphere. The values of K_1 and K_2, calculated from these experiments, were found to be the same as previously. This result is not intended to show that there was no absorption of gases from the air, but rather that the method of correction for alkali was a valid one.

A more accurate determination of these constants would require temperature control, a more sensitive method of determining *p*H and higher purification of reagents and conductivity water. The error introduced by neglecting activity effects was probably small since the ionic strength of the solutions was low. In any case, a correction for activity based on theoretical considerations would be of questionable value since the ions are very large and the nature of the solvent is complex.

TABLE IV

CALCULATED VALUES OF K_2

$K_2 \times 10^{-4}$	$(H^+) \times 10^5$	$C_M \times 10^3$	$C_B \times 10^3$	$T \times 10^5$	$(BM^-) \times 10^5$	$A \times 10^5$
2.2	2.63	117.5	5.88	4.92	0.50	2.30
2.4	2.09	93.8	6.25	4.37	.36	2.30
2.4	0.043	2.87	7.65	1.20	.98	2.30
2.5	3.31	139	5.56	5.60	.45	2.30
2.9	0.742	35.7	7.14	2.92	.66	2.30
3.0	1.20	51.7	6.90	3.46	.57	2.30
3.0	0.158	11.3	7.52	2.16	1.02	2.30
3.1	.417	22.9	7.34	2.61	0.78	2.30
3.1	1.00	43.8	7.01	3.26	.59	2.30
3.2	0.316	18.5	7.41	2.47	.83	2.30
3.3	.96	3.90	190	4.0	2.8	5.44
3.3	.117	8.50	7.56	2.01	1.04	2.30
3.5	.055	3.82	7.63	1.47	1.02	2.30
3.5	.066	4.76	7.62	1.63	1.05	2.30
3.5	.246	14.9	7.46	2.36	0.87	2.30
3.5	.575	27.3	7.27	2.80	.66	2.30
3.7	1.15	4.80	190	4.6	2.9	5.44
4.2	1.55	6.50	190	5.5	2.9	5.44
4.2	0.81	2.90	190	3.44	2.45	5.44
4.5	.098	6.65	7.60	1.99	1.99	2.30
5.0	1.18	5.76	195	6.08	3.12	6.72
5.1	0.0282	0.96	7.68	0.58	0.50	2.30
5.6	2.34	11.2	190	8.25	2.70	6.72
5.6	2.35	9.10	180	6.8	2.5	5.44
6.4	45.0	1150	3.90	47	0.19	2.5
6.6	3.71	16.5	185	9.98	2.19	6.72
7.1	240	1150	95.8	242	0.88	2.5
7.1	5.13	21.5	181	11.55	1.92	6.72
7.6	209	1150	68.4	211	0.72	2.5
7.9	7.94	30.8	173	14.50	1.60	6.72
8.2	0.62	12.87	7.25	1.31	0.29	0.824
8.6	10.5	39.4	166	17.10	1.40	6.72
8.7	0.398	8.74	7.39	1.10	0.31	0.824
8.8	9.3	62.5	50.0	12.3	.65	3.0
8.8	0.85	16.86	7.12	1.62	.27	0.824
8.8	.162	3.58	7.56	0.69	.32	.824
8.9	.316	7.05	7.44	.99	.32	.824

Summary

Evidence has been presented to show that boric acid and mannitol form two complexes, consisting of one and two moles of mannitol per mole of borate. The equilibrium constants for the formation of these complexes from mannitol and borate ion have been calculated to be 3.0 × 10^2 and 5.1 × 10^4, respectively.

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