

Equilibrium Studies of Polyanions

10. On the First Equilibrium Steps in the Acidification of $B(OH)_4^-$, an Application of the Self-Medium Method

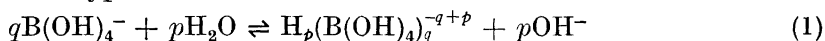
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In the present work the "self-medium" method¹ has been used to study the reactions, $qB(OH)_4^- + pH_2O \rightleftharpoons H_p(B(OH)_4)_q^{-q+p} + pOH^-$. The acidification was followed to $Z = 0.05$ for $B = 3.0, 2.5, 2.4, 1.2$ and 0.6 M. Z is the average number of H^+ bound to $B(OH)_4^-$ assuming no hydrolysis and B the total borate concentration. In the range over which it was studied, Z is mainly determined by p . The data indicated for $B = 2.5$ M, main species with $p = 2$ ($B_3O_3(OH)_4^-$ or $B_4O_5(OH)_4^{2-}$ or $B_5O_6(OH)_6^{3-}$ etc) and for $B \leq 1.2$ M, additional species with $p = 1$ ($B(OH)_3$ or $B_2O(OH)_5^-$ or $B_3O_3(OH)_5^{2-}$ etc). The data have been explained on the basis of the formation of the complexes $B(OH)_3$, $B_4O_5(OH)_4^{2-}$ and $B_3O_3(OH)_5^{2-}$ and the following equilibrium constants have been deduced: $\log K_1 = -5.31 \pm 0.02$, $\log K_{24} = -7.34 \pm 0.11$ and $\log K_{13} = -4.64 \pm 0.19$ (see Table 2). The constants have been refined using the least squares program LETAGROP³ and the errors given are 3σ (σ is the standard deviation).

It has been found¹ that the "self-medium" method is a valuable complement to the "inert medium" method and may be used to give additional or confirmatory information about the composition of complexes. Even if the information obtained is restricted it is of such character that it certainly could not be better obtained by any other method. The main principles of the method have been described in a paper by Hietanen and Sillén¹.

In Part 2² in this series the borate equilibria were studied using the "inert medium" method (3 M $Na(ClO_4)$) and formulae and formation constants were deduced for the formation of the complexes, $B(OH)_4^-$, $B_3O_3(OH)_4^-$ and $B_3O_3(OH)_5^{2-}$ or $B_4O_5(OH)_4^{2-}$ from $B(OH)_3$ and OH^- . With the data then available it was not possible to decide whether $B_3O_3(OH)_5^{2-}$, $B_4O_5(OH)_4^{2-}$ or both were formed. However, by using the self-medium method we can obtain data with which a decision possibly can be made. By using a concentrated medium where the greater part of the negative ions are $B(OH)_4^-$ and studying reactions of the type,



we obtain curves $Z(\log[\text{OH}^-])_B$, the shape of which gives p for the main reactions; Z is the average number of H^+ bound to every $\text{B}(\text{OH})_4^-$; B is the total concentration of boron. For $\text{B}_3\text{O}_3(\text{OH})_5^{2-}$, $p=1$ and for $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$, $p=2$. The method gives meagre information about q and the aim of the present work is to complete our previous inert-medium investigation² with self-medium data and deduce p for the main reaction according to (1). In this way we may get an answer on the question whether it is $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$, $\text{B}_3\text{O}_3(\text{OH})_5^{2-}$ or both.

CHOICE OF EXPERIMENTAL CONDITIONS

We decided to use Na^+ as the inert cation. By addition of NaClO_4 the solutions were made to contain 3 M Na^+ (except in one titration where $[\text{Na}^+] = 3.4$ M). Z was allowed to reach a value of *ca.* 0.05 only. In attempts to use higher Z -values, borax $\text{Na}_2\text{B}_4\text{O}_7(\text{OH})_4(\text{H}_2\text{O})_8$ was precipitated.

The NaClO_4 , HClO_4 , NaOH and boron solutions used in the present investigation were prepared and analysed as described previously². The experiments were performed as a series of potentiometric titrations in which $\log[\text{OH}^-]$ was measured using a hydrogen electrode. The hydrogen electrode was used in combination with the half-cell,

$\text{RE} = \text{Ag}, \text{AgCl} | 0.010 \text{ M NaCl}, B \text{ M NaB}(\text{OH})_4, (2.990 - B) \text{ M NaClO}_4 | \text{S} |$
where S was either

$\text{S} = B \text{ M NaB}(\text{OH})_4, (3.0 - B) \text{ M NaClO}_4$ or

$\text{S} = B \text{ M NaB}(\text{OH})_4, c \text{ M NaOH}, (3.0 - B - c) \text{ M NaClO}_4$

The emf of the cell used,

$-\text{Pt}, \text{H}_2(1 \text{ atm}) | \text{equilibrium solution} | \text{RE}+,$

was measured with a Vernier potentiometer to ± 0.05 mV. The hydrogen electrodes were prepared as described in Part 2² and all experiments were carried out with the cell immersed in a paraffin oil thermostat at $25 \pm 0.1^\circ\text{C}$. The potential of the hydrogen electrode always rapidly attained a constant value (within 30–45 min).

The relationship between the measured E and $[\text{OH}^-]$ is given by the equation

$$E = E_{oa} + 59.155 \log [\text{OH}^-] + E_j \quad (2)$$

where E_{oa} is a constant and E_j the liquid junction potential. Before or after every titration, E_{oa} was determined in the most alkaline solution where $[\text{OH}^-] \approx -H$; H is the analytical excess of H^+ over $\text{B}(\text{OH})_4^-$; thus in these points we assumed that all boron existed as $\text{B}(\text{OH})_4^-$. For E_j , we used in all titrations the relation $E_j = -8[\text{OH}^-]$ (see Ref.²).

In a titration with, *e.g.*, $B = 1.2$ M we started with a solution containing 1.2000 M boron, added as $\text{B}(\text{OH})_3$, and 1.1767 M NaOH in 1.8233 M NaClO_4 , and a solution containing 1.2000 M $\text{B}(\text{OH})_3$, 1.6720 M NaOH and 1.3280 M NaClO_4 was added from a buret. From the last points in this titration, the E_{oa} in (2) could be calculated.

In another type of titration we started with an alkaline solution and added a more acid one. *E.g.* for $B = 3.0000$ M we titrated a solution containing 3.0000 M $B(OH)_3$ and 3.3400 M NaOH and 3.4 M $NaClO_4$, with two more acid solutions I and II. When 1 ml of I was added, 0.4 ml of II was added at the same time. I contained, $B = 3.0000$ M, $[OH^-] = 3.1000$ M, $[ClO_4^-] = 1.4000$ M, $[Na^+] = 4.5000$ M and II, $B = 3.0000$ M, NaOH = 0.6600 M. This way of reversed titration was necessary because of the low solubility of borax.

The quantity Z , which is the average number of H^+ bound per $B(OH)_4^-$ was calculated [using the relationship, $BZ \approx -H - [OH^-]$, where H is the analytical excess of H^+ over $B(OH)_4^-$].

SYSTEMATIC ERRORS

It must be pointed out that the Z - and $\log[OH^-]$ -values obtained may be impaired by errors which may give serious systematic errors in the shape of the curves $Z(\log[OH^-])_B$. We have to consider the following errors: (a) a possible error in the analytical determination of H , which is the difference between two large numbers, $[OH^-]_{tot}$ and B . The chemical determination of these concentrations were always reproducible within $\pm 0.2\%$; (b) a small error in E_{oa} , determined in the most alkaline solutions where the boron is practically unhydrolysed, $B \approx [B(OH)_4^-]$. There is also an uncertainty in the

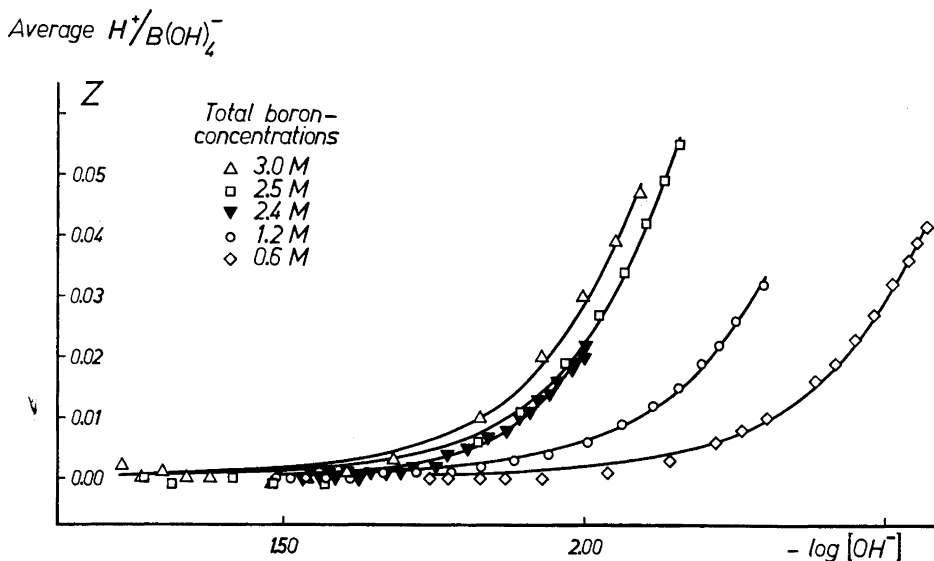


Fig. 1. Selfmedium of $B(OH)_4^-$. Data, $Z(\log[OH^-])_B$, compared with calculated curves for formation of $B(OH)_3$, $B_4O_5(OH)_4^{2-}$, and $B_3O_3(OH)_3^{2-}$. The full curves calculated with the constants in Table 2.

E-measurements at high $[\text{OH}^-]$; (c) an incorrect value of the constant j in the expression for the liquid junction potential, $E_j = j[\text{OH}^-]$.

Due to these errors we can not expect the ordinates of the curves, $Z(\log[\text{OH}^-])_B$ to be accurate to better than ca. 3–4 %.

TREATMENT OF EXPERIMENTAL DATA

The Z - and $\log[\text{OH}^-]$ -data obtained are plotted in Fig. 1 and given in Table 1. In the present case when H^+ is added to $\text{B}(\text{OH})_4^-$ a number of complexes H_pB_q ($\text{H} = \text{H}^+$ and $\text{B} = \text{B}(\text{OH})_4^-$), will be formed. Let K_{pq} be the equilibrium constant for the reaction (1). From the conditions for the concentrations, B

Table 1. Data for acidification of $\text{B}(\text{OH})_4^-$. For the points used in LETAGROP,

$10^3(Z_{\text{calc}} - Z)$ is given. Z' have been calculated assuming $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$, $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$ and Z' assuming $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$, $\text{B}_3\text{O}_3(\text{OH})_5^{2-}$, $\text{B}(\text{OH})_3$ and $\text{B}(\text{OH})_4^-$.

$B = 3.0 \text{ M}$; $10^3(Z'_{\text{calc}} - Z)$, $10^3(Z'_{\text{calc}} - Z)$, $-\log[\text{OH}^-]$: 0.047, -1, -4, 2.184; 0.039, 0, 0, 2.103; 0.030, 2, 3, 1.995; 0.020, 1, 4, 1.858; 0.010, 0, 4, 1.650; 0.003, -1, -1, 1.363; 0.001, -2, 0, 1.209; 0.000, -2, -1, 1.078; -0.001, -3, -1, 0.957; 0.000, -1, -1, 0.757; 0.000, -1, -1, 0.678; 0.001, 0, 1, 0.599; 0.000, -1, 0, 0.529; 0.002, 2, 2, 0.462. ($\log \beta_1 = 5.223$, $\log \beta_{24} = 13.673$, Z'_{calc}), ($\log \beta_1 = 5.271$, $\log \beta_{24} = 13.705$; $\log \beta_{23} = 10.998$, Z'_{calc})

$B = 2.5 \text{ M}$; Z ; $10^3(Z'_{\text{calc}} - Z)$, $10^3(Z'_{\text{calc}} - Z)$, $-\log[\text{OH}^-]$: 0.055, -1, -4, 2.316; 0.049, 0, -2, 2.267; 0.042, 1, 1, 2.206; 0.034, 1, 2, 2.134; 0.027, 1, 3, 2.049; 0.019, 1, 4, 1.936; 0.011, 0, 3, 1.784; 0.006, -1, 1, 1.645; -0.001, -3, -2, 1.138; -0.001, -2, -1, 0.967; 0.000, -1, 0, 0.832; -0.001, -2, -1, 0.629; 0.000, 0, 0, 0.538. ($\log \beta_1 = 5.217$, $\log \beta_{24} = 13.709$, Z'_{calc}), ($\log \beta_1 = 5.289$, $\log \beta_{24} = 13.878$, $\log \beta_{23} = 11.062$, Z'_{calc})

$B = 2.4 \text{ M}$; Z ; $10^3(Z'_{\text{calc}} - Z)$, $10^3(Z'_{\text{calc}} - Z)$, $-\log[\text{OH}^-]$: 0.020, -1, -2, 2.001; 0.018, 0, -1, 1.959; 0.014, 0, 0, 1.887; 0.011, 0, 0, 1.819; 0.008, 0, 0, 1.739; 0.005, 0, 1, 1.611; 0.001, -1, -1, 1.504; 0.001, -1, -1, 1.389; 0.001, 0, 0, 1.291; 0.001, 0, 0, 1.212; 0.001, 0, 0, 1.149; 0.001, 0, 1, 1.089; 0.022, 0, 0, 2.004; 0.019, 0, -1, 1.970; 0.016, 1, 1, 1.910; 0.013, 1, 1, 1.844; 0.010, 1, 1, 1.783; 0.007, 1, 1, 1.678; 0.004, 0, 0, 1.543; 0.002, 0, 0, 1.430; 0.001, -1, -1, 1.340; 0.000, -1, -1, 1.249; 0.000, -1, -1, 1.172; 0.000, -1, -1, 1.123; 0.000, -1, 0, 1.067. ($\log \beta_1 = 5.199$, $\log \beta_{24} = 13.759$, Z'_{calc}) ($\log \beta_1 = 5.314$, $\log \beta_{24} = 14.170$, $\log \beta_{23} = 10.542$, Z'_{calc})

$B = 1.2 \text{ M}$; Z ; $10^3(Z'_{\text{calc}} - Z)$, $10^3(Z'_{\text{calc}} - Z)$, $-\log[\text{OH}^-]$: 0.032, -1, -4, 2.599; 0.026, 1, 0, 2.507; 0.022, 0, 1, 2.451; 0.019, 1, 2, 2.390; 0.015, 0, 3, 2.314; 0.012, 0, 3, 2.229; 0.009, 0, 3, 2.125; 0.006, 0, 3, 2.008; 0.004, -1, 2, 1.881; 0.003, 0, 1, 1.763; 0.002, -1, 1, 1.653; 0.001, -1, 1, 1.554; 0.001, -1, 0, 1.441; 0.001, 0, 1, 1.330; 0.000, -1, 0, 1.219; 0.000, -1, 0, 1.140; 0.000, -1, 0, 1.076; 0.000, -1, 0, 1.023; 0.000, -1, 0, 0.976. ($\log \beta_1 = 5.211$, $\log \beta_{24} = 13.752$, Z'_{calc}) ($\log \beta_1 = 5.333$, $\log \beta_{24} = 13.969$, $\log \beta_{23} = 11.495$, Z'_{calc}).

$B = 0.6 \text{ M}$; Z ; $10^3(Z'_{\text{calc}} - Z)$, $10^3(Z'_{\text{calc}} - Z)$, $-\log[\text{OH}^-]$: 0.042, 0, -3, 3.130; 0.039, 0, -2, 3.103; 0.036, -1, -1, 3.075; 0.032, 1, 1, 3.019; 0.027, 1, 2, 2.961; 0.023, 1, 3, 2.901; 0.019, 1, 3, 2.835; 0.016, 1, 3, 2.766; 0.011, -1, 1, 2.692; 0.010, 0, 3, 2.611; 0.008, 0, 3, 2.527; 0.006, 0, 2, 2.440; 0.003, -1, 1, 2.287; 0.001, -1, 0, 2.078; 0.000, -1, -1, 1.861; 0.000, -1, 0, 1.735; 0.000, -1, 0, 1.652; 0.000, -1, 0, 1.547; 0.000, -1, 0, 1.484. ($\log \beta_1 = 5.227$, $\log \beta_{24} = 13.705$, Z'_{calc}) ($\log \beta_1 = 5.344$, $\log \beta_{24} = 14.021$, $\log \beta_{23} = 11.593$, Z'_{calc}).

(the total concentration of boron), BZ (the moles of H^+ bound to B per liter) and the law of mass action we get:

$$B = [B] + \sum_p \sum_q q [H_p B_q] = b + \sum_p \sum_q q K_{pq} a^p b^q \quad (4)$$

$$BZ = \sum_p \sum_q p [H_p B_q] = \sum_p \sum_q p K_{pq} a^p b^q \quad (5)$$

where $a = [OH^-]^{-1}$.

If Z is kept at such low values that practically $b \approx B$ the shape of the curves $Z(\log[OH^-])_B$ given in Fig. 1 will mainly be determined by the p -values of the complexes $H_p B_q$. In Part 2² in this series, we found for the reaction, $B(OH)_4^- \rightleftharpoons B(OH)_3 + OH^-$, $\log K_1 = -5.22$. It means that, when considering $B = 3.0, 2.4$, and 2.5 M, the contribution to Z due to the formation of $B(OH)_3$ may in the first approximation be neglected compared with the contribution due to the polyanion formation; thus by analysing the shape of the curves $Z(\log[OH^-])_B$ for the concentrations of these polyanions we could hope to obtain p in the dominating polynuclear complexes, $H_p B_q$.

Main p in the polynuclear complexes $H_p B_q$. In a first attempt we shall assume the formation of only one of the polyanions $H_p B_q$. For this case normalization of eqns. (4) and (5) and elimination of b give

$$Z(1 - ZQP^{-1})^{-Q} = u^P \text{ where } u^P = a^P P K_{PQ} B^{Q-1} \quad (6)$$

Using (6) a number of normalized curves, $Z(\log u)$ were calculated for $P = 1, 2$, and 3 with Q ranging between 2 and 8. These theoretical curves were then compared with the experimental curves, $Z(\log[OH^-])_B$. In Fig. 2 the experimental points for $B = 2.5$ M are compared with the three sets of calculated curves and given in the position of best fit. From this comparison we concluded, that the experimental curve for $B = 2.5$ M fits only the family

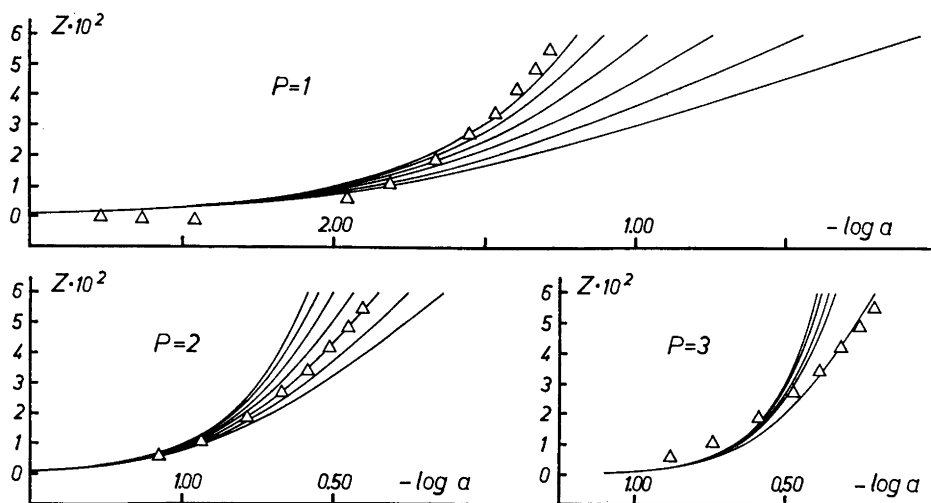


Fig. 2. Selfmedium of $B(OH)_4^-$. Determination of p in the reaction, $q B(OH)_4^- + p H_2O \rightleftharpoons H_p(B(OH)_4)_{q-p} + p OH^-$. Full curves calculated for $q = 2, 3, 4, \dots$

of calculated curves with $P = 2$. Thus, necessarily, one or more of the complexes in the series, H_2B^+ , H_2B_2 , $H_2B_3^-$, $H_2B_4^{2-}$, $H_2B_5^{3-}$,, $H_2B_q^{2-q}$, must be formed. A tetraborate ion, $B_4O_5(OH)_4^{2-}$, belongs to this series. With $P = 1$ and $P = 3$ no fit was obtained. $P = 1$ means formation of complexes of the series, HB , HB_2^- , HB_3^{2-} ,, HB_q^{1-q} . It may be noted that the complex $B_3O_3(OH)_5^{2-}$, belongs to this series. However a mixture of complexes with $P = 1$ and $P = 2$ may be possible. For $B = 1.2$ M we surely have such a mixture since for these concentrations appreciable amounts of HB ($B(OH)_3$) are also formed ($\log K_1 = -5.22$).

The q -values in the complex H_2B_q . The information we can get about q from the present data is restricted. Even if, in the family of calculated curves for $P = 2$, the experimental data for $B = 2.5$ M (see Fig. 2) fit well for $Q = 6$ it is necessary to test not only this Q -value but also some other Q -values over a considerably larger range of concentrations. For this analysis we used the computer program LETAGROP³ and assumed the formation of two complexes, HB and H_2B_Q . The Q -values between 3 and 6 were tested and every B -value of the data in Table 1 was treated separately. We found that the combination $HB + H_2B_4$ gave the best constancy of K_1 and K_{24} over the whole B -range, in addition to this the agreement between these constants and the constants obtained using "inert medium" data^{2,4} was satisfactory. The constants deduced from "inert medium" data using LETAGROP³ were $\log \beta_1 = 5.28 \pm 0.02$ and $\log \beta_{24} = 13.70 \pm 0.12$. These constants correspond

Table 2. Equilibrium constants of polyborates in $B(OH)_4^-$ -medium.

B M	$\sigma(Z)$	$\log \beta_1 \pm 3\sigma$	$\log \beta_{24} \pm 3\sigma$	$\log \beta_{23} \pm 3\sigma$
0.6	± 0.0020	5.227 ± 0.008	13.705 ± 0.034	—
	± 0.0009	5.344 ± 0.015	14.021 ± 0.087	11.59 ± 0.13
1.2	± 0.0020	5.211 ± 0.010	13.752 ± 0.043	—
	± 0.0009	5.333 ± 0.015	13.969 ± 0.099	11.50 ± 0.10
2.5	± 0.0025	5.217 ± 0.009	13.709 ± 0.036	—
	± 0.0015	5.289 ± 0.027	13.878 ± 0.111	11.06 ± 0.27
3.0	± 0.0024	5.223 ± 0.011	13.673 ± 0.044	—
	± 0.0016	5.271 ± 0.030	13.705 ± 0.138	11.00 ± 0.27

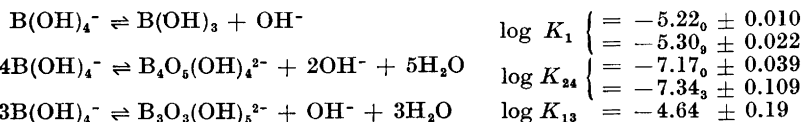
Mean values: $5.22_0 \pm 0.01_0$ $13.71_0 \pm 0.03_0$ —
 $5.30_0 \pm 0.02_2$ $13.89_3 \pm 0.10_0$ 11.29 ± 0.19

$$\beta_1 = [B(OH)_4^-][OH^-]^{-1}[B(OH)_3]^{-1}$$

$$\beta_{24} = [B_4O_5(OH)_4^{2-}][OH^-]^{-2}[B(OH)_3]^{-4}$$

$$\beta_{23} = [B_3O_3(OH)_5^{2-}][OH^-]^{-2}[B(OH)_3]^{-3}$$

Using the mean values we may calculate the constants for acidification of $B(OH)_4^-$



to the reactions $\text{B(OH)}_3 + \text{OH}^- \rightleftharpoons \text{B(OH)}_4^-$ and $4\text{B(OH)}_3 + 2\text{OH}^- \rightleftharpoons \text{B}_4\text{O}_5(\text{OH})_4^{2-} + 5\text{H}_2\text{O}$. The present self-medium data gave for these reactions the constants collected in Table 2. For all ranges we may write (the mean value),

$$\log\beta_1 = 5.22 \pm 0.01 \quad \text{and} \quad \log\beta_{24} = 13.71 \pm 0.04$$

In the Table 1 the differences are given between the calculated Z and the experimental Z , ($Z''_{\text{calc}} - Z$). By examining these differences we found that the experimental curves $Z(\log[\text{OH}^-])_B$ are flatter than the calculated ones and the differences are slightly greater than the differences one would expect considering only experimental errors. In an attempt to explain the deviations we assumed that $\text{B}_3\text{O}_3(\text{OH})_5^{2-}$ was also formed, besides $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$. This assumption is reasonable as, in the investigations using other media (3 M $\text{Na}(\text{ClO}_4)$, 3 M $\text{Na}(\text{Br})$ and 3 M $\text{Li}(\text{Br})$), this combination gave a better explanation of data than only $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$.

The combination satisfactorily explained our data and on addition of the complex $\text{B}_3\text{O}_3(\text{OH})_5^{2-}$ the error square sum decreased around 50 %. The constants deduced for this constant combination are collected in Table 2. The differences between the calculated Z and the experimental Z , ($Z'_{\text{calc}} - Z$) for this case are given in Table 1. For the whole range we may write

$$\log\beta_1 = 5.31 \pm 0.02 \quad \log\beta_{24} = 13.89 \pm 0.11 \quad \text{and} \quad \log\beta_{23} = 11.29 \pm 0.19$$

It should surely be possible also to explain the deviations by assuming some other complex than $\text{B}_3\text{O}_3(\text{OH})_5^{2-}$. However, we think that self-medium data do not permit determination of minor complexes. The composition of these must be obtained from other data, *e.g.* as in this case from ionic inert medium data.

CONCLUSIONS

The present data enable us with some confidence to reach a conclusion on the value $p = 2$ for the predominating complex $\text{H}_p(\text{B(OH)}_4)_q$, whereas the assignment of q cannot be made with certainty from self-medium data alone. However, using LETAGROP³ and assuming the formation of one polynuclear complex besides the mononuclear one we found that $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$ gave the best constancy of the equilibrium constants for different B , and the $\log\beta_{24}$ so obtained is of the same order of magnitude as the $\log\beta_{24}$ obtained for other ionic media⁴: 3.0 M $\text{Na}(\text{ClO}_4)$, $\log\beta_{24} = 13.53$, 3.0 M $\text{Na}(\text{Br})$, $\log\beta_{24} = 13.43$, 3.0 M $\text{Li}(\text{Br})$, $\log\beta_{24} = 13.37$, 3.0 M $\text{K}(\text{Br})$, $\log\beta_{24} = 13.41$. Formation of a tetranuclear complex with the charge minus two is also probable for structural reasons; the ion $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$ has been found to form separate units in crystals of borax. However, we found that the present self-medium data were, like the data in other media, better explained by assuming that $\text{B}_3\text{O}_3(\text{OH})_5^{2-}$ was also formed.

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