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Equilibrium Studies of Polyanions

11. Polyborates in 3.0 M Na(Br), 3.0 M Li(Br) and 3.0 M K(Br), a Comparison with Data Obtained in 3.0 M Na(ClO_4)

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Using a hydrogen electrode, the borate equilibria have been studied at 25°C in the three media, 3.0 M Na(Br), 3.0 M Li(Br), and 3.0 M K(Br). The total boron concentration, *B*, has been varied, usually between 0.01 M and 0.400 M. These data as well as the data we obtained earlier for 3.0 M Na(ClO_4) medium could be explained by the species, $B(OH)_3$, $B(OH)_4^-$, $B_3O_3(OH)_4^-$, $B_4O_5(OH)_4^{2-}$ and small amounts of $B_5O_6(OH)_4^-$. However, for 3.0 M Na(ClO_4), 3.0 M Na(Br) and 3.0 M Li(Br), the data are slightly better explained by assuming that $B_3O_3(OH)_5^{2-}$ is also formed. There is no evidence for formation of $B_3O_3(OH)_5^{2-}$ in 3.0 M K(Br). Equilibrium constants and standard deviations have been calculated for these combinations using the computer program LETAGROP [2]; the results of the calculations are collected in Table 2.

Sometimes fears have been expressed about using ionic media, as misleading conclusions might be obtained owing to specific interactions between the ions of the medium and the reacting molecules. By studying the equilibria in different ionic media one can investigate such effects. The aim of the present work is to study the borate equilibria in 3.0 M Na(Br), 3.0 M Li(Br), 3.0 M K(Br) and compare these data with those obtained previously for 3.0 M Na$(ClO)_4$ medium [1].

LIST OF SYMBOLS

B	total concentration of B
E	measured emf in mV, $E = E_0 + 59.155 \log [OH^-] + E_j$
E_0	a constant in the expression for *E*
E_j	liquid junction emf
H	total analytical excess concentration of hydrogen ions assuming no hydrolysis; in most experiments *H* was negative.
Z	average number of OH^- bound per $B(OH)_3$ = average negative charge per boron

β_{pq} equilibrium constant for formation of A_pB_q from $B = B(OH)_3$ and $A = OH^-$.
$\beta_1 = [B(OH)_4^-]\ [B(OH)_3]^{-1}\ [OH^-]^{-1}$
$\beta_{13} = [B_3O_3(OH)_4^-]\ [B(OH)_3]^{-3}\ [OH^-]^{-1}$
$\beta_{15} = [B_5O_6(OH)_4^-]\ [B(OH)_3]^{-5}\ [OH^-]^{-1}$
$\beta_{24} = [B_4O_5(OH)_4^{2-}]\ [B(OH)_3]^{-4}\ [OH^-]^{-2}$
$\beta_{23} = [B_3O_3(OH)_5^{2-}]\ [B(OH)_3]^{-3}\ [OH^-]^{-2}$
$\sigma\ (Z)$ standard deviation in Z as defined in Ref.[3]
$\sigma(\beta_{pq})$ standard deviation in β_{pq} as defined in Ref.[3]

Chemical symbols are in Roman, concentrations in italic type. Concentrations and equilibrium constants will be expressed in M (mole/l).

EXPERIMENTAL

Methods and apparatus in these titrations were essentially the same as described in Part 2 [1] in this series. However, in the present set of titrations we found that the hydrogen electrode for some reason did not give a stable potential in acid solutions although it always did in neutral and alkaline solutions. For this reason the E_0-values were always determined on the alkaline side. In the range where E_0 was determined all boron was in the form of the complex $B(OH)_4^-$. Only in 3.0 M Na(Br) was it possible to use total boric acid concentrations, B, as high as 0.600 M. In the other media B must be kept below or equal to 0.4 M, because of the low solubility of $Na_2B_4O_5(OH)_4(H_2O)_8$.

The measurements were carried out as a series of potentiometric titrations. In every titration the total boron concentration, B, was kept constant. The temperature was kept at 25 ± 0.1°C using an oil thermostat. The salt bridge described by Forsling, Hietanen and Sillén [4] was used and the reference halfcell was,

$$\mathrm{RE} = \mathrm{Hg}\ |\ 3.0\ \mathrm{M\ Br^-},\ 2.98\ \mathrm{M\ X^+},\ 0.01\ \mathrm{M\ Hg^{2+}}\ ||\ 3.0\ \mathrm{M\ XBr}\ |$$

where X^+ is Li^+, Na^+, or K^+. This cell was used in combination with a hydrogen electrode; thus the E-value was measured with the cell

$$-\mathrm{Pt,H_2(1\ atm)}\ |\ \text{alkaline } \mathrm{B(OH)_3}\text{-solution}\ |\ \mathrm{RE}\ +$$

Assuming the activity factors to be constant, E may be represented by the equation,

$$E = E_0 + 59.155 \log [OH^-] + E_j$$

where E_0 is a constant and E_j the liquid junction potential. E_0 and E_j have been determined before or after every titration as described in Part 2 [1]. The quantity, Z, the average negative charge per boron, was calculated for each point of the titration using the relationship

$$BZ = -H - [OH^-]$$

where $-H$ is the analytical proton deficiency.

Chemicals and analysis

Pro analysi grade (Mallinckrodt) *NaBr, KBr and LiBr* was used after recrystallisation by evaporation.

NaOH and borate solutions were prepared and analysed as described in Part 2 [1]. Commercial *KOH* (KEBO) and *LiOH* (B.D.H) were used. The carbonate in these products was removed with a cation exchanger (Dowex 50) and recrystallised $Ba(OH)_2$. The commercial product was dissolved in distilled and boiled water and a small amount of $Ba(OH)_2$ was added. After the $BaCO_3$-precipitate had settled the supernantant liquid was passed through the K- or Li-saturated ion-exchanger. The eluate was tested for Ba^{2+} and CO_3^{2-} ions. Solutions of the hydroxides more concentrated than 0.9 M could not be prepared in this way. In all these manipulations, the solutions were carefully protected with N_2 from CO_2.

RESULTS AND CONCLUSIONS

In Part 2 [1] of this series we studied the borate equilibria in 3.0 M $NaClO_4$ and concluded that the main species were $B(OH)_3$, $B(OH)_4^-$, $B_3O_3(OH)_4^-$, and either $B_4O_5(OH)_4^{2-}$ or $B_3O_3(OH)_5^{2-}$ or both. With data available then, it was not possible to decide whether $B_3O_3(OH)_5^{2-}$, $B_4O_5(OH)_4^{2-}$ or both were formed. This earlier investigation gave the following main reactions and equilibrium constants (see Ref.[1]):

$B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+$ $\quad \log{}^*\beta_1 = -\ 9.00 \pm 0.05$
$3B(OH)_3 \rightleftharpoons B_3O_3(OH)_4^- + H^+ + 2H_2O$ $\quad \log{}^*\beta_{13} = -\ 6.84 \pm 0.10$
and either
$3B(OH)_3 \rightleftharpoons B_3O_3(OH)_5^{2-} + 2H^+ + H_2O$ $\quad \log{}^*\beta_{23} = -16.44 \pm 0.20$
or
$4B(OH)_3 \rightleftharpoons B_4O_5(OH)_4^{2-} + 2H^+ + 3H_2O$ $\quad \log{}^*\beta_{24} = -14.66 + 0.20$

and with $\log K_w = -14.22$, $\log\beta_1 = 5.22 \pm 0.05$, $\log\beta_{13} = 7.38 \pm 0.10$, $\log\beta_{23} = 12.00 \pm 0.20$ and $\log\beta_{24} = 13.78 \pm 0.20$. Due to a miscalculation in Part II (Ref.[1]), $\log{}^*\beta_{24}$ and $\log{}^*\beta_{23}$ are erroneously given as, -15.71 ± 0.20 and -15.44 ± 0.20, respectively.

In a later work [5] using the self-medium method (3.0 M $B(OH)_4^-$-medium), data were obtained that indicated that the main complex formed was $B_4O_5(OH)_4^{2-}$. However, the data could be better explained by assuming that small amounts of $B_3O_3(OH)_5^{2-}$ were also formed. The following equilibrium constants were deduced: $\log\beta_1 = 5.29 \pm 0.03$, $\log\beta_{24} = 13.88 \pm 0.11$, $\log\beta_{23} = 11.06 \pm 0.27$. ($B = 2.5$ M).

In another selfmedium study [6] we used a medium consisting mainly of $B(OH)_3$ and in this work we found evidence for formation of small amounts of an additional complex, either $B_5O_6(OH)_4^-$ (best fit) or $B_4O_5(OH)_3^-$. We found:

$\log{}^*\beta_1 = -8.98 \pm 0.01$, $\log{}^*\beta_{13} = -7.29 \pm 0.02$, $\log{}^*\beta_{15} = -6.77 \pm 0.10$ (0.1 M $NaClO_4$)
or $\log{}^*\beta_1 = -8.98 \pm 0.01$, $\log{}^*\beta_{13} = -7.36 \pm 0.04$, $\log{}^*\beta_{14} = -7.14 \pm 0.11$ (0.1 M $NaClO_4$)
and $\log{}^*\beta_1 = -9.00 \pm 0.02$, $\log{}^*\beta_{13} = -6.91 \pm 0.03$, $\log{}^*\beta_{15} = -6.62 \pm 0.16$ (3.0 M $NaClO_4$)
or $\log{}^*\beta_1 = -9.00 \pm 0.02$, $\log{}^*\beta_{13} = -6.94 \pm 0.05$, $\log{}^*\beta_{14} = -6.96 \pm 0.18$ (3.0 M $Na(ClO_4)$)

Graphical analysis of the data obtained for 3 M Na(Br), 3 M K(Br) and 3 M Li(Br) indicated the same main species as in 3 M $Na(ClO_4)$. The computer program LETAGROP [2] (a least squares program) was used to test which of the following combinations gave the best agreement with the experimental results

(*a*) $B(OH)_3$, $B(OH)_4^-$, $B_3O_3(OH)_4^-$, $B_3O_3(OH)_5^{2-}$ or
(*b*) $B(OH)_3$, $B(OH)_4^-$, $B_3O_3(OH)_4^-$, $B_4O_5(OH)_4^{2-}$ or
(*c*) $B(OH)_3$, $B(OH)_4^-$, $B_3O_3(OH)_4^-$, $B_3O_3(OH)_5^{2-}$, $B_4O_5(OH)_4^{2-}$.

LETAGROP was also used to refine our previous data for 3.0 M $Na(ClO_4)$. LETAGROP gives, β_{pq}, the "best" formation constant for the complex $(B(OH)_3)_q(OH)_p$, $\sigma(Z)$, the standard deviation in Z and $\sigma(\beta_{pq})$, the standard

Table 1. Equilibrium data for borates in different media. For the points used in Letagrop $10^3(Z_{\mathrm{calc}}-Z)$ is given.

Data with 3.0 M Li(Br) medium. For calculating Z_{calc}, $\log\beta_1 = 5.26$, $\log\beta_{13} = 7.29$, $\log\beta_{24} = 13.37$ and $\log\beta_{23} = 11.88$ have been used.

$B = 0.010$ M; Z, $-\log[\mathrm{OH}^-]$, $10^3\ (Z_{\mathrm{calc}})-Z)$; 0.065, 6.406, 3; 0.150, 6.031, −3; 0.232, 5.789, −1; 0.292, 5.649, 1; 0.370, 5.491, 3; 0.445, 5.353, 5; 0.518, 5.224, 6; 0.590, 5.097, 5; 0.657, 4.971, 6; 0.757, 4.755, 7; 0.836, 4.540, 5; 0.925, 4.164, 2; 0.963, 3.860, −1; 0.982, 3.598, −3; 1.006, 2.245; 1.005, 1.975; 1.002, 1.911; 1.009, 1.842; 0.7890; 0.044, 6.585, 2; 0.087, 6.270, 4; 0.123, 6.081, 4; 0.191, 5.880, 5; 0.252, 5.728, 5; 0.331, 5.560, 6; 0.408, 5.416, 6; 0.482, 5.282, 8; 0.554, 5.154, 9; 0.624, 5.026, 10; 0.708, 4.856, 11; 0.805, 4.622, 9; 0.882, 4.360, 7; 0.952, 3.938, 3; 0.975, 3.777; 1.002; 2.244; 1.002, 1.974; 1.003, 1.887; 1.005, 1.842;

$B = 0.050$; Z, $-\log\ [\mathrm{OH}^-]$, $10^3[Z_{\mathrm{calc}}-Z)$; 0.022, 6.991, 1; 0.054, 6.589, 0; 0.175, 5.989, −1; 0.250, 5.773; 0.338, 5.566, 1; 0.420, 5.398; 0.497, 5.249, 3; 0.602, 5.047; 0.729, 4.786, 5; 0.841, 4.493; 0.963, 3.870, −4; 0.999, 3.214; 1.002, 1.612; 1.002, 1.566; 1.002, 1.520; 0.033, 6.865, −3; 0.085, 6.378; 0.136, 6.135, −2; 0.204, 5.904; 0.295, 5.669, −3; 0.380, 5.481; 0.456, 5.323, 4; 0.568, 5.116; 0.668, 4.919, 4; 0.786, 4.651; 0.892, 4.308, 1; 0.940, 4.054; 0.984, 3.607, −7; 1.006, 2.267; 1.005, 2.037; 1.003, 1.845; 1.002, 1.697; 1.001, 1.601;

$B = 0.100$; Z, $-\log\ [\mathrm{OH}^-]$, $10^3\ (Z_{\mathrm{calc}}-Z)$; 0.044, 6.877, −1; 0.127, 6.302, −3; 0.252, 5.838, −5; 0.342, 5.590, −4; 0.422, 5.394, −2; 0.537, 5.142, −1; 0.671, 4.848, 3; 0.756, 4.634, 9; 0.826, 4.455, 3; 0.877, 4.267, 5; 0.977, 3.454, 4; 0.998, 2.086, 1; 1.001, 1.801; 1.002, 1.642; 0.890; 0.096, 6.494, −7; 0.201, 6.022, −10; 0.304, 5.709, −12; 0.392, 5.485, −11; 0.474, 5.296, −10; 0.556, 5.121, −10; 0.642, 4.932, −7; 0.723, 4.747, −5; 0.787, 4.583, −3; 0.828, 4.461, −1; 0.896, 4.199, 2; 0.941, 3.924, 3; 0.982, 3.309, 4; 1.000, 2.117; 1.007, 1.924; 1.008, 1.745;

$B = 0.200$ Z, $-\log\ [\mathrm{OH}^-]$, $10^3\ (Z_{\mathrm{calc}}-Z)$; 0.034, 7.391, −2; 0.099, 6.750, −5; 0.224, 6.083, −6; 0.313, 5.742; 0.384, 5.508, −4; 0.467, 5.267; 0.532, 5.089, 0; 0.621, 4.861; 0.693, 4.677, −1; 0.751, 4.521; 0.893, 4.047, −4; 0.924, 3.886; 0.945, 3.746, −3; 0.974, 3.416; 0.995, 2.677, 0; 1.000, 1.625; 1.002, 1.385; 1.004, 1.240; 0.934; 0.053, 7.183, −6; 0.131, 6.558; 0.193, 6.231, −8; 0.268, 5.917; 0.355, 5.616, −9; 0.425, 5.401; 0.491, 5.213; −6; 0.568, 5.027; 0.655, 4.789, −6; 0.714, 4.637; 0.771, 4.479, −7; 0.815, 4.345; 0.858, 4.198, −6; 0.911, 3.967; 0.961, 3.584, −1; 0.999, 2.065; 1.003, 1.648; 1.007, 1.408;

$B = 0.400$; Z, $-\log\ [\mathrm{OH}^-]$, $10^3\ (Z_{\mathrm{calc}}-Z)$; 0.152, 6.841, −13; 0.220, 6.373, −9; 0.284, 6.012, −6; 0.343, 5.728, −4; 0.398, 5.491, −2; 0.450, 5.289, 0; 0.498, 5.111, 2; 0.566, 4.884, 2; 0.631, 4.686, −1; 0.685, 4.508, 0; 0.738, 4.342, −2; 0.787, 4.187, −5; 0.832, 4.032, −8; 0.879, 3.847, −11; 0.926, 3.618, −14; 0.961, 3.351, −13; 1.000, 1.958; 1.000, 1.464; 1000, 1.313; 1.000, 1.209;

Data with 3.0 M Na(Br) medium. For calculating Z_{calc}, $\log\beta_1, = 5.26$, $\log\beta_{13} = 7.35$, $\log\ \beta_{24} = 13.43$ and $\log\ \beta_{23} = 11.86$ have been used.

$B = 0.010$; Z, $-\log\ [\mathrm{OH}^-]$, $10^3\ (Z_{\mathrm{calc}}-Z)$; 0.021, 6.869, 4; 0.043, 6.550, 7; 0.085, 6.271, 5; 0.144, 6.016, 7; 0.226, 5.780, 9; 0.299, 5.618, 8; 0.384, 5.450, 11; 0.476, 5.283, 13; 0.567, 5.123, 13; 0.662, 4.948, 12; 0.729, 4.829, 2; 0.800, 4.637, 9; 0.888, 4.342, 5; 0.933, 4.110, 1; 0.969, 3.787, −1; 0.986, 3.501, −3; 0.992, 3.298, −3; 1.021, 2.535; 1.000, 2.329;

$B = 0.050$; Z, $-\log\ [\mathrm{OH}^-]$, $10^3\ (Z_{\mathrm{calc}}-Z)$; 0.010, 7.322; 0.025, 6.942, 1; 0.046, 6.666; 0.081, 6.397, 1; 0.135, 6.134, 0; 0.040, 6.723, 2; 0.099, 6.302, 0; 0.163, 6.034, −1; 0.228, 5.802, 11; 0.311, 5.630, −2; 0.458, 5.324, 0; 0.527, 5.189, 3; 0.588, 5,070, 4; 0.662, 4.923; 0.740, 4.752, 7; 0.826, 4.485; 0.920, 4.145, 4; 0.970, 3.749; 1.001, 2.078; 1.003, 1.791; 0.059, 6.551; 0.135, 6.136, 0; 0.211, 5.884; 0.278, 5.706, −2; 0.345, 5.557; 0.431, 5.375, 0; 0.558, 5.131; 0.635, 4.980, 4; 0.718, 4.805; 0.778, 4.660, 7; 0.827, 4.524; 0.874, 4.361, 6; 0.899, 4.222; 0.954, 3.905, 1; 0.988, 3.417; 0.999, 2.763, −2; 1.001, 2.444; 1.002, 2.116; 1.002, 1.962; 1.003, 1.791;

Table 1 continued.

$B = 0.100$; Z, $-\log [\mathrm{OH^-}]$, $10^3(Z_{\mathrm{calc}}-Z)$; 0.007, 7.656; 0.022, 7.181; 0.033, 7.000; 0.053, 6.774; 0.079, 6.567; 0.108, 6.391; 0.135, 6.256; 1.005, 1.940; 0.082, 6.538, 3; 0.158, 6.153, 2; 0.238, 5.871; 0.402, 5.435, −2; 0.535, 5.137; 0.685, 4.805, 3; 0.776, 4.666; 0.854, 4.350, 4; 0.935, 3.966; 0.972, 3.609, 1; 0.994, 3.027; 0.999, 2.370, −10; 1.000, 2.093; 1.001, 1.947; 0.048, 7.285, −29; 0.124, 6.314, 0; 0.188, 6.045, −1; 0.273, 5.775, −3; 0.340, 5.593, −4; 0.483, 5.254; 0.605, 4.987, 0; 0.745, 4.663; 0.830, 4.427, 5; 0.895, 4.185; 0.924, 4.033, 4; 0.957, 3.782, 2; 0.972, 3.595, 2; 0.990, 3.193, 0; 0.996, 2.823, 0; 0.999, 2.536, −1; 1.000, 2.186; 1.000, 1.984; 1.000, 1.860;

$B = 0.200$; Z, $-\log [\mathrm{OH^-}]$, $10^3(Z_{\mathrm{calc}}-Z)$; 0.007, 8.59; 0.020, 7.63 0.050, 7.14; 0.081, 6.86; 0.115, 6.63; 0.183, 6.27; 1.008, 1.700; 1.008, 1.431; 1.014, 1.222; 0.933; 0.058, 7.082, 2; 0.168, 6.346, −3; 0.272, 5.906, −8; 0.365, 5.585; 0.479, 5.248, −12; 0.558, 5.034; 0.642, 4.811, −9; 0.797, 4.391; 0.861, 4.180, −8; 0.901 – 4.014; 0.955, 3.659, −4; 0.991, 2.945; 0.999, 2.020, 0; 1.001, 1.693; 1.003, 1.546; 1.006, 1.431; 0.027, 7.477, 2; 0.144, 6.474; 0.230, 6.070, −6; 0.325, 5.715; 0.419, 5.419, −11; 0.522, 5.129; 0.608, 4.898, −9; 0.684, 4.700; 0.753, 4.513, −7; 0.826, 4.297; 0.877, 4.114, −7; 0.944, 3.759; 0.987, 3.119, −1; 0.996, 2.564; 0.998, 2.198, 0; 0.999, 1.828; 1.000, 1.693; 1.001, 1.535;

$B = 0.400$; Z, $-\log [\mathrm{OH^-}]$, $10^3(Z_{\mathrm{calc}}-Z)$; 0.010, 8.564, −1; 0.022, 8.191, −2; 0.042, 7.821, −2; 0.061, 7.584; 0.084, 7.365, −4; 1.002, 1.369; 1.006, 1.090; 1.008, 1.002; 0.034, 7.972, −3; 0.083, 7.387, −5; 0.131, 6.960; 0.184, 6.588, −3; 0.247, 6.213; 0.325, 5.818, −6; 0.382, 5.564; 0.427, 5.381, −6, 0.479, 5.183, 0.529, 4.998, −2; 0.592, 4.782, 0; 0.658, 4.567, 1; 0.712, 4.397, 0; 0.759, 4.242; 0.817, 4.050, −4; 0.881, 3.805, −8; 0.911, 3.664, −9; 0.934, 3.536; 0.954, 3.385, −10; 0.995, 2.548, −4; 1.000, 1.691; 1.002, 1.377; 1.002, 1.241;

$B = 0.600$; Z, $-\log [\mathrm{OH^-}]$, $10^3(Z_{\mathrm{calc}}-Z)$; 0.036, 8.393, −10; 0.106, 7.527, −10; 0.176, 6.906, −5; 0.246, 6.392, −4; 0.318, 5.952, −6; 0.397, 5.475, 6; 0.480, 5.141, −2; 0.550, 4.843; 0.611, 4.603, 4; 0.698, 4.284, 4; 0.799, 3.926; 0.885, 3.587, −11; 0.933, 3.332, −15; 0.984, 2.772; 1.000, 1.535; 1.002, 1.208; 1.003, 1.076; 0.000, 10.429; 0.007, 9.243, −3; 0.042, 8.320, −12; 0.063, 8.047, −15; 0.169, 7.008, −11; 0.269, 6.308, −15; 0.300, 6.066, −8; 0.443, 5.341, −11; 0.521, 4.992, −7; 0.611, 4.632, −4; 0.688, 4.355, −6; 0.793, 3.988, −12;

Data with 3.0 M $\mathrm{Na(ClO_4)}$ medium. Data have been taken from our previous work (see Ref.[1,5,6]). For calculating Z_{calc}, $\log\beta_1 = 5.27$, $\log\beta_{13} = 7.41$, $\log\beta_{24} = 13.53$ and $\log\beta_{23} = 11.67$ have been used.

$B = 0.600$; Z, $-\log [\mathrm{OH^-}]$, $10^3(Z_{\mathrm{calc}}-Z)$; 1.000, 1.861, −2; 0.999, 2.078, −3; 0.997, 2.287, −3; 0.994, 2.440, −3; 0.992, 2.527, −3; 0.990, 2.611, −4; 0.989, 2.692, −6; 0.984, 2.766, −4; 0.981, 2.835, −4; 0.977, 2.901, −5; 0.973, 2.962, −5; 0.968, 3.019, −5; 0.964, 3.075, −5; 0.961, 3.103, −6; 0.958, 3.130, −6; 0.933, 3.346, −9; 0.872, 3.642, −7; 0.862, 3.692, −9; 0.803, 3.896, −2; 0.793, 3.951, −8; 0.733, 4.153, −4; 0.715, 4.221, −6; 0.653, 4.434, −4; 0.631, 4.523, −6; 0.005, 9.500, −11; 0.009, 9.175, −1; 0.014, 8.980, −2; 0.018, 8.835, −3; 0.022, 8.723, −3; 0.026, 8.632, −3; 0.029, 8.556, −3; 0.039, 8.376, −4; 0.049, 8.042, 2; 0.055, 8.138, −5; 0.064, 8.027, −6; 0.073, 7.918, −6; 0.080, 7.829, −6; 0.092, 7.710, −7; 0.032, 8.520, −5; 0.053, 8.200, −7; 0.090, 7.800, −13; 0.102, 7.628, −9; 0.148, 7.178, −7; 0.177, 6.944, −8; 0.240, 6.449, −7; 0.266, 6.268, −6; 0.283, 6.155, −6; 0.348, 5.767, −6; 0.369, 5.656, −6; 0.405, 5.469, −5; 0.431, 5.348, −6; 0.466, 5.180, −5; 0.536, 4.888, −6; 0.565, 4.767, −4;

$B = 0.400$; Z, $-\log [\mathrm{OH^-}]$, $10^3(Z_{\mathrm{calc}}-Z)$; 0.597, 4.753, −5; 0.655, 4.576, −8; 0.711, 4.430, −18; 0.745, 4.287, −7; 0.787, 4.138, −3; 0.826, 4.016, −6; 0.868, 3.848, −3; 0.901, 3.723, −7; 0.983, 3.492, −47; 0.035, 7.998, 0; 0.066, 7.615, −3; 0.102, 7.245, −3; 0.119, 7.123, −6; 0.149, 6.867, −3; 0.178, 6.678, −7; 0.201, 6.508, −5; 0.222, 6.392, −8; 0.281, 6.037, −5; 0.333, 5.791; −9; 0.374, 5.591, −7; 0.415, 5.415, −7; 0.471, 5.203, −8; 0.545, 4.932, −7;

Table 1 continued.

$B = 0.200$; Z, $-\log [OH^-]$, $10^3(Z_{calc}-Z)$; 0.557, 4.967, 10; 0.603, 4.901, −11; 0.730, 4.567, −8; 0.753, 4.444, 14; 0.849, 4.200, −1; 0.852, 4.138, 14; 0.947, 3.679, 6; 0.040, 7.326, 3; 0.050, 7.170, 6; 0.099, 6.760, 4; 0.130, 6.532, 8; 0.173, 6.340, −1; 0.186, 6.236, 6; 0.241, 6.030, −5; 0.263, 5.900, 5; 0.304, 5.795, −9; 0.357, 5.559, 5; 0.374, 5.553, −10; 0.427, 5.392, −12; 0.482, 5.231, −12; 0.550, 5.043, −12;

$B = 0.100$; Z, $-\log [OH^-]$, $10^3(Z_{calc}-Z)$; 0.563, 5.050, 11; 0.626, 4.912, 12; 0.678, 4.794, 14; 0.732, 4.666, 15; 0.775, 4.554, 17; 0.838, 4.363, 18; 0.881, 4.211, 15; 0.944, 3.855, 10; 0.973, 3.447, 10; 0.068, 6.640, 7; 0.119, 6.330, 7; 0.168, 6.099, 10; 0.261, 5.790, 7; 0.366, 5.505, 7; 0.444, 5.320, 7;

$B = 0.50$; Z, $-\log [OH^-]$, $10^3(Z_{calc}-Z)$; 0.611, 5.107, 11; 0.709, 4.775, 30; 0.812, 4.537, 19; 0.869, 4.356, 14; 0.197, 4.139, 10; 0.972, 3.637, 4; 0.990, 2.787, 7;

Data with 3.0 M K(Br) medium. For calculating Z_{calc}, $\log \beta_1 = 5.11$ $\log \beta_{13} = 7.19$, $\log \beta_{24} = 13.41$ and $\beta_{23} = 0$ have been used.

$B = 0.010$ M; Z, $-\log [OH^-]$, $10^3(Z_{calc}-Z)$; 0.072, 6.154, 11; 0.141, 5.855, 12; 0.208, 5.661, 12; 0.309, 5.433, 13; 0.393, 5.273, 13; 0.473, 5.132, 13; 0.558, 4.982, 14; 0.659, 4.796, 13; 0.753, 4.599, 10; 0.842, 4.367, 4; 0.930, 3.998, −2; 0.942, 3.918, −3; 0.961, 3.770, −5; 0.979, 3.579, −8; 0.994, 3.277, −9; 1.005, 2.432, −7; 1.003, 2.204; 1.000, 2.079; 1.000, 2.000;

$B = 0.050$ M; Z, $-\log [OH^-]$, $10^3(Z_{calc}-Z)$; 0.043, 6.558, 0; 0.114, 6.109; 0.194, 5.782, −3; 0.284, 5.541; 0.369, 5.351, −4; 0.559, 4.973; 0.661, 4.768, 4; 0.756, 4.553; 0.836, 4.330, 10; 0.904, 4.066; 0.936, 3.877, 6; 0.978, 3.387; 0.966, 2.739, 30; 0.999, 1.742; 0.031, 6.717, −1; 0.072, 6.325; 0.141, 5.975, −5; 0.233, 5.674; 0.333, 5.430, −5; 0.427, 5.230; 0.506, 5.076, −2; 0.611, 4.871; 0.709, 4.665, 6; 0.801, 4.439; 0.875, 4.199, 8; 0.943, 3.828; 0.966, 3.618, 2; 0.984, 3.310; 0.999, 2.614, −2; 1.001, 1.728; 1.003, 1.504, −3; 1.003, 1.381; 1.003, 1.302;

$B = 0.100$ M; Z, $-\log [OH^-]$, 10^3 $(Z_{calc}-Z)$; 0.007, 7.522, 1; 0.014, 7.258, 1; 0.028, 6.976, −1; 0.040, 6.786, 0; 0.051, 6.678, −2; 0.072, 6.504, −3; 0.099, 6.330, −5; 0.186, 5.928, −7; 0.262, 5.676, −10; 0.367, 5.380, −8; 0.556, 4.936, −7; 0.667, 4.688, 5; 0.792, 4.382, 1; 0.924, 3.888, 6; 1.002, 2.924, −9; 1.003, 1.835; 1.003, 1.521; 1.002, 1.367; 1.001, 1.197; 0.058, 6.613; 0.114, 6.247, −5; 0.220, 5.807; 0.319, 5.508, −9; 0.412, 5.269; 0.504, 5.053, −8; 0.614, 4.806; 0.720, 4.561, 0; 0.848, 4.208; 0.935, 3.819, 6; 0.962, 3.599; 1.003, 2.017, −4; 1.002, 1.714; 1.001, 1.496; 1.001, 1.404; 1.000, 1.308;

$B = 0.200$ M; Z, $-\log [OH^-]$, $10^3(Z_{calc}-Z)$; 0.046, 7.122, −3; 0.088, 6.721, −4; 0.170, 6.215, −5; 0.246, 5.863, −5; 0.350, 5.468, −4; 0.444, 5.167, −5; 0.544, 4.880, −8; 0.632, 4.641, −9; 0.723, 4.399, −9; 0.804, 4.167, −5; 0.890, 3.873, 1; 0.928, 3.689, 4; 0.951, 3.531, 5; 0.974, 3.310, 3; 1.001, 2.419, −3; 1.002, 1.562; 1.001, 1.355; 1.000, 1.181; 1.000, 1.106;

$B = 0.400$ M; Z, $-\log [OH^-]$, 10^3 $(Z_{calc}-Z)$; 0.066, 7.474, −11; 0.132, 6.920, −16; 0.211, 6.317, −5; 0.286, 5.870, 1; 0.355, 5.525, 2; 0.436, 5.169, 0; 0.508, 4.888, −4; 0.573, 4.654, −7; 0.644, 4.414, −11; 0.719, 4.172, −13; 0.784, 3.960, −11; 0.841, 3.765, −7; 0.907, 3.499, −1; 0.950, 3.252, 4; 0.975, 3.004, 5; 1.002, 1.650, −2; 1.001, 1.466; 1.001, 1.347; 1.001, 1.236;

deviation in β_{pq}. Here the "best" combination means that one which gives the lowest error square sum.

We found that of the two combinations (*a*) and (*b*), the combination (*b*) gave for all media the lowest square sum, thus indicating that the combination

Table 2. Formation constants for borates in 3 M Na(ClO$_4$), 3 M Na(Br), 3 M Li(Br) and 3 M K(Br). The constants and the errors have been obtained by using the least squares program LETAGROP[2]. The experimental points, which have been used in the calculation are denoted in Table 1 and all points have been given the weight, $w = 1$. It is three different combinations which have been tested. In the table, $\beta_1 = [B(OH)_4^-][B(OH)_3]^{-1}[OH^-]^{-1}$; $\beta_{13} = [B_3O_3(OH)_4^-][B(OH)_3]^{-3}[OH^-]^{-1}$; $\beta_{24} = [B_4O_5(OH)_4^{2-}][B(OH)_3]^{-4}[OH^-]^{-2}$; $\beta_{23} = [B_3O_3(OH)_5^{2-}][B(OH)_3]^{-3}[OH]^{-2}$ and so on.

In the first three calculations for Na(ClO$_4$) mainly polynuclear complexes are considered and the B-range used $\geqq 0.050$ M and in the fourth calculation all data (62 points) at low concentrations, $B \leq 0.050$ M, and 58 points in the B-range > 0.050 M have been used. Calculation for data $B \leq 0.025$ M (the mononuclear curve) gave $\log\beta_1 \pm 3\sigma = 5.24_8 \pm 0.014$.

Medium	Number of points	σ (Z)	log β_1 $\pm$ 3 σ	log β_{13} $\pm$ 3 σ	log β_{24} $\pm$ 3 σ	log β_{23} $\pm$ 3 σ	log β_{15} $\pm$ 3 σ
Na(ClO$_4$)	120	0.0152	$5.27_3 \pm 0.021$	7.54 ± 0.08	—	12.09 ± 0.13	7.42
3.0 M	120	0.0113	$5.28_4 \pm 0.015$	7.47 ± 0.11	13.70 ± 0.08	—	7.42
	120	0.0095	$5.27_4 \pm 0.012$	7.41 ± 0.07	13.53 ± 0.12	11.67 ± 0.24	7.42 ± 0.70
	120	0.0097	$5.25_3 \pm 0.014$	7.38 ± 0.08	13.45 ± 0.13	11.96 ± 0.23	7.52
Na(Br)	114	0.0109	$5.26_3 \pm 0.012$	7.48 ± 0.06	—	12.17 ± 0.12	—
3.0 M	114	0.0094	$5.26_9 \pm 0.011$	7.26 ± 0.08	13.59 ± 0.10	—	—
	114	0.0069	$5.26_4 \pm 0.009$	7.35 ± 0.06	13.43 ± 0.12	11.86 ± 0.16	—
Li(Br)	100	0.0082	$5\ 26_6 \pm 0.008$	7.42 ± 0.06	—	12.16 ± 0.10	—
3.0 M	100	0.0080	$5.26_7 \pm 0.008$	7.17 ± 0.09	13.57 ± 0.10	—	—
	100	0.0059	$5.26_6 \pm 0.005$	7.29 ± 0.07	13.37 ± 0.16	11.88 ± 0.18	—
K(Br)	84	0.0106	$5.10_6 \pm 0.013$	7.38 ± 0.08	—	11.84 ± 0.15	—
3.0 M	84	0.0078	$5.10_9 \pm 0.010$	7.19 ± 0.08	13.41 ± 0.10	—	—
	84	0.0078	$5.10_9 \pm 0.010$	7.19 ± 0.08	13.41 ± 0.10	($\beta_{23} = -0.69$)	—

containing the complex $B_4O_5(OH)_4^{2-}$ is a better explanation of the data than that containing $B_3O_3(OH)_5^{2-}$. The results of our LETAGROP analysis of the combinations (*a*) and (*b*) are collected in Table 2.

In order to see if our data could be better explained by assuming the formation of both $B_3O_3(OH)_5^{2-}$ and $B_4O_5(OH)_4^{2-}$ we carried out a LETAGROP analysis assuming the formation of the complexes in the combination (*c*). We found that this combination gave a better explanation of the data than (*b*) for data for 3.0 M NaClO$_4$, 3.0 M NaBr, 3.0 M LiBr, but not for 3.0 M KBr. The result of our analysis is collected in Table 2, and the difference between Z_{calc} and Z_{obs} is given in Table 1. In Fig. 1 the experimental points obtained in 3 M NaBr are given and the full curve is that calculated with the set of constants in Table 2.

The formation constant for $B_3O_3(OH)_5^{2-}$ in 3.0 M K(Br) was found to be ≈ 0 (-0.69), but in 3.0 M Na(ClO$_4$), 3.0 M Na(Br) and 3.0 M Li(Br), 4.65×10^{11}, 7.25×10^{11} and 7.60×10^{11}, respectively, and, in addition, the formation constant for $B(OH)_4^-$ in 3.0 M K(Br) is significantly different from the values for the other media ($1.28_5 \times 10^5$ compared with $1.87_8 \times 10^5$ (NaClO$_4$), $1.83_8 \times 10^5$

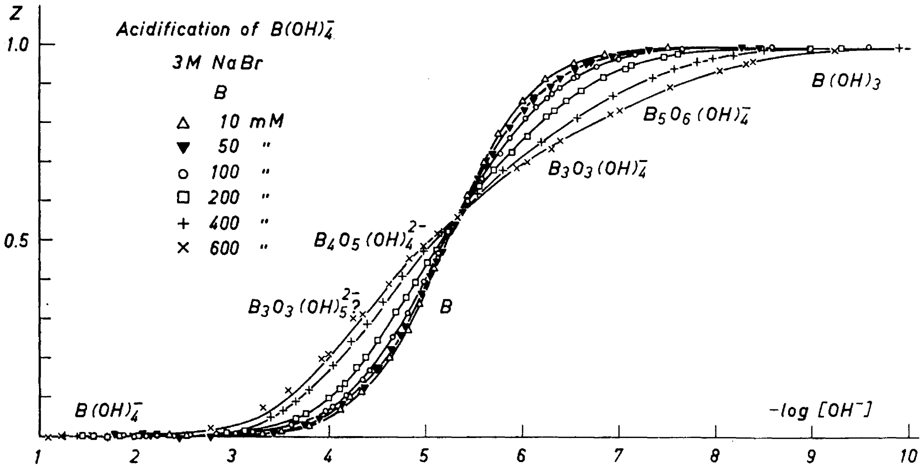

Fig. 1. Experimental data. $Z(\log\,[\mathrm{OH}])_B$, for borates in 3 M Na(Br). Z is the average number of H^+ bound per $B(OH)_4^-$ (note that Z is different from Z given in the text). Full curves calculated with the set of best constants in Table 2.

(NaBr), $1.84_4 \times 10^5$ (LiBr)). Thus we conclude that an exchange of the perchlorate-ions in 3.0 M $NaClO_4$ for Br^--ions results in only small changes in the equilibrium constants, and that the substitution of the sodium-ions in the media, 3.0 M NaBr with Li^+ and K^+ results in measurable changes of the composition of the borate solution only in the case of potassium-ions.

From Table 1 we see that for the highest concentrations and in all media Z_{calc} is always slightly lower than Z_{obs}, thus indicating a systematic deviation. This deviation is probably due to the fact that the equilibrium-constant for the mononuclear reaction, β_1 (and for the other reactions also), may be slightly different in a solution with $B = 0.020$ M and in a solution with $B = 0.600$ M. In other words the activity factors seem to change when the total boric acid concentration increases from $B = 0.020$ M to $B = 0.600$ M. This deviation might be examined by analysing each curve, $Z(\log\,[\mathrm{OH}^-])_B$, independently of the others, a new set of equilibrium constants being obtained for every B. However, such a calculation has not been carried out. The deviations are not of such magnitude that they change our main conclusions and we conclude that concentrated borate solutions contain the species, $B(OH)_3$, $B(OH)_4^-$, $B_3O_3(OH)_4^-$, $B_4O_5(OH)_4^{2-}$ and probably also $B_3O_3(OH)_5^{2-}$ and $B_5O_6(OH)_4^-$.

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