REACTIONS OF BORIC ACID WITH OXALIC, GLYCOLIC AND TARTARIC ACIDS

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Dedicated to Professor S. Stankovianský on the occasion of his 70th birthday.

Formation of chelates of B(III) with oxalic acid (composition $OxB(OH)_2^-$), glycolic acid (composition $(GH_{-1})B(OH)_2^-$), and tartaric acid (composition $(HTH_{-1})B(OH)_2^-$, $(TH_{-1})B(OH)_2^-$, $(HO)_2B(TH_{-2})B(OH)_2^+$ and $(TH_{-1})B(TH_{-2})^4^-$) has been studied in diluted aqueous solutions by the method of potenciometric neutralization titration, and the equilibrium constants values are given. Conditions of formation of the chelates of B(III) with organic hydroxy acids are discussed.

Boric acid reacts¹ with organic reagents (H₂L) containing 2 hydroxyl groups and able of formation of 5- and 6-membered chelate cycles. The hydroxyl groups in the reagent H₂L can have phenolic or alcoholic character or they can be hydroxyl groups of carboxylic or amide groups^{2,3}. Reaction of H₂L with H₃BO₃ in aqueous solutions produces the complexes LB(OH)₂⁻ or BL₂⁻. Conjugated acids of these complex boron anions are known only in solid state, whereas on dissolving in water they split off the proton or decompose into components H₂L and H₃BO₃ (ref.⁴). In aqueous solutions the complexes of B : L = 1 : 1 ratio are most usual. Those of 1 : 2 ratio are less usual, a considerable excess of the reagent H₂L being needed for their formation. A number of reagents whose chelates 1 : 2 were isolated as solids form only 1 : 1 complexes in aqueous

Complex salts of B(111) with oxalic acid (H_2Ox) and with hydroxyacetic acid (HG) were isolated, their composition corresponding to formulas K[OxB(OH)₂] (ref.^{6,7}) and H[G₂B] (ref.²). Formation of these complexes in aqueous solution was not studied in more detail.

Tartaric acid (H_2T) is a weak dibasic acid $(pK_{a1} 2.4 \text{ to } 3.0, pK_{a2} 3.4 \text{ to } 4.4; \text{ref.}^{20})$; its carboxyl groups easily split off protons in aqueous solutions to give the ions HT^- and T^{2-} . Dissociation of the both alcoholic groups to give the ions TH^{2-}_{-1} and TH^{4-}_{-2} was observed by Frei⁸ in concentrated alkali hydroxides $(pK_{a3} \approx 15, pK_{a4} \approx 16)$. Structure of tartaric acid molecule allows to bind the central B(III) atom to two oxygen atoms of neighbouring alcoholic groups, the chelates formed being analogous to those of B(III) with glycols⁴ in which the ligands are ions $H_2TH^{2-}_{-2}$, HTH^{3-}_{-2} and TH^{4-}_{-2} (the non-split off hydrogen atoms of carboxylic groups is given after this symbol with negative index). The second possibility consists in linking of born to one carboxyl and one alcoholic oxygen atoms (the chelate formed being analogous to that of glycolic acid²), ions HTH^{2-}_{-1} or TH^{3-}_{-1} are the ligand; in this way one tartaric acid molecule can be bound to two born atoms. Another possibility — linking of B(III) to oxygen atoms of the both carboxyl groups, atoms of the both carboxyl groups, how both carboxyl groups atoms to that of glycolic acid²), ions HTH^{2-}_{-1} or TH^{3-}_{-1} are the ligand; in this way one tartaric acid molecule can be bound to two born atoms. Another possibility — linking of B(III) to oxygen atoms of the both carboxyl groups, in the second possibility and the second possibility and the second possibility and the second poster atoms of the both carboxyl and one alcoholic oxygen atoms (the chelate formed being analogous to that of glycolic acid²), ions HTH^{2-}_{-1} or TH^{3-}_{-1} are the ligand; in this way one tartaric acid molecule can be bound to two born atoms. Another possibility — linking of B(III) to oxygen atoms of the both carboxyl groups, glycolic acid² = 1 atom and the two born atoms.

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 T^{2-} being the ligand — is little likely, as ring-closure of the 7-membered chelate ring in such a compound would not contribute to increasing of the stability of the complex9. Complexes of B(III) with tartaric acid were studied in detail. Salts of alkali metals of the type $Me(HTH_{-1})_{3}B$ were isolated¹⁰. In complexes with tartrate and also malate¹¹ the bond of boron to one carboxylic and one alcoholic oxygen was reported. Bond of boron to two neighbouring alcoholic oxygen atoms is suggested¹² in the case of diethyl tartrate and tartrate anion in strongly alkaline medium. Reaction of H₂T with H₂BO₂ is accompanied by acidity increase of the aqueous solution¹¹. which indicates that a considerably strong acid is formed. Solubility increase of boric acid in water in the presence of tartrate¹³ indicates formation of the complex $(HO)_2B(TH_{-2})B(OH)_2^2$. Reactions of H₃BO₃ with H₂T were studied on the basis of acidity change of aqueous solutions^{11,14,15}, cryoscopically¹⁵, conductometrically^{14,16}, and from the change of optical activity^{12,14}. Equilibrium constants of formation of the complexes HTBO₂H⁻, TBO₂H²⁻, TBO₂³⁻ and TBO₂(OH)⁴⁻ are given in ref.¹⁵, and those of $(TH_{-1})B$, $(TH_{-2})B^{-}$, $(TH_{-2})B(OH)^{2-}$, $(TH_{-2})B(OH)^{2-}$, $(TH_{-2})B(OH)^{2-}$, $(TH_{-2})B(OH)^{2-}$, $(TH_{-1})_2B^{-3}$ and $(TH_{-2})_2B^{5-}$ are given in ref.¹⁴. The complexes described in ref.¹⁵ can be considered to be the protonation products of the ion $(TH_{-1})BO_2^{4-}$, whereas those given in ref.¹⁴ are various protonated species of $(TH_{-2})B(OH)_{2}^{3^{-1}}$ and $(TH_{-2})_{2}B^{5^{-1}}$. Lack of uniformity in formulation of these complexes was a hint for the present work.

EXPERIMENTAL

Solutions of acids were titrated with standard 0.0940M NaOH solution using an automatic apparatus for potenciometric titration PHM 26, TTT 11, ABU 12 and SBR with a glass G 200 B and a saturated calomel electrode (Radiometer, Copenhagen). Titration of a strong acid with a strong base (HNO₃ + NaOH) was used for calibration, and the pH meter was adjusted with the use of a phosphate buffer pH 6:50 before each measurement. Titrations were carried out at 21 \pm 1°C. Ionic strength (1) of the solutions was adjusted by addition of potassium nitrate (sodium nitrate in the case of tartaric acid).

Sodium salt of glycolic acid was prepared by reaction of 0-1 mol monochloroacetic acid with 0-2 mol sodium hydroxide in aqueous solution at increased temperature. d-Tartaric acid and the other reagents used were commercial chemicals of p.a. purity grade (Lachema, Brno). Concentration of solutions of acids was checked by potenciometric alkalimetric titration.

Boric acid solutions were titrated in alkaline medium in the presence of varying excess of neutral salt of the organic acid, and the value \bar{z} was determined¹⁷ giving the average number of protons split off from the boric acid molecule. In acid media the organic acids were titrated in the presence of various excesses of boric acid, and the function $_{L}\bar{z}$ was determined¹⁸ giving the average number of protons split off from the organic acid. The approximations $c_{\rm B} \approx [{\rm H}_3 {\rm BO}_3]$ at pH < 7, and $c_{\rm L} \approx [{\rm G}^-]$ or $c_{\rm L} \approx [{\rm T}^{2^-}]$ at pH > 7 suit well the solutions studied. The total analytical concentrations of boron and reagent — organic acid — are denoted $c_{\rm B}$ and $c_{\rm L}$, respectively. In the calculations of equilibrium constants activities of the proton and concentrations of the other components were used.

RESULTS AND DISCUSSION

Reactions of Oxalic Acid

A series of 0.02M-H₂Ox solutions were titrated in the presence of various concentrations of boric acid, c_B 0, 0.127, 0.160, 0.255, 0.382 and 0.510M at *I* 0.11. Increasing content of boric acid in the solution shifts the titration curves to more acidic region (at pH < 2.9) or to more alkaline region (at pH > 2.9) (Fig. 1), consumption of base for neutralization of oxalic acid being unchanged. Oxalic acid is a weak dibasic acid, pK_{a1} 1.2 and pK_{a2} 4.0; at pH < 2.9 it is present in the solution as H_2Ox and HOx^- , at pH ≈ 2.9 it is neutralized to the first degree, and at pH > 2.9 the ions HOx^- and Ox^{2-} are in solution. The acidity increase of solution containing H_2Ox molecules after addition of boric acid is explained by Eq. (A), The complex $OxB(OH)_2^-$ is formed also by reaction (B) not liberating protons.

$$H_2Ox + H_3BO_3 = OxB(OH)_2^- + H^+ + H_2O$$
 (A)

$$HOx^{-} + H_3BO_3 = OxB(OH)_2^{-} + H_2O \quad K_B \equiv \beta_1 \qquad (B)$$

$$2 H_2Ox + H_3BO_3 = Ox_2B^- + H^+ + 3 H_2O$$
 (C)

Therefore, addition of boric acid to a solution of pH 2-9 containing oxalate only in the form HOx⁻ does not cause any acidity change of the solution. After finished reaction of the anion HOx⁻ with boron (Eq. (B)) the neutralization of oxalic acid to the second degree is more difficult, *i.e.* it takes place in more alkaline medium than in solutions without H₃BO₃. At pH < 3 formation of the complex Ox₂B⁻ according to Eq. (C) cannot be excluded. The consumption of base for attaining pH 2-9 was found to be the same in all the solutions studied ($c_B = 0$ and $c_B \neq 0$, too). It means that, if the complex Ox₂B⁻ was formed at the beginning of tiration in acid medium, at



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pH 2·9 it is already decomposed. If the formed complex Ox_2B^- were not decomposed, the consumption of base for neutralization to pH 2·9 would be proportional to the total oxalic acid concentration minus concentration of Ox_2B^- complex.

Titration curves of the studied series make it possible to evaluate the formation of $OxB(OH)_2^-$ complex from the acidity increase of the solutions in the region of neutralization of oxalic acid to the first degree or from acidity decrease of these solutions in the region of neutralization to the second degree. Oxalic acid itself is, in its solutions, considerably dissociated into H⁺ and HOx⁻ ions and, therefore, the acidity change due to addition of boric acid in the region of neutralization of oxalic acid to the first degree is smaller than that in the region of neutralization to the second degree. Values of the function $_L\bar{z}$ in interval 1 to 2 were evaluated from titration curves in the pH region 3.0 to 5.5. The quantity $_L\bar{z}$ is defined by relation (1) (charges of ions are omitted for simplicity) which gives Eq. (2) by introduction of constans, and Eq. (3) holds for $[H]_{L\bar{z}=1.5}$ which equals to 10^{-pH} at $_L\bar{z} = 1.5$.

$$_{L}\tilde{z} - 1 = [Ox]/([Ox] + [HOx] + [OxB(OH)_{2}]), \qquad (1)$$

$$(_{L}\bar{z} - 1)[H]/(2 - _{L}\bar{z}) = K_{a2}/(1 + K_{B}[H_{3}BO_{3}]),$$
 (2)

$$1/[H]_{L^{\bar{z}}=1.5} = (1 + K_{B}[H_{3}PO_{3}])/K_{a2}.$$
(3)

Graphical transformation of $\log[(_{L}\bar{z} - 1)/(2 - _{L}\bar{z})] = f(pH)$ at constant c_{B} is linear in the pH region 3.5 to 4.7, its slope being close to unity. From these linear dependences the values pH_{LZ=1.5} were read: 4.02, 4.10, 4.17, 4.20, 4.29, and 4.32 for c_{B} 0, 0.127, 0.160, 0.255, 0.372, and 0.510, respectively. Dependence $1/[H]_{L\bar{z}=1.5} = f(c_{B})$ is linear, its slope gives the value $K_{B} = 10^{0.35}$.

Solutions of malonic acid were titrated under the same conditions as those of oxalic acid. Addition of boric acid caused only a slight shift of the titration curve to acid region, malonic acid does not practically react with boric acid in weakly acidic aqueous solution at $c_{\rm L}$ 0.22M and $c_{\rm B}$ 0.5M.

Reactions of Glycolic Acid

A series of 0.035M glycolic acid solutions were titrated having $c_{\rm B}$ 0 to 0.5M at I = 0.09. Titration curves of this monobasic acid shift to more acidic region with increasing $c_{\rm B}$. Consumption of base for neutralization of HG in the presence of boric acid does not change, *i.e.* complex type L₂B is not formed. The quantity $_{\rm L}\bar{z}$ in the interval 0.10 to 0.98 was measured in the pH region 2.9 to 5.3. Dependence $\log[_{\rm L}\bar{z}/(1 - _{\rm L}\bar{z})] = f(pH)$ at constant $c_{\rm B}$ is linear, its slope being unity. From graph of this dependence the values pH_{1,z=0.5} were read: 3.81, 3.74, 3.66, 3.60, and 3.55 for $c_{\rm B}$ 0.014, 0.28, 0.42, and

Reactions of Boric Acid

0.56M, respectively. For the solutions in which the reactions (D) and (E) take place the function $_{L}\overline{z}$ is defined by Eq. (4), and Eq. (5) is valid.

$$HG = G^- + H^+ \quad K_{a1} \tag{D}$$

$$HG + H_3BO_3 = (GH_{-1})B(OH)_2 + H^+ + H_2O K_E$$
 (E)

$$L\bar{z} = [G]/([HG] + [G] + [(GH_{-1}) B(OH)_2])$$
 (4)

$$[H]_{L^{\bar{z}}=0.5} = K_{a1} + K_{E}[H_{3}BO_{3}]$$
(5)

Graph of the function $[H]_{L^{\xi=0.5}} = f(c_B)$ is linear and gives, on the basis of Eq. (5), the values pK_{a1} 3.81 and pK_E 3.64.

Solutions of 0.0032*M* boric acid were titrated at pH > 7.5 in the presence of various concentrations of glycolate at I = 0.21. With increasing glycolate content the titration curves shift to more alkaline region. Function $\log[\bar{z}/(1-\bar{z})] = f(pH)$ at c_L constant is linear with the slope equal to unity. The values pH_{z=0.5} 9.08, 9.11, 9.14, and 9.22 were found for $c_L 0$, 0.021, 0.053, and 0.106M, respectively. If the reactions (F) and (G) take place in the solution, then Eqs (6) and (7) hold.

$$H_3BO_3 + H_2O = B(OH)_4^- + H^+ K_b$$
 (F)

$$H_3BO_3 + G^- = (GH_{-1})B(OH)_2^- + H_2O \quad K_G \equiv \beta_1$$
 (G)

$$\bar{z} = [B(OH)_{4}^{-}]/([H_{3}BO_{3}] + [B(OH)_{4}^{-}] + [(GH_{-1})B(OH)_{2}^{-}])$$
(6)

$$1/[H]_{z=0.5} = (1 + K_G[G])/K_b.$$
⁽⁷⁾

The experimentally found dependence $1/[H]_{z=0.5} = f([G])$ is linear in accord with the presumed equilibria (F) and (G); from the respective plot the values log $K_b = -9.08$ and log $K_G = 0.54$ were read.

Reactions of Tartaric Acid

In dilute aqueous solutions tartaric acid is a weak dibasic acid, in the presence of excess boric acid the curve of neutralization titration of tartaric acid shifts to more acidic region, its dibasicity being, however, maintained. No pH change was observed during mixing tartrate (NaKT) and boric acid solutions. Neutralization of boric acid in the presence of excess tartrate takes place in a more alkaline region than that in the absence of tartrate. These facts indicate that boron is not bound to the both carboxyl groups of tartrate; if such bond were formed, the titration curves of the

solutions having $c_{\rm B} = 0$ and $c_{\rm B} \neq 0$ in acid medium would cross each other at pH = $(pK_{a1} + pK_{a2})/2$, as it is the case with oxalic acid. Bond of boron to 2 alcoholic groups would affect probably only slightly acidity of carboxyl groups, and the complex $(TH_{-2}) B(OH)_2^{3^-}$ thus formed would be a tribasic acid. By analogy with reaction of glycoles the formation of $(TH_{-2}) B(OH)_2^{3^-}$ complex can by expected first in weakly alkaline medium, and in this case boric acid would be a stronger acid in the presence of tartrate than at $c_{\rm L} = 0$. Experimentally observed acidity increase of H_2T in the presence of H_3BO_3 and acidity decrease of boric acid at $[T^{2^-}] > 0$ indicates boron to be bound to one oxygen of carboxylic group and one oxygen of alcoholic group, which is similar to the glycolate complex.

In acid media with excess H_3BO_3 the reactions (*H*) to (*L*) can be considered to take place. Eq. (8) defining the quantity $_L\bar{z}$ can be modified to the form Eq. (9) the graphical transformation (Eq. (10)) of which enables determination of equilibrium constants of the reactions (*H*) to (*L*). The straight line according to Eq. (10) has the intercept *p* and slope *q* given by Eqs (11) and (12), respectively.

$$H_2T = HT^- + H^+ K_{a1}$$
 (H)

$$HT^{-} = T^{2-} + H^{+} K_{a2}$$
 (1)

$$H_2T + H_3BO_3 = (HTH_{-1})B(OH)_2^- + H^+ K_J$$
 (J)

$$H_2T + H_3BO_3 = (TH_{-1})B(OH)_2^2 + 2H^+ K_K$$
 (K)

$$H_2T + 2 H_3BO_3 = (HO)_2B(TH_{-2})B(OH)_2^{2-} + 2 H^+ K_L$$
 (L)

$$_{L}\bar{z} = ([HT] + [(HTH_{-1}) B(OH)_{2}] + 2[T] + 2[(TH_{-1}) B(OH)_{2}] +$$

+ $2[(HO)_2B(TH_{-2})B(OH)_2])/([H_2T] + [HT] + [T] + [(HTH_{-1})B(OH)_2] +$

+

$$+ [(TH_{-1}) B(OH)_2] + [(HO)_2 B(TH_{-2}) B(OH)_2])$$
(8)

$$_{L}\bar{z} + (_{L}\bar{z} - 1) [H]^{-1} (K_{a1} + K_{J}[H_{3}BO_{3}]) + (_{L}\bar{z} - 2) [H]^{-2} (K_{a1}K_{a2} + K_{J}[H_{3}BO_{3}])$$

+
$$K_{\rm K}[{\rm H}_{3}{\rm BO}_{3}] + K_{\rm L}[{\rm H}_{3}{\rm BO}_{3}]^{2}) = 0$$
 (9)

$$_{L}\bar{z}[H]/(1 - _{L}\bar{z}) = f((_{L}\bar{z} - 2)/[H](_{L}\bar{z} - 1))_{[H_{3}BO_{3}]=const.}$$
 (10)

$$p = K_{a1} + K_{J} [H_{3}BO_{3}]$$
⁽¹¹⁾

$$q = K_{a1}K_{a2} + K_{K}[H_{3}BO_{3}] + K_{L}[H_{3}BO_{3}]^{2}$$
(12)

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The values $_{L}\bar{z}$ 0.24 to 1.93 were found by measuring the titration curves of the solutions of c_{L} 0.018M, c_{B} 0 to 0.46M and I 0.1 at pH 2.2 to 5.2. Graphical transformation (Eq. (10), Fig. 2) gives straight lines from which the p and q values were read. The graph $p = f(c_{B})$ is linear and indicates pK_{a1} 2.89 and pK_{J} 1.87. Graph $q = f(c_{B})$ is not linear and gives only the value ($pK_{a1} + pK_{a2}$) = 6.92. The linear dependence ($q - K_{a1}K_{a2}$)/ $|c_{B} = f(c_{B})$ yields pK_{K} 6.00 and pK_{L} 4.98.

Titration curves of 0.0036M boric acid in the presence of various concentrations of the Seignett salt (c_1 , 0, 0.012, 0.024, 0.036 and 0.060M) were measured at pH 7.6 to 10.0, \overline{z} 0.02 to 0.92 at I = 0.2. The linear dependence $\log[\overline{z}/(1-z)] = f(pH)$ at constant c_1 has the slope equal to unity and gives the pH_{z=0.5} values 9.05, 9.07, 9.11, 9.15 and 9.25 for the respective above c_1 values. Change of pH_{2=0.5} value with increasing $c_{\rm L}$ is of similar type as in the system boric acid-glycolate, therefore, we presume the reaction (M) analogous to the equilibrium (G). Dependence $1/[H]_{z=0.5} =$ $= f(c_1)$ of the tartrate is visibly curved, which indicates the presence of a further equilibrium not observed in the system $H_3BO_3-G^-$. The linear dependence (Eq. (16)) indicates also co-ordination of 2 tartrate ions per 1 boron atom. Protons are neither liberated nor consumed in the reaction of H₃BO₃ with T²⁻, hence the equation describing formation of the complex with two tartrate ions does not involve protons. This requirement is met by Eq. (N), the complex formed containing 2 tartrate anions bound in non-equivalent ways. In medium of excess tartrate formation of the complex with the ratio B : L = 2 : 1 is little likely, and the linearity of the dependence $\log [\bar{z}](1 - z)$ $(-\tilde{z}) = f(pH)$ at constant c_L confirms experimentally the absence of a greater amount of the 2:1 complex. If equilibria (M) and (N) are established in solution, then Eqs



FIG. 2

Graphical Transformation (10) for the System Boric Acid-Tartaric Acid at pH < 7

$$\begin{split} Y &= {}_{L}\bar{z}[H] (1 - {}_{L}\bar{z})^{-1} \cdot 10^2; X = (2 - {}_{L}\bar{z})/(1 - {}_{L}\bar{z}) [H] 10^4 c_L 0.018M; c_B 0 (1), 0.187 (2), \\ 0.327 (3) and 0.467M (4). \end{split}$$

(13) to (15) are valid. From the linear graphical transformation (Eq. (16)) on the basis of Eq. (15) the values log $K_{\rm M}$ 0.65 and log $K_{\rm N}$ 0.86 were read.

$$H_3BO_3 + T^{2-} = (TH_{-1})B(OH)_2^{2-} + H_2O \quad K_M \equiv \beta_1$$
 (M)

$$H_3BO_3 + 2T^{2-} = (TH_{-1})B(TH_{-2})^{4-} + 3H_2O K_N$$
 (N)

$$\bar{z} = [B(OH)_4]/([H_3BO_3] + [B(OH)_4] + [(TH_{-1}) B(OH)_2] + [(TH_{-1}) B(TH_{-2})])$$
(13)

$$K_{\rm b} / [{\rm H}]_{\bar{z}=0.5} = 1 + K_{\rm M} [{\rm T}] + K_{\rm N} [{\rm T}]^2$$
(14)

$$([H]_{\bar{i}=0.5}^{-1} - K_{b}^{-1})/[T] = K_{M}/K_{b} + K_{N}[T]/K_{b}$$
(15)

$$([H]_{\bar{z}=0.5}^{t} - K_{b}^{-1})/c_{L} = f(c_{L})$$
(16)

CONCLUSIONS

Chelates of B(III) with oxalic, glycolic and tartaric acids are formed analogously as those with reagents of gylcol⁴, *o*-dihydroxybenezene^{5,18} or *o*-carboxyphenolic types¹⁹. Formation of 1 : 1 complex in aqueous solutions can be observed in a somewhat more acidic region than the region of dissociation of the most acidic group taking part directly in formation of complex bond of boron atom with oxygen of the ligand; in reactions of organic acids with B(III) this strongest acidic group is carboxyl, whereas in reactions with glycols it is boric acid. Decomposition of the 1 : 1 complex proceeds at somewhat higher pH than the pH of dissociation of the second most acidic group participating in the bond formation; in complexes of B(III) with hydroxycarboxylic acids it is boric acid, and in reaction with oxalic acid it is the second less acidic carboxyl. Therefore, complex of boron with oxalic acid is decomposed already in slightly acidic medium, whereas the complex with glycolic acid decomposes in alkaline medium.

In the studied acid solutions no co-ordination of two reagents per one boron atom was observed. Measurement at pH < 7 was carried out in solutions of $c_{\rm B} > c_{\rm L}$, *i.e.* medium little suited for formation of complexes type BL₂. For formation of the complexes BL₂ the best medium is that containing excess of reagent in the form H₂L, and if organic acid is the reagent, then such medium is not suitable for study of formation of complexes by means of potenciometric neutralization titration. The complex type BL₂ was not observed in alkaline solutions with excess glycolate, too. Glycolate anion corresponds to the species HL, whereas the species H₂L is needed for coordination of the second ligand to the complex LB(OH)₂ (Eq. (P)); coordination of the species HL would have to proceed with consumption of proton, but reaction of this type is not known. The BL_2 complex was proved in alkaline medium only with tartrate the anion of which (T^{2^-}) contains a glycol arrangement, corresponding thus to the species H_2L .

$$LB(OH)_{2}^{-} + H_{2}L = BL_{2}^{-} + 2 H_{2}O$$
(P)

From the β_1 values given in Table I it follows that oxalic and glycolic acids form approximately equally little stable complexes with B(III), the complex with tartaric acid having the highest stability of the studied series (still more stable complexes are formed form salicylic acid¹⁹ (log β_1 1·4) and chromotropic acid¹⁸ (log β_1 3·8)). Table I gives β_1 values evaluated from measurements in alkaline and acidic media at different ionic strengths. The difference in logarithms of these values (0·3) can be considered

TABLE I		
Summary of the	Equilibria	Studied

Equilibrium ^a	log K	
Oxalic acid		
$HOx^- = Ox^{2-} + H^+$	$\log K_{a2} = -4.02$	
$HOx^{-} + H_{3}BO_{3} \rightarrow OxB(OH)_{2}^{-}$	$\log \beta_1 = 0.35^b$	
Glycolic acid		
$\mathrm{HG}=\mathrm{G}^{-}~+~\mathrm{H}^{+}$	$\log K_{a1} = -3.81$	
$G^{-} + H_3BO_3 \rightarrow (GH_{-1})B(OH)_2^{-}$	$\log \beta_1 = 0.17^b \ 0.54^c$	
Tartaric acid		
$H_2T = HT^- + H^+$	$\log K_{a1} = -2.89$	
$HT^{-} = T^{2-} + H^{+}$	$\log K_{a2} = -4.02$	
$HT^{-} + H_{3}BO_{3} \rightarrow (HTH_{-1})B(OH)_{2}^{-}$	$\log \beta_{1\mathrm{H}} = 1.02^{b}$	
$T^{2-} + H_3BO_3 \rightarrow (TH_{-1})B(OH)_2^{2-}$	$\log \beta_1 = 0.92^b \ 0.65^c$	
$(TH_{-1}) B(OH)_2^2 + H_3 BO_3 \rightarrow (HO)_2 B(TH_{-2}) B(OH)_2^2$	$\log K_{1,2} = 1.04^{h}$	
$(TH_{-1}) B(OH)_2^2 + T^2 \rightarrow (TH_{-1}) B(TH_{-2})^4$	$\log K_2 = 0.21^c$	
$(\text{HTH}_{-1}) \text{ B}(\text{OH})_{2}^{-} = (\text{TH}_{-1}) \text{ B}(\text{OH})_{2}^{2^{-}} + \text{H}^{+}$	$\log K_{ak} = -4.13^{b}$	

^{*a*} In the schemes of equilibria water is not given; water concentration was not involved in the calculation of constants, too, ^{*b*} found at pH < 7, ^{*c*} found at pH > 7.

to represent an acceptable agreement of two independent ways of measurement of one quantity.

The values of constants given in Table I show that coordination of B at "one end" of tartrate anion affects negligibly acid-base and complex-forming properties of "the other end" of the anion. Acidity constant of the less acidic carboxyl is practically the same, whether the reagent is free (K_{a2}) or bound in complex (K_{ay}) . Also the affinity to B(III) is almost the same for the protonated (HT^-) , non-protonated (T^{2^-}) and complex-bound tartrate $(TH_{-1}) B(OH)_2^{2^-}$, as it follows from slight differences between β_{111} , β_1 , and $K_{1,2}$. Attempt to compare the constants of tartrate complexes of B(III) measured in this work with those published in refs^{14,15} failed, as for the latter the complex equilibria are formulated in a fundamentally different way.

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