

# Reaction of boric acid with salicylic and chromotropic acids and with their derivatives

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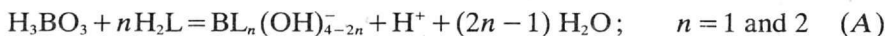
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*Dedicated to Professor F. Čůta, Corresponding Member of the Czechoslovak Academy of Sciences, on his 80th birthday*

The formation constants of the boron chelates 1:1 with salicylate, sulfosalicylate, *p*-aminosalicylate, 1,2-, 2,1-, and 2,3-hydroxynaphthoate were evaluated from potentiometric curves of the acid-base titrations at pH 8–10. The difference 4 orders of magnitude between determined constants for the chelates  $\text{BL}(\text{OH})_2$  with 1,8-dihydroxynaphthalene-3,6-disulfonate and 8-amino-1-naphthol-3,6-disulfonate indicates that the affinity of the central boron atom for the nitrogen donor atom is much smaller than for the oxygen one.

Из кривых нейтрализации в области pH 8–10, исследованных потенциометрически, были определены константы образования хелатов 1:1 бора с салицилатом, сульфосалицилатом, *p*-аминосалицилатом, 1,2-, 2,1-, и 2,3-гидроксинафтоатом. Разница в четыре порядка у полученных значений констант хелатов  $\text{BL}(\text{OH})_2$  с 1,8-дигидроксинафталин-3,6-дисульфонатом и 8-амино-1-нафтол-3,6-дисульфонатом показывает, что сродство центрального атома бора к донорному атому азота гораздо меньше, чем к кислороду.

Boric acid forms chelates  $\text{BL}(\text{OH})_2$  and  $\text{BL}_2$  (the charges of ions are omitted for the sake of simplicity) with organic oligohydroxy compounds ( $\text{H}_2\text{L}$ ) in aqueous solution. The acidity of function groups participating directly in complex formation is characterized by the constants  $K_b = [\text{B}(\text{OH})_4][\text{H}]/[\text{H}_3\text{BO}_3]$ ,  $K_{a1} = [\text{HL}][\text{H}]/[\text{H}_2\text{L}]$ , and  $K_{a2} = [\text{L}][\text{H}]/[\text{HL}]$ . The relations among these constants is the criterion for dividing the  $\text{H}_2\text{L}$  reagents into 4 groups [1]. Hydroxy acids and peri-diphenols (like disodium 1,8-dihydroxynaphthalene-3,6-disulfonate, that is chromotropic acid) are members of the third group in which  $K_{a1} \gg K_b \gg K_{a2}$ . The acidity of these reagents solutions in the region of the more acid group neutralization ( $\text{H}_2\text{L} \rightarrow \text{HL} + \text{H}$ ) increases in presence of boric acid (reaction (A)). Boric acid coordinates one anion HL in neutral medium and no protons take part in the reaction (B).



Neutralization of boric acid bounded in the complex (reaction (C)) takes place in more alkaline medium than that of free  $\text{H}_3\text{BO}_3$ . This acidity decrease of boric acid solutions in presence of reagents from the third group gives the possibility to determine [2] the equilibrium constants of the reaction (B). Boron chelates with salicylic and chromotropic acid have already been studied in acid aqueous solutions [3, 4]. Similar complex systems in alkaline medium are investigated in the present paper.

H-acid (HR) is disodium salt of 8-amino-1-naphthol-3,6-disulfonic acid, this compound may be obtained by replacement of one phenolic group by the amino group in chromotropic acid. The comparison of boric acid reaction with catechol and *o*-aminophenol, both these reagents form 5-membered chelate rings, indicates [5] small affinity of boron for the nitrogen donor atom; its affinity for the oxygen donor atom is larger. The 6-membered chelate rings with boron are more stable than the 5-membered ones [6]. Therefore comparison of the stability of boron chelates with reagents forming 6-membered chelate rings like chromotropic acid and H-acid can give better information on the affinity of boron for the nitrogen from an amino group.

### Experimental

Boric, salicylic, and sulfosalicylic acids of anal. grade and other chemically pure reagents (all products of Lachema, Brno) were used in the present work. The *o*-phenolcarboxylic acids were recrystallized from ethyl alcohol and their contents were determined by potentiometric neutralization of the carboxylic group with base. Solutions of reagents neutralized to pH 7–8 (NaHL) were added to the solution of boric acid. Ionic strength  $I = 0.1$  was reached by addition of  $\text{KNO}_3$  to the measured solution; the few cases with  $I \neq 0.1$  are mentioned in the text. The concentration of boric acid in the studied solutions was sufficiently low ( $< 0.02 \text{ M}$ ), therefore no oligonuclear borates [4] were formed.

Automatic registration assembly ABU-12, PHM-26, TTT-11, and SBR (Radiometer, Denmark) was used for titration with  $0.1 \text{ M-NaOH}$  at  $293 \pm 1 \text{ K}$ . The electrode response of the glass electrode G-202B used in combination with SCE was checked by evaluation of the titration of strong acid ( $\text{HNO}_3$ ) with strong base ( $\text{NaOH}$ ). The phosphate buffer having pH 6.50 (the electrodes and the buffer made by Radiometer) was used for adjusting the pH-meter before every titration. The values  $\bar{z}$  and  ${}_R\bar{z}$  indicate the average number of  $\text{H}^+$  moles split off per one mole of boric acid and one mole of ligand, respectively, the determination of these values was described elsewhere [7, 4]. Hydrogen ion activity and concentrations of all other components were used in computation of constants.

## Results and discussion

### Reaction of salicylate and its derivatives

The HL anions of salicylate and of its derivatives listed in Table 1 neither split off nor bind protons in aqueous medium at pH 7–10. Reaction (B) takes place in neutral medium and it is the reason why boric acid becomes a weaker acid in presence of salicylate derivatives. The definition of the  $\bar{z}$  function is given in eqn (1). The values of  $\bar{z}$  were evaluated from titration curves, typical titration curves are in Fig. 1.

$$\bar{z} = [\text{B}(\text{OH})_4] / ([\text{H}_3\text{BO}_3] + [\text{B}(\text{OH})_4] + [\text{BL}(\text{OH})_2]) \quad (1)$$

$$\log [\bar{z} / (1 - \bar{z})] = \text{pH} - \text{p}K_b - \log (1 + K[\text{HL}]) \quad (2)$$

Table 1

Experimental conditions and results in the study of *o*-phenolcarboxylic complexes with boron

Reagent	$c_L$ mM	$c_B$ mM	$\text{pH}_{\bar{z}=0.5}$	$\text{tg } \beta$	$\log K$
Salicylate	0	5.6	9.04	0.91	1.23 <sup>a</sup>
	21.9		9.15	0.92	
	43.8		9.26	0.91	
	65.7		9.34	0.95	
	87.7		9.42	0.92	
Sulfosalicylate	0	5.6	9.00	0.91	0.98 <sup>b</sup>
	22.0		9.10	0.91	
	43.0		9.17	0.98	
	65.0		9.22	0.96	
	87.0		9.28	1.00	
1,2-Hydroxynaphthoate	0	3.85	9.00	1.00	1.31
	3.85		9.03	1.00	
	8.65		9.07	1.00	
2,1-Hydroxynaphthoate	0	3.64	9.01	0.98	1.83
	3.64		9.10	0.95	
	8.18		9.20	0.97	
2,3-Hydroxynaphthoate	0	3.85	9.02	0.98	1.29
	3.85		9.05	0.99	
	8.65		9.09	1.00	
<i>p</i> -Aminosalicylate	0	8.0	9.02	0.93	1.31
	20.0		9.17	0.97	
	40.0		9.27	0.98	
	60.0		9.36	0.97	
	80.0		9.45	0.97	

a)  $\log K = 1.38$  evaluated at  $\text{pH} < 7$  in [3]; b)  $I = 0.3$ .

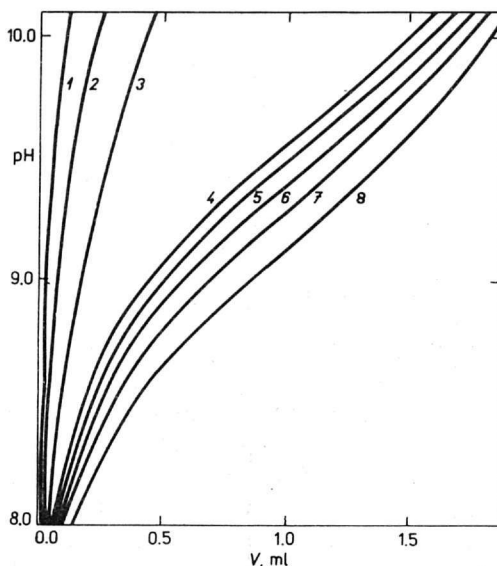


Fig. 1. Titration curve for the system boric acid with chromotropic (1—3) and *p*-aminosalicylic acid (4—8).

$c_B$  (mM): 0 (1); 5 (2, 3); 8 (4—8).  
 $c_L$  (mM): 8 (1, 2); 5 (3); 80 (4); 60 (5); 40 (6); 20 (7); 0 (8).

Experimental values give linear plots  $\log [\bar{z}/(1-\bar{z})] = f(\text{pH})$  at  $[\text{HL}] = \text{const}$  and  $\bar{z} = 0.2-0.8$ . These plots based on eqn (2) have the slopes  $\text{tg } \beta = 1$ , which is typical for neutralization of monobasic acid. The value  $[\text{HL}]$  remains constant either for  $c_L \gg c_B$  ( $c_L$  and  $c_B$  are the total concentrations of ligand and of boron, respectively) or for  $c_L \approx c_B$  only when a small part of boron is converted into the complex. The more complex is formed, the more shifts the titration curve for  $c_L \neq 0$  into alkaline region when compared with a curve for  $c_L = 0$ . It holds  $\bar{z}/(1-\bar{z}) = 1$  at  $\text{pH}_{\bar{z}=0.5}$  and eqn (2) can be transformed into eqn (3)

$$1/[\text{H}]_{\bar{z}=0.5} = (1 + K[\text{HL}])/K_b \quad (3)$$

Experimental values give linear plots  $[\text{H}]_{\bar{z}=0.5} = f([\text{HL}])$  indicating coordination of only one ligand to the central atom. The slope of the last mentioned plots give the  $K$  values listed in Table 1. Eqn (3) means that  $\text{pH}_{\bar{z}=0.5} = \text{p}K_b$  at  $c_L = 0$ . The measurement of  $\text{pH}_{\bar{z}=0.5}$  at  $c_L = 0$  was repeated for every reagent (Table 1), it gives the average  $K_b = 10^{-9.01}$  and corresponding relative standard deviation 1.5%.

#### Reaction of chromotropic acid at $\text{pH} > 7$

The titration curves in Fig. 1 show that the boron chelate with chromotropic acid is much more stable than that with salicylic acid derivative, therefore eqns (1—3)

are no more useful in this study. Concentrations of the particular components were calculated from eqns (4—6) and used for computation of the constant  $K$  by means of eqn (7).

$$[\text{H}_3\text{BO}_3] = \bar{z} c_B [\text{H}] / K_b \quad (4)$$

$$[\text{BL}(\text{OH})_2] = c_B - \bar{z} c_B (1 + [\text{H}] / K_b) \quad (5)$$

$$[\text{HL}] = c_L - [\text{BL}(\text{OH})_2] \quad (6)$$

$$K = [\text{BL}(\text{OH})_2] / [\text{H}_3\text{BO}_3][\text{HL}] \quad (7)$$

The solutions of boric acid and of chromotropic acid trisodium salt (NaHL) having  $\text{pH} > 7$  were mixed for titration. The  $\bar{z}$  values determined in presence of chromotropic acid salt are much smaller than those found at  $c_L = 0$  (Table 2). The  $K$  values in Table 2 have the same order of magnitude as  $K = 10^{3.9}$  determined from measurement in acid solution [4]. The drift in  $K$  values with decreasing acidity of the solution is probably due to the decomposition of reagent taking slowly part in alkaline medium in course of titration. Therefore the  $K$  value from paper [4] is more reliable than these values in Table 2.

Table 2

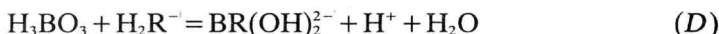
Values  $\bar{z}$  and  $K$  determined in the system boric acid—chromotropic acid at  $\text{pH} 9-10$ ;  $c_B$  5 mM;  $I = 0.2$

$c_L$	0			5 mM		8 mM	
$\text{pH}$	$\bar{z} \cdot 10^2$	$\bar{z} \cdot 10^2$	$K \cdot 10^{-4}$	$\bar{z} \cdot 10^2$	$K \cdot 10^{-4}$	$\bar{z} \cdot 10^2$	$K \cdot 10^{-4}$
9.00	50	8	1.2	2	1.2		
9.09	55	9	1.3	3	1.4		
9.18	60	10	1.4	3	1.6		
9.27	65	11	1.6	3	1.7		
9.36	69	12	1.7	3.5	1.9		
9.45	74	12.5	1.9	4	2.0		
9.54	77	13.5	2.1	4.5	2.2		
9.63	81	14	2.5	5	2.4		
9.72	84	15	2.7	5.5	2.7		
9.81	87	16	3.2	6	3.0		
9.90	89	17	3.7	6.5	3.4		
9.99	91	17.5	4.3	7	3.7		

### Reaction of H-acid

The form  $\text{H}_2\text{R}$  prevails in acid solution of H-acid. The more acid proton from the amino group splits off in weakly acid medium and the phenolic one in weakly

alkaline medium,  $pK'_{a1}$  3.6,  $pK'_{a2}$  7.7 [8]. The interaction of boric acid with H-acid (reaction (D)) is indicated by acidity increase of the ammonium group in presence of boric acid



2.5 mM H-acid solution was titrated at pH 2.9–6.0. The amount of base necessary for neutralization of H-acid is not changed by addition of boric acid. The half neutralization for the reaction  $H_2R \rightarrow HR + H$  is reached at pH 3.52, 3.49, 3.46, and 3.42 when  $c_B$  0, 88, 175, and 263 mM, respectively. The value  $K' = [BR(OH)_2^-]/[H_3BO_3][HR] = 10^{-0.07}$  was evaluated using eqns (8) and (9)

$${}_R\bar{z} = ([BR(OH)_2^-] + [HR])/([BR(OH)_2^-] + [H_2R] + [HR]) \quad (8)$$

$${}_R\bar{z}[H]/(1 - {}_R\bar{z}) = K'_{a1} + K'[H_3BO_3] \quad (9)$$

For the similar boron chelate with chromotropic acid  $K = 10^{3.9}$  was determined. The difference 4 orders of magnitude between these constants indicates a significant decrease in reagent affinity for boric acid when one hydroxyl group is replaced by the amino group.

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