

Fig. 2. Melting point diagram of (—)- α -(3-chloro-2-naphthoxy)propionic acid (I) and (+)- α -(1-chloro-2-naphthoxy)propionic acid (II).

Experimental. — Melting point diagrams. Weighed quantities of the components were dissolved in acetone. After evaporation to dryness the residue was powdered and the melting point determined with a hot stage microscope according to Kofler¹¹.

The author thanks Dr. D. Woodcock for samples of optically active α -(3-chloro-2-naphthoxy) propionic acid.

1. Pope, P. and Woodcock, D. *J. Chem. Soc.* 1955 577.
2. Matell, M. *Ann. Roy. Agr. Coll. Sweden* 20 (1953) 205.

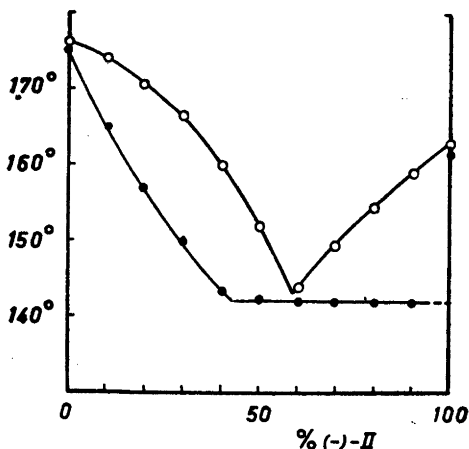


Fig. 3. Melting point diagram of (—)- α -(3-chloro-2-naphthoxy)propionic acid (I) and (—)- α -(1-chloro-2-naphthoxy)propionic acid (II).

3. Matell, M. *Arkiv Kemi* 7 (1954) 437.
4. Matell, M. *Ibid.* 8 (1955) 79.
5. Åberg, B. *Ann. Roy. Agr. Coll. Sweden* 20 (1953) 241.
6. Fredga, A. *The Svedberg 1884 30/8 1944*, Uppsala 1944, p. 261.
7. Matell, M. *Mikrochimie ver. Microchim. Acta* 38 (1951) 532.
8. Timmermans, J. *J. Chim. Phys.* 49 (1952) 162.
9. Matell, M. and Larsson, S. *Arkiv Kemi* 5 (1953) 379.
10. Matell, M. *Ibid.* 6 (1953) 355.
11. Kofler, L., Kofler, A. and Brandstätter, M. *Thermo-Mikro-Methoden*, 3rd Ed. Innsbruck 1954, pp. 4, 17.

Received June 10, 1955.

On the Formation of Boric Acid-Mannitol Complexes

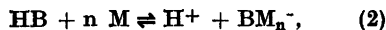
P. J. ANTIKAINEN

Institute of Chemistry, University of Helsinki, Helsinki, Finland

The formation of boric acid-mannitol complexes has been the object of many studies, but only a few quantitative investigations of the reaction in question have been published. The author of this paper has previously studied¹ the influence of mannitol on the ionization of boric acid in aqueous solutions of some alkali salts and shown that the apparent ionization constant K^* of boric acid in dilute boric acid solutions can be expressed in the form:

$$K^* = K \cdot C^n, \quad (1)$$

where C is the stoichiometric concentration of mannitol, n the average number of mannitol molecules which combine with one molecule of boric acid and K the equilibrium constant for the reaction:



where HB and M designate boric acid and mannitol, respectively, and BM_n^- the anion of the acid formed.

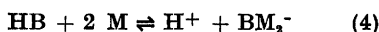
The values of the complex formation constant K obtained by previous workers²⁻⁶ show a considerable variation with varying concentration of mannitol. Most probably one reason for this variation lies in the

fact that the value 2 generally has been used for the constant n , although recent findings indicate that this constant should have a value of about 1.81¹. Using this value for the constant n the complex formation constant K can be calculated according to the author¹ with an average accuracy of 0.01 pK-units at different concentrations of mannitol.

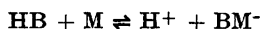
The above-mentioned deviation of the term n from the whole number can be explained by assuming that besides the main complex HBM₂ small quantities of the complex HBM are formed simultaneously. Thus equation (1) can be written in the form:

$$K^* = K_1 \cdot C^a + K_2 \cdot C, \quad (3)$$

where K_1 and K_2 are the equilibrium constants for the reactions:



and



respectively. For the determination of these constants by means of equation (3) it is necessary to know the values for the apparent ionization constants at at least two different concentrations of mannitol. These values can be obtained from equation (1) using the already known values¹ for the constants K and n . Results of calculations are given in Table 1, where C' and C'' designate the two different concentrations of mannitol and K' and K'' the corresponding apparent ionization constants of boric acid. The concentrations C' and C'' have been selected so that the differences between them are as great as possible insuring that the calculations are correct. Furthermore these concentrations are so high that equation (1) is in good agreement with theory¹.

As can be seen from Table 1 the values for the complex formation constant K_2 can be calculated with an average accuracy of 0.02–0.05 pK-units using the above-mentioned method. Thus it is apparent that a complex of the type HBM also exists in solutions of boric acid and mannitol confirming previous statements^{1,3,4}.

For the constant pK₂ the values 5.65 and 6.70 were obtained by Böeseken³ and

Table 1. Determination of the complex formation constants of mannitoboric acid in aqueous potassium chloride solutions at 25° C.

C'	C''	$K' \cdot 10^5$	$K'' \cdot 10^5$	pK ₂	Average
0.3	1.0	0.564	4.975	5.256	
0.3	0.8	0.564	3.320	5.287	$\sqrt{I} = 0.0$
0.5	1.0	1.421	4.975	5.153	pK ₁ = 4.359
0.5	0.8	1.421	3.320	5.182	pK ₂ = 5.218
0.3	1.0	0.837	7.500	5.113	
0.3	0.8	0.837	5.008	5.106	$\sqrt{I} = 0.316$
0.5	1.0	2.100	7.500	5.046	pK ₁ = 4.181
0.5	0.8	2.100	5.008	5.115	pK ₂ = 5.095
0.3	1.0	0.904	8.020	5.062	
0.3	0.8	0.904	5.340	5.093	$\sqrt{I} = 0.632$
0.5	1.0	2.282	8.020	4.956	pK ₁ = 4.149
0.5	0.8	2.282	5.340	4.978	pK ₂ = 5.022
0.3	1.0	0.655	5.803	5.198	
0.3	0.8	0.655	3.870	5.297	$\sqrt{I} = 1.412$
0.5	1.0	1.652	5.803	5.097	pK ₁ = 4.289
0.5	0.8	1.652	3.870	5.137	pK ₂ = 5.128

Deutsch⁸, respectively. The corresponding thermodynamic constant has now been calculated and found to be 5.218 ± 0.05 at 25° C and thus for the thermodynamic constant K_1 the value 4.357 ± 0.02 can be calculated by means of equation (3).

The values for the complex formation constants at different ionic strengths agree with Debye-Hückel's equation from which the values $a = 2.375$ and 2.115 and $B = 0.133$ and 0.108 for the constants K_1 and K_2 can be calculated.

1. Antikainen, P. *Ann. Acad. Sci. Fennicae*, Ser. A II (1954) 56.
2. Böeseken, J. *Ber.* **46** (1913) 2612; *Chem. Zentr.* **314** (1924) 2778.
3. Böeseken, J. and Vermaas, N. *Rec. trav. chim.* **54** (1935) 853.
4. Mehta, S. M. and Kantak, K. V. *J. Am. Chem. Soc.* **74** (1952) 3470.
5. Ross, S. and Catotti, A. J. *Ibid.* **71** (1949) 3563.
6. Schäfer, H. *Z. anorg. allgem. Chem.* **247** (1941) 96.
7. Thung, J. and Chang, H. *J. Chinese Chem. Soc.* **9** (1942) 125.
8. Deutsch, A. and Osoling, S. *J. Am. Chem. Soc.* **71** (1949) 1673.

Received June 10, 1955.