

## Potentiometric and Polarimetric Studies of the Reaction of Boric Acid and Tetrahydroxyborate Ion with Polyhydroxy Compounds

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Received 16th November, 1981

Values of the association constant,  $K_n$ , for the reaction of boric acid with sorbitol, mannitol, D-glucose, glycerol and ethylene glycol have been evaluated from a modified Antikainen equation using values of the dissociation constant,  $K^*$ , obtained by the half-neutralisation method. This procedure gives values of  $K_n$  which are easily compared with each other, and which have trends which are compatible with other previously determined values. Measurements of  $pK^*$  at various temperatures for the complexes of sorbitol and mannitol with boric acid allow estimates to be made of  $\Delta H^*$  and  $\Delta S^*$  for complexation. Polarimetric studies of the sorbitol and mannitol complexes in solution indicate that the tetrahydroxyborate ion,  $B(OH)_4^-$ , is more effectively complexed than boric acid and do not suggest any major differences in complexing ability between sorbitol and mannitol.

The reaction of boric acid and borates with polyhydroxy compounds (polyols) has been known for many years, particularly as a means of increasing the acid strength of boric acid for its analysis by volumetric titration.<sup>1</sup> The relationship between the structural characteristics of the polyol and its influence upon the acidity of boric acid was reviewed by Boiseken<sup>2,3</sup> and it was he who suggested that the formation of boric-acid-polyol complexes occurred in two stages, first the formation of a mono-chelated borate complex, followed by a bichelated complex. It has also been suggested<sup>4-7</sup> that it is the borate ion, rather than boric acid, which is complexed by the polyol. Because the stoichiometry of the complexes is not clearly defined<sup>8-10</sup> discrepancies occur among values derived for the association constants, since assumptions made about the complex stoichiometry lead to varying methods of calculation.<sup>5, 11-13</sup>

In order to compare association constants it has been suggested<sup>8</sup> that the Antikainen<sup>11</sup> equation be used, *i.e.*

$$K^* = K_1 K_n C_2^n + K_1 \quad (1)$$

where  $K^*$  is the measured dissociation constant of the polyol +  $H_3BO_3$  solution,  $K_n$  is the association constant of the complex,  $K_1$  is the dissociation constant of  $H_3BO_3$ ,  $C_2$  is the stoichiometric concentration of all species containing the polyol and  $n$  is the coordination number of the complex. However, for the complexes of mannitol and glucose with boric acid<sup>8</sup> the value of  $K^*$  varied with the extent of dissociation, a mixture of acidic complexes being formed, the composition of which varied as the ratio of undissociated boric acid to borate ions changed. Similar effects are also observed with complexes of mannitol and borate ion.<sup>13</sup> To overcome this problem, Davis and Mott<sup>8</sup> used a modified Antikainen equation (in its logarithmic form)

$$p(K^* - K_1) = -n \log_{10} C_2 + p(K_1 K_n) \quad (2)$$

where  $C_2$  is the total stoichiometric concentration of polyol at half-neutralisation of the acid with NaOH, and  $K^*$  is the dissociation constant of the polyol-boric-acid complex at half-neutralisation.  $pK^*$  was obtained from the pH of the solution using the well-known Henderson-Hasselbalch equation, for which  $pH = pK^*$  at half-neutralisation.

The purpose of this work was to extend the studies made by Davis and Mott<sup>8</sup> to other polyols and also to study the effect of temperature upon  $pK^*$ . In addition, the formation of complexes of mannitol and sorbitol with  $H_3BO_3$  and with tetrahydroxyborate ion have been compared by polarimetric measurements.

## EXPERIMENTAL

### MATERIALS

The materials used and their grades of purity were as follows: boric acid (AR), sodium chloride (AR), sodium hydroxide (AR), D-glucose (AR), glycerol (AR), ethylene glycol (GPR), mannitol (GPR) and sorbitol (GPR). The materials were used without further purification.

### POTENTIOMETRIC TITRATIONS

Solutions of  $0.05 \text{ mol dm}^{-3} H_3BO_3$  in  $0.1 \text{ mol dm}^{-3} NaCl$  were prepared containing a range of concentration of polyol from  $0.01$  to  $0.5 \text{ mol dm}^{-3}$ .  $50 \text{ cm}^3$  aliquots of these solutions were titrated with  $0.1 \text{ mol dm}^{-3} NaOH$ . The pH titration curves were obtained using an EIL (model 7050) expanded-scale pH-meter. This model has a 2 pH-unit expanded-scale facility enabling pH readings to be estimated to 0.005, and includes both automatic and manual temperature compensation and also a fully adjustable isopotential facility. A combined glass/Ag/AgCl electrode was used to measure the pH. The values of  $pK^*$  were interpolated from the pH-titration curves at the half-neutralisation point.

### CHANGE OF $pK^*$ WITH TEMPERATURE

The effect of temperature on  $pK^*$  was studied for the mannitol and sorbitol complexes. Solutions of  $H_3BO_3$  containing various amounts of polyol were prepared and standardised NaOH added to each solution corresponding to the half-neutralisation point. The pH of each solution was measured at 50, 40, 30, 25 and 20 °C, making appropriate adjustments to the temperature and isopotential controls of the pH-meter. The temperatures were maintained at  $\pm 0.5$  °C over a period of *ca.* 2-3 min while the pH was measured.

### POLARIMETRIC MEASUREMENTS

Solutions were made up containing  $0.25 \text{ mol dm}^{-3}$  mannitol plus  $H_3BO_3$  in amounts varying from 0 to  $1.0 \text{ mol dm}^{-3}$ . The optical rotations of the solutions were measured with a Bellingham and Stanley model A photoelectric polarimeter using a 200 mm polarimeter tube. Angular rotations could be estimated to  $0.001^\circ$ . The measurements were made at a wavelength of 435.8 nm using a low-pressure Hg lamp with other wavelengths filtered out by a cobalt glass filter plus a solution of  $NaNO_2$ .<sup>14</sup> This wavelength was used rather than the sodium D-lines since it gave larger differences in angular rotation between successive solutions. The measurements were repeated with the  $H_3BO_3$  neutralised with NaOH to give  $B(OH)_4^-$ , in amounts again varying from 0 to  $1.0 \text{ mol dm}^{-3}$ .

The whole series of polarimetric measurements was then repeated using sorbitol instead of mannitol. Thus the measurements were monitoring the changes in optical rotation of the polyol, with its total stoichiometric concentration kept constant, as it complexed with increasing amounts of added  $H_3BO_3$  or  $B(OH)_4^-$ .

## RESULTS AND DISCUSSION

The pH-titration curves for each solution were plotted and the values of  $pK^*$  at half-neutralisation obtained from these graphs. The curves for sorbitol and ethylene

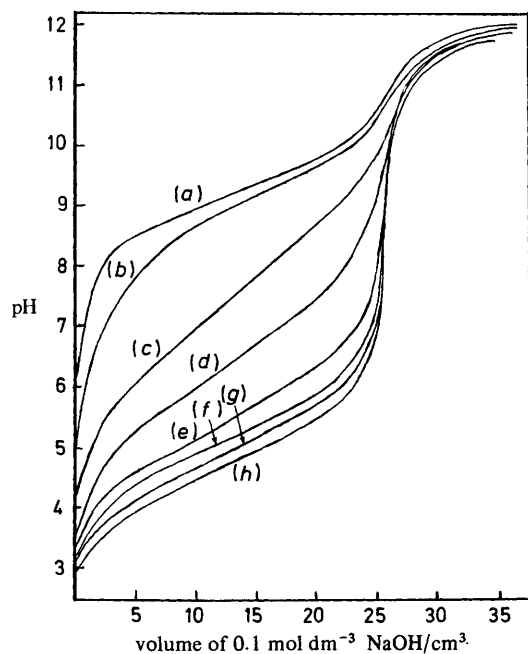


FIG. 1.—Potentiometric titrations of  $0.05 \text{ mol dm}^{-3} \text{ H}_3\text{BO}_3 + x \text{ mol dm}^{-3}$  sorbitol where  $x = (a) 0, (b) 0.01, (c) 0.05, (d) 0.1, (e) 0.2, (f) 0.3, (g) 0.4$  and  $(h) 0.5$ .

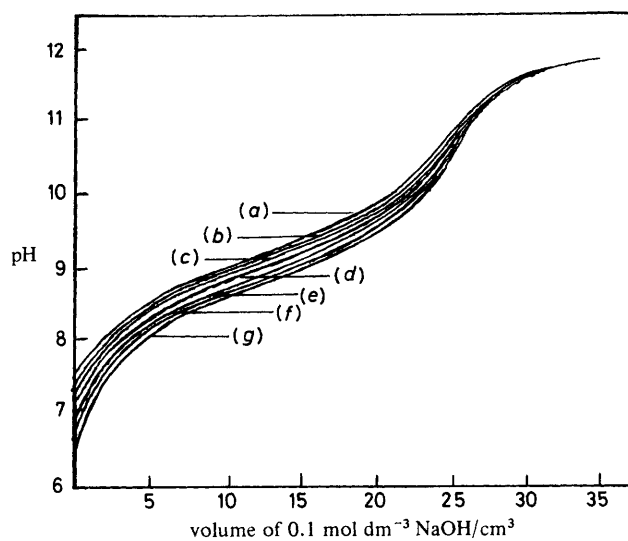
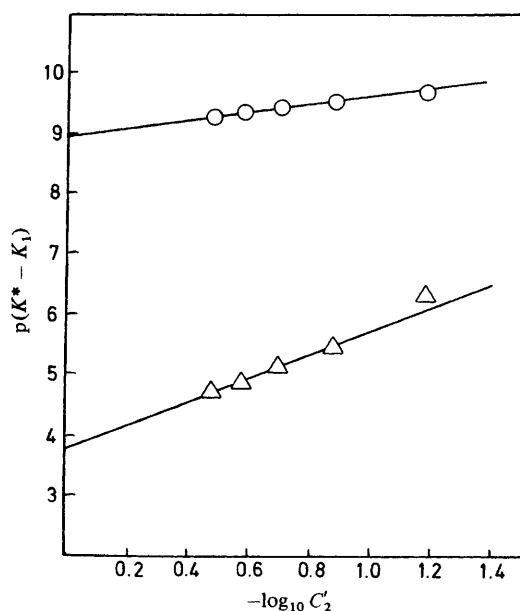


FIG. 2.—Potentiometric titration of  $0.05 \text{ H}_3\text{BO}_3 + x \text{ mol dm}^{-3}$  ethylene glycol where  $x = (a) 0, (b) 0.05, (c) 0.1 (d) 0.2, (e) 0.3, (f) 0.4$  and  $(g) 0.5$ .

TABLE 1.— $pK^*$  VALUES AT HALF-NEUTRALISATION FOR VARIOUS POLYOLS IN BORIC ACID SOLUTIONS

[polyol]/mol dm <sup>-3</sup>	$pK^*$ with polyol				
	sorbitol	mannitol	D-glucose	glycerol	ethylene glycol
0	9.15	9.15	9.15	9.15	9.15
0.01	8.98	9.00	—	—	—
0.05	7.50	7.94	8.60	8.90	—
0.10	6.40	6.88	8.35	8.70	9.04
0.20	5.52	5.99	8.05	8.36	9.00
0.30	5.16	5.58	7.92	8.14	8.97
0.40	4.90	5.22	7.80	8.00	8.94
0.50	4.75	5.05	7.34	7.83	8.90

FIG. 3.—Antikainen plots for  $\circ$ , ethylene glycol and  $\Delta$ , sorbitol.

glycol are shown in fig. 1 and 2. The  $pK_a$  of boric acid ( $pK_1$ ) was found to be 9.15, which is close to other reported values.<sup>8, 15, 16</sup> The  $pK^*$  values obtained for various polyol–boric-acid systems at half-neutralisation are given in table 1.

The modified Antikainen equation [eqn (2)] predicts that graphs of  $p(K^* - K_1)$  against  $\log_{10} C'_2$  should be linear;  $n$ , the coordination number, is obtained as the slope, and  $p(K_1 - K_n)$  is obtained as the intercept, from which  $K_n$  can be evaluated. Linear plots were in fact obtained when the polyol concentration was greater than *ca.* 0.1 mol dm<sup>-3</sup>, *i.e.* when the polyol concentration is high relative to that of the H<sub>3</sub>BO<sub>3</sub>, and for which eqn (2) is valid. The graphs for sorbitol and ethylene glycol are shown in fig. 3. The data derived from the Antikainen plots are summarised in table 2.

TABLE 2.—RESULTS FROM ANTIKAINEN PLOTS [EQN (2)]

complexant	slope, ( <i>n</i> )	intercept, $p(K_1K_n)$	$pK_n$	$K_n$	other values of $K_n$
sorbitol	1.95	3.80	-5.35	$2.24 \times 10^5$	—
mannitol	2.27	3.99	-5.16	$1.45 \times 10^5$	$1.38 \times 10^{5a}$ $1 \times 10^4$ and $8.24 \times 10^{4b}$
D-glucose	1.03	7.24	-1.91	81.3	$186^a$ 188 and $574^b$ 8 and $770^c$
glycerol	1.25	7.32	-1.83	67.6	$36.4$ and $81.3^b$ $16.0$ and $41.2^c$
ethylene glycol	0.67	8.98	-0.17	1.48	$1.85$ and $0.1^c$

<sup>a</sup> Ref. (8); <sup>b</sup> ref. (11); <sup>c</sup> ref. (5).

TABLE 3.— $pK^*$  FOR  $H_3BO_3$  + SORBITOL AT VARIOUS TEMPERATURES

<i>T</i> /°C	$pK^*$ at [sorbitol]/mol dm <sup>-3</sup>				
	0	0.05	0.1	0.2	0.5
50	8.86	7.50	6.54	5.76	4.98
40	8.94	7.44	6.44	5.65	4.85
30	9.04	7.35	6.28	5.50	4.70
25	9.09	7.28	6.18	5.38	4.58
20	9.15				

The values of *n* when glucose, glycerol and ethylene glycol were used as complexants correspond to the formation of a 1:1 complex with boric acid. For sorbitol and mannitol, however, *n* is *ca.* 2, indicating the formation of a bichelated complex. The values of the association constants ( $K_n$ ) for the various complexants, evaluated from the Antikainen equation, are compared in table 2. There is broad agreement between the values of  $K_n$  evaluated by this method and those determined by other methods for which certain association equilibria are assumed. However, the Antikainen method, based upon the  $pK^*$  at half-neutralisation,<sup>8</sup> allows a comparison to be made between various complexants without assumptions having to be made concerning the association equilibria. The value of  $K_n$  for sorbitol is only slightly larger than that for mannitol, indicating that there is not a major difference in the complexing abilities of these two polyols for boric acid. The values of  $K_n$  for the other polyols studied (table 2) are considerably lower than those for sorbitol and mannitol and follow trends similar to those found in other studies.<sup>5, 8, 11</sup>

The values of  $pK^*$  at various temperatures and at various concentrations of sorbitol and mannitol are given in tables 3 and 4. It can easily be shown from the van't Hoff isochore that

$$pK^* = \Delta H^*/2.303 RT + \text{constant.}$$

Thus the enthalpy of ionisation of the polyol- $H_3BO_3$  complex,  $\Delta H^*$ , can be obtained from a graph of  $pK^*$  against  $1/T$ . The values of  $\Delta H^*$  obtained in this way are plotted

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