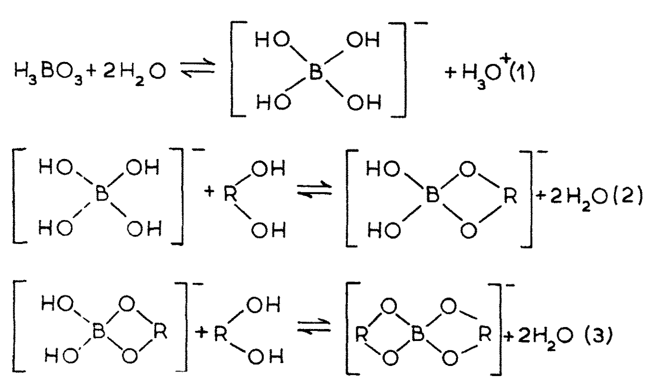
# The pH Dependence of the Boron-11 Chemical-shift of Borate–Boric Acid Solutions

M. J. HOW,* G. R. KENNEDY, and E. F. MOONEY

*(Department of Chemistry, The University, P.O. Box 363, Birmingham 15)*

OUR interest in the formation of anionic complexes by neutral polyhydroxy-compounds, such as carbohydrates, in alkaline borate prompted investigations of direct methods for studying the structure and stability of such complexes in solution by $^{11}B$ and $^{1}H$ n.m.r. Complex formation depends upon the pH of the electrolyte and the structure of the polyhydroxy-compound.[1] The structure of such complexes involving sugars has been inferred[1,2] from studies of the electrophoretic mobilities of derivatives of the sugars in which hydroxy-groups were selectively substituted *e.g.* by methylation.

The following equilibria between borate ions and polyhydroxy-compounds have been suggested.[3]



The pH dependence of (1) determines the concentration of the complexed forms of the polyhydroxy-compound $R(OH)_2$ as indicated by (2) and (3). This was investigated for aqueous solutions (50 g.l.$^{-1}$) of sodium tetraborate, pH 2—12, at 33° by measurement of the $^{11}B$ chemical shift at 12·83 Mc./sec., with the dimethyl ether–boron trifluoride complex as external standard. The results (Figure) show that the chemical shift at high pH corresponds to that of the tetrahedral $B(OH)_4^-$ ion[4] and, at low pH, to that of boric acid. Only one $^{11}B$ resonance signal is observed, indicative of a rapidly interconverting equilibrium. The measured chemical-shift corresponds to a mean of those of $H_3BO_3$ and $B(OH)_4^-$ weighted according to their relative concentrations. The extreme sensitivity of equilibrium (1) to pH in the region 7—10 confirms that complex formation is pH dependent. p*K* Values at 33° for equilibrium (1), calculated from the $^{11}B$ n.m.r. data presented are summarised in the Table. From electrochemical data Owen and King[5]

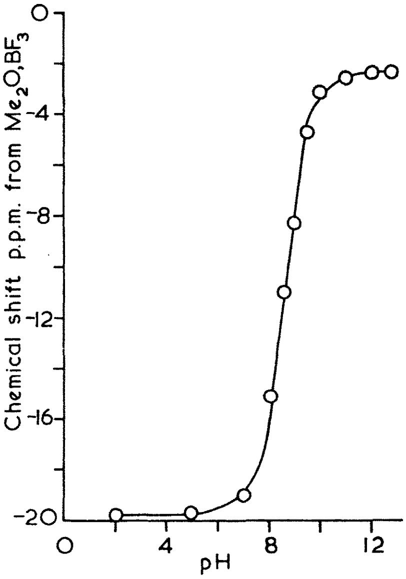


FIGURE. pH *Dependence of* $^{11}B$ *chemical shift of borate–boric acid solutions.*

*The effect of* pH *on the equilibrium constant of equilibrium* (*I*)

| $\delta^{11}B$[a] | pH | $[B(OH)_4^-]/[H_3BO_3]$ | $K \times 10^{-9}$ (g. ion l.$^{-1}$) | p$K$ |
|---|---|---|---|---|
| − 3·15 | 10·0 | 19·0 | 1·90 | 8·72 |
| − 4·70 | 9·5 | 6·40 | 2·02 | 8·69 |
| − 8·3 | 9·0 | 1·93 | 1·93 | 8·71 |
| −12·0 | 8·5 | 0·807 | 2·55 | 8·59 |
| −15·8 | 8·0 | 0·298 | 2·98 | 8·52 |
| −18·1 | 7·5 | 0·108 | 3·42 | 8·46 |
| −18·8 | 7·0 | 0·045 | 4·50 | 8·35 |

[a] Minus sign indicates to low field of $Me_2O, BF_3$.

calculated p$K$ values of 8·850 and 8·814, respectively, for equilibrium (1) in 0·36M-sodium chloride, at 30 and 35°, and showed that p$K$ values decreased on increasing the sodium chloride concentration. The apparent dependence of p$K$ on pH (Table) probably reflects the increased chloride ion concentration which results from addition of hydrochloric acid to aqueous solutions of sodium tetraborate to produce solutions of pH $< 9·5$.

(*Received, January* 15*th*, 1969; *Com.* 050.)

---

[1] A. B. Foster, *Adv. Carbohydrate Chem.*, 1957, **12**, 81.
[2] H. Bouveng and B. Lindberg, *Acta Chem. Scand.*, 1956, **10**, 1283.
[3] J. Boeseken, *Rec. Trav. chim.*, 1942, **6**, 82; H. S. Isbell, J. F. Brewster, N. B. Holt, and H. L. Frush, *J. Res. Nat. Bur. Stand.*, 1948, **40**, 129.
[4] T. P. Onak, H. Landesman, R. E. Williams, and I. Shapiro, *J. Phys. Chem.*, 1959, **63**, 1533.
[5] B. B. Owen and E. J. King, *J. Amer. Chem. Soc.*, 1943, **65**, 1612.