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STUDIES ON BORATE ESTERS I

THE pH DEPENDENCE OF THE STABILITY OF ESTERS OF BORIC ACID AND BORATE IN AQUEOUS MEDIUM AS STUDIED BY ^{11}B NMR

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ABSTRACT - The pH dependent stability of esters of boric acid and borate with glycol, glycolic acid, oxalic acid and glyceric acid as dihydroxy compounds has been studied. ^{11}B NMR provides a suitable analytical tool for the quantitative determination and structure elucidation of the various esters in aqueous medium. The pH dependent stability of esters of boric acid and borate is formulated in a general rule of thumb: esters of boric acid and borate with dihydroxy compounds in aqueous medium show the highest stability at that pH where the sum of the charges of the free esterifying species is equal to the charge of the ester.

Esters of boric acid and borate have found widespread use as a tool in configurational analysis, for instance of carbohydrates,[1] and in a variety of separation and chromatography techniques.[2] This class of compounds has been studied for more than a century,[3] using several analytical techniques.[4] The possible equilibria between boric acid, borate and the corresponding esters are summarized in Fig. 1. Boric acid (B^o) is a Lewis acid and can bind a hydroxyl ion forming the borate anion (B^-). Both boric acid and borate can react with a suitable dihydroxy compound (L), resulting in the boric acid ester (B^oL) and the borate monoester (B^-L), respectively. Subsequently, these two esters can react with another dihydroxy compound to give the borate diester (B^-L_2).

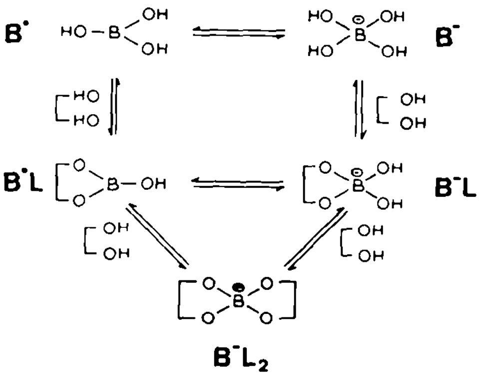

Fig. 1. Equilibria between boric acid, borate and dihydroxy compounds in aqueous medium.

Throughout this paper a distinction between esters of boric acid and of borate is made by the use of B^o and B^-, respectively. The indices "o" and "-" do not always stand for the actual charge of the ester but denote the charge of the BO_3 or BO_4 moiety. As dihydroxy compounds diols, hydroxycarboxylic acids and dicarboxylic acids are possible. The corresponding esters possess structures as shown in Fig. 2.

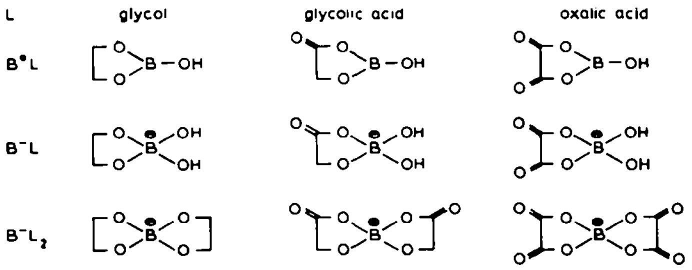

Fig. 2. Esters of boric acid and borate for glycol, glycolic acid and oxalic acid.

The association constants for the various equilibria involved are defined as follows:

$$B^0 + OH^- \rightleftarrows B^- \qquad K^{B^0}_{B^-} = [B^-]/[B^0]*[OH^-] = 8.5*10^4 \qquad (I)^5$$

$$B^0 + L \rightleftarrows B^0L + 2\ H_2O \qquad K^{B^0}_{B^0L} = [B^0L]/[B^0]*[L] \qquad (II)$$

$$B^- + L \rightleftarrows B^-L + 2\ H_2O \qquad K^{B^-}_{B^-L} = [B^-L]/[B^-]*[L] \qquad (III)$$

$$B^-L + L \rightleftarrows B^-L_2 + 2\ H_2O \qquad K^{B^-L}_{B^-L_2} = [B^-L_2]/[B^-L]*[L] \qquad (IV)$$

Boric acid and boric acid esters are neutral compounds. In the crystalline phase the central boron atom is surrounded by three oxygen atoms in an almost planar fashion with O-B-O angles of about 118°.[6] In aqueous solutions, however, we propose these compounds to form an adduct with one water molecule. The central boron atom is then surrounded by four oxygen atoms but the system still remains without charge. The central boron atom in borate and borate esters is coordinated by four oxygen atoms. The geometry is tetrahedral because the O-B-O angles are circa 109°.[6] Borate and borate esters are negatively charged.

Boric acid and boric acid-like structures are considered to be the reactive species in the esterification due to the ease of substitution of the relative loosely bound water molecule by a dihydroxy compound in comparison with substitution of a hydroxyl ion in borate or borate-like structures. The mechanism of the formation of esters of boric acid and borate proposed by Kustin and Pizer[7] is given more extensively in Fig. 3. The rate of exchange between boric acid and borate is very fast and diffusion controlled.[8,9] At low pH it only consists of proton transfer and at high pH of hydroxyl transfer. All the other steps involving proton transfer are assumed to be fast too. The nucleophilic substitution reactions are relatively slow. The bound water molecule is displaced and a new B-O bond is formed. At the moment it cannot be decided what the kinetic order of the nucleophilic substitution reaction is. As a result of the chelate effect the subsequent ring closure is relatively fast in comparison with the attack of a free dihydroxy compound at a reactive boric acid-like species. Thus the latter steps are considered to be the rate determining steps in the formation of esters of boric acid and borate. The equilibria between B^- and B^-L and between B^-L and B^-L_2 as given in Fig. 1 are therefore not realistic from a kinetical point of view but can be defined thermodynamically.

Some 30 papers have dealt with the stability of esters of boric acid and borate. The influence of the pH on the stability, however, has not been studied systematically. In addition, most of the techniques used (such as potentiometry and polarimetry) give no direct information concerning the identity of the esters involved.

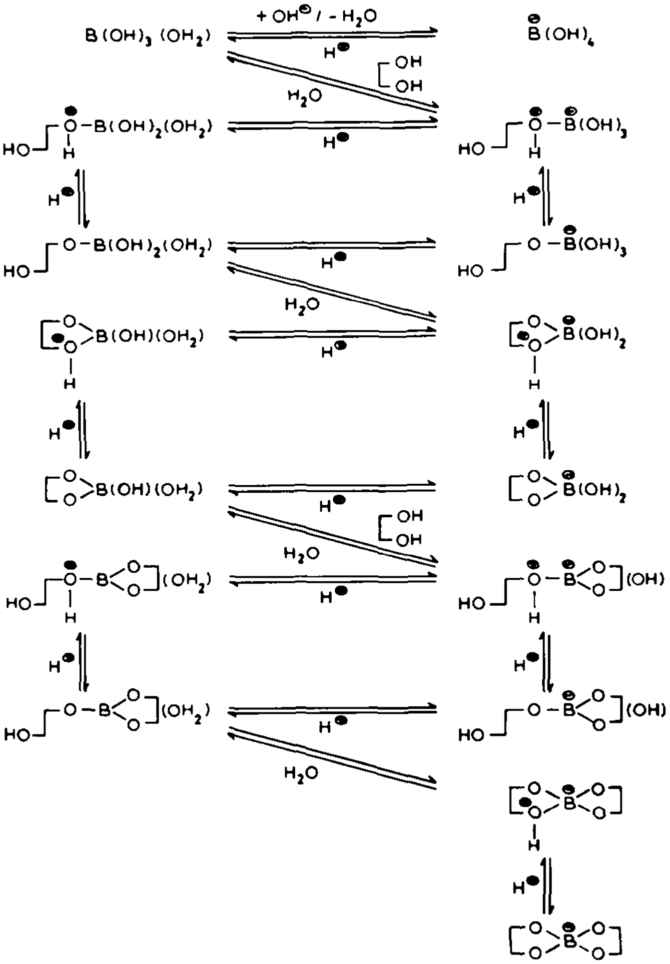

Fig. 3. Mechanism of formation of esters of boric acid and borate.

In our laboratory several multinuclear NMR techniques are applied to study cation complexation phenomena of (poly)hydroxy(poly)carboxylic acids[10] and of combinations of these acids with borate. B NMR was therefore an obvious choice in the study of esters of boric acid and borate, especially because this technique provides direct information concerning ester formation. Table 1 gives some important physical data of the two boron isotopes, ^{10}B and ^{11}B, which are both NMR sensitive.

Table 1. Physical data for ^{10}B and ^{11}B nuclei.[11]

Nucleus	^{10}B	^{11}B
Spin	3	3/2
Resonance frequency at 4.60 T (MHz)	21.06	64.16
Natural abundance (%)	18.83	81.17
Relative sensitivity at constant field for equal number of nuclei (^1H - 1.00)	$1.88*10^{-2}$	0.165
Relative sensitivity in one molar aqueous solution (^1H - 1.00)	$3.5*10^{-3}$	0.12
Electric quadrupole moment (10^{-28} m^2)	0.111	0.0355

^{11}B NMR is more suitable than ^{10}B NMR for two reasons. Firstly, the NMR sensitivity in a one molar solution for ^{11}B is approximately 40 times larger than that for ^{10}B. This is due to the difference in natural abundance and to the NMR sensitivity for an equal number of nuclei. Secondly, the resolution in ^{11}B NMR spectra is better. This is a result of the higher resonance frequency of ^{11}B NMR and of the smaller quadrupole moment of ^{11}B which rules the linewidth.

Until now ^{11}B NMR was mostly used in the studies of boranes, carboranes, heterocyclic (N, O, P) boron compounds and metallo derivatives in organic solvents.[11,12] ^{11}B NMR studies of compounds with boron coordinated only by oxygen atoms are scarce and have been usually performed in organic solvents. ^{11}B NMR was used to study the equilibria between boric acid, borate and several polyborate species in water, especially with respect to the dependence of total boron concentration, pH,[13,14,15] and the presence of metal ions.[16,17] In dilute solutions only one average signal was observable and therefore the exchange of boric acid ($\delta = 0.0$ ppm) and borate ($\delta = -17.6$ ppm) is fast on the ^{11}B NMR time scale. Furthermore, it was shown that polyborate formation occurs only at total boron concentrations above 0.2 mole/l. Henderson et al.[18] were the first to use ^{11}B NMR for identifying borate esters of diols in water. These results were applied in the carbohydrate field.[19] Borate ester formation and hydrolysis was found to be slow on the ^{11}B NMR time scale. Chemical shifts for borate mono- and diesters of 1,2- and 1,3-diols were measured. The determined association constants showed good correspondence with values obtained by other techniques.[18]

In this paper a ^{11}B NMR study is presented dealing with the influence of pH on the stability of esters of boric acid and borate in aqueous solution. As dihydroxy compounds a 1,2-diol (glycol), an α-hydroxycarboxylic acid (glycolic acid), a dicarboxylic acid (oxalic acid) and a compound combining a 1,2-diol and an α-hydroxycarboxylic acid function (glyceric acid = 2,3-dihydroxypropanoic acid) are used. A general rule for determining pH dependent concentration optima of esters of boric acid and borate will be put forward.

RESULTS AND DISCUSSION

In Figs. 4, 5, 6, and 7 the influence of the pH on the concentration of the different boron compounds is given for L = glycol,[20] glycolic acid, oxalic acid and glyceric acid, respectively. The points were determined experimentally with ^{11}B NMR while the curves are calculated from the association constants obtained (except for L = glyceric acid). Chemical shifts ($\delta_{B^o} = 0.0$ ppm) are given in Table 2. The association constants (Table 3) were calculated using equations (I)-(IV) together with the pKa's of the dihydroxy compounds and the following material balance equations:

$$C_B = [B^o] + [B^-] + [B^oL] + [B^-L] + [B^-L_2] \quad (V)$$

$$C_L = [L] + [B^oL] + [B^-L] + 2\,[B^-L_2] \quad (VI)$$

Glycol

For L = glycol (Fig. 4) only one signal is observed for pH < 8. This signal shows an upfield shift upon an increase of pH and is assigned to the equilibrium between B^o and B^- which is fast on the ^{11}B NMR time scale. At pH > 8 two new signals are observed which are assigned to B^-L and B^-L_2. Thus the exchange between B^- and B^-L and between B^-L and B^-L_2 is slow on the ^{11}B NMR time scale. A further increase of pH above 11 has no effect on the concentrations of B^-L and B^-L_2.

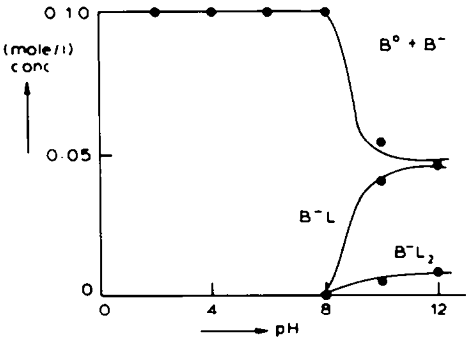

Fig. 4. Glycol (L; 1.0 M) and boric acid/borate (B^o/B^-; 0.1 M): distribution of species as function of pH.

These phenomena can be explained by rewriting the equilibria from Fig. 1 as

$$B^o + L \rightleftharpoons B^-L + H^+ + H_2O$$
$$B^o + 2\ L \rightleftharpoons B^-L_2 + H^+ + 3\ H_2O$$

B^-L and B^-L_2 are formed at high pH which means in practice that B^- is present in solution. Consequently borate esters of glycol can only be expected in the region where pH > pK_a(boric acid) (9.07); experimentally pH > 8 is found. At pH = 11, $[B^-] \approx C_B$ and a further increase of pH has no effect on $[B^-]$. Therefore, $[B^-L]$ and $[B^-L_2]$ reach maxima.

The presence of B^oL could not be demonstrated. When this ester does exist $K^{B^o}_{B^oL}$ should be small or $\delta_{B^oL} \approx 0$ ppm. In the latter case the experimental signal at $\delta = 0.0$ ppm has to be attributed to the equilibrium between B^o and B^oL (fast exchange on the ^{11}B NMR time scale). Paŝl,[21] however, has shown that the former explanation is correct: $K^{B^o}_{B^oL} \approx 0$.

Glycolic acid

When L = glycolic acid the pH dependence is quite different (Fig. 5). At low pH a single signal is observed with a chemical shift between +0.4 and 0.0 ppm. It is assigned to the equilibrium between B^o and B^oL which is fast on the ^{11}B NMR time scale. Rise of pH results in a second signal, attributed to B^-L_2 with a maximal intensity at pH = 3. A third signal appears for B^-L with a maximal intensity at pH 7. A further increase of pH results in the disappearance of the B^-L and B^-L_2 signals and only the signal for B^- remains. The difference in pH dependence for L = glycolic acid in comparison with L = glycol is due to the easy deprotonation of the former compound.

$$L \rightleftharpoons L^- + H^+ \qquad pK_a(\text{glycolic acid}) = 3{,}82.$$[22]

The amount of B^oL will be large when $[B^o]$ and $[L]$ are large, therefore at pH < pKa(glycolic acid). When both $[L]$ and $[L^-]$ are large, formation of B^-L_2 according to

$$B^o + L + L^- \rightleftharpoons B^-L_2 + 3\ H_2O$$

will be optimal. At pH = pK_a (glycolic acid), where $[L] = [L^-]$, a maximum in $[B^-L_2]$ is reached. In principle B^-L can be formed either from B^o and L^- or from B^- and L. The latter possibility, however, can be excluded because pK_a(glycolic acid) < pK_a(boric acid). This means that B^-L exists when L^- is present, i.e. upon dissociation of glycolic acid:

$$B^o + L^- \rightleftharpoons B^-L + H_2O$$

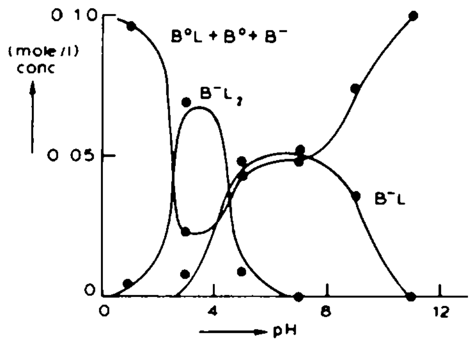

Fig. 5. Glycolic acid (L; 1.0 M) and boric acid/borate (B^0/B^-; 0.1 M): distribution of species as function of pH.

When the pH reaches pK_a (boric acid) $[B^-]$ increases. The equilibrium for B^-L then may be rewritten as

$$B^- + L^- \rightleftharpoons B^-L + OH^- + H_2O$$

It is obvious that an increase of the pH causes dissociation of B^-L. In other words, the pH optimum for B^-L is attained when pK_a(glycolic acid) < pH < pK_a(boric acid). Our experimental results fully agree with this picture.

As was stated above the difference in pH dependence of the stabilities of the borate esters of glycol and glycolic acid can be understood by their difference in pK_a (~ 14 and 3.82, respectively). This is in agreement with the results of Sienkiewicz and Roberts,[23] who studied the influence of pH on the phenylboronate ester stability of 4,5-dihydroxynaphthalene-2,7-disulfonic acid and 2,3-dihydroxynaphthalene-6-sulfonic acid. Boronate ester formation with these aromatic diols shows also optima, viz. at pH = 6-7 and 8-9, which are close to the corresponding pK_a values (5.45 and 8.12, respectively).

Oxalic acid

When L = oxalic acid (Fig. 6) only one signal could be observed besides the signal for the equilibrium between B^0 and B^-. This signal is attributed to B^-L. A maximum for $[B^-L]$ has to be found at the pH where $[L^-]$ and $[B^0]$ are maximal

$$B^0 + L^- \rightleftharpoons B^-L + H_2O$$

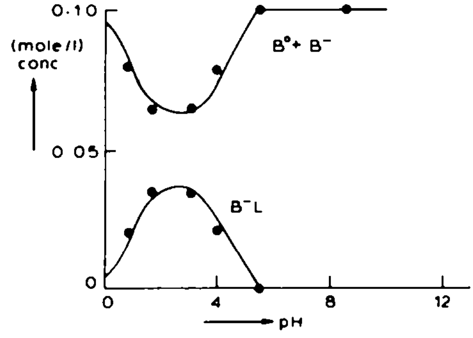

Fig. 6. Oxalic acid (L; 0.25 M) and boric acid/borate (B^0/B^-; 0.1 M): distribution of species as function of pH.

Since oxalic acid is a dicarboxylic acid ($pK_1 = 1.23$; $pK_2 = 4.19^{22}$) the pH optimum for B^-L has to be $pH = (pK_1 + pK_2)/2 = 2.7$. This value is close to the experimental maximum for $[B^-L]$ at pH = 3. ^{11}B NMR gave no indication for the occurrence of B^-L_2 which would be expected at $pH = pK_1$. Therefore only the upper limit for $K^{B^-L}_{B^-L_2}$ could be calculated. Again B^0L could not be detected either.

Glyceric acid

Although glyceric acid is the simplest molecule in which 1,2-diol and α-hydroxycarboxylic acid functions are combined, its picture for ester formation as a function of pH is rather complicated as shown in Fig. 7. Here two types of ester formation are possible as depicted in Fig. 8, which generally holds for polyhydroxy(poly)carboxylic acids.

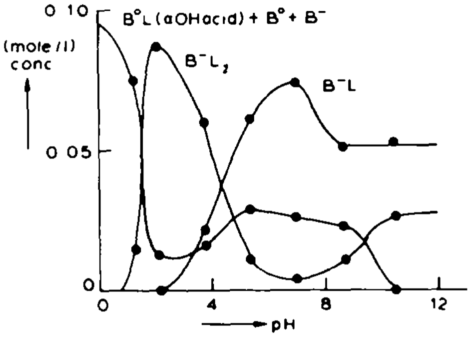

Fig. 7. Glyceric acid (L; 1.0 M) and boric acid/borate (B^0/B^-; 0.1 M): distribution of species as function of pH.

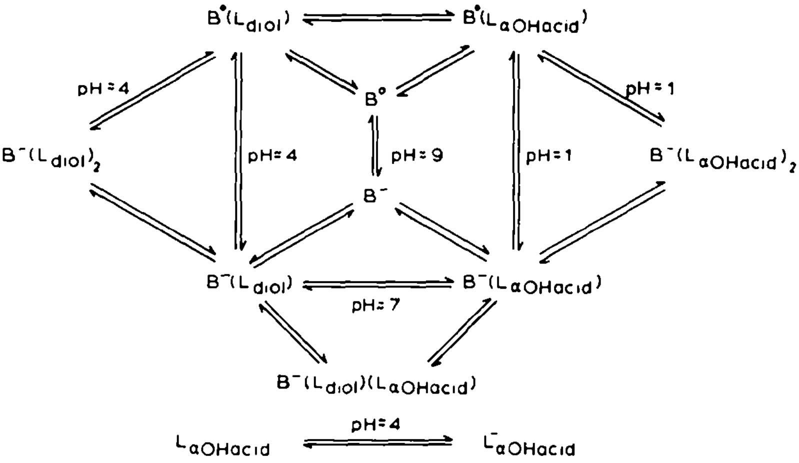

Fig. 8. Equilibria between boric acid, borate, glyceric acid and glycerate in aqueous solution.

The notations L_{diol} and $L_{\alpha OHacid}$ indicate the way glyceric acid is esterified, viz. as a 1,2-diol or as an α-hydroxycarboxylic acid. At low pH an average signal for the equilibrium between B^0 and B^0L is observed. Since $K^{B^0}_{B^0L}$ for L = glycol is smaller than that for L = glycolic acid, glyceric acid will be bound as an α-hydroxycarboxylic acid in B^0L. Between pH 1 and 8 glyceric acid behaves like glycolic acid and signals for $B^-(L_{\alpha OHacid})$ and $B^-(L_{\alpha OHacid})_2$ are observed. Maximal concentrations of these two species are found at pH = 2 and 6, respectively. A further increase of pH reduces the stability of the borate esters of the α-hydroxycarboxylic acid type but enhances the stability of the borate esters of the diol type. A new signal for

$B^-(L^-_{diol})_2$ appears while the chemical shift of B^-L changes slightly, probably as a result of a shift from $B^-(L_{\alpha OHacid})$ to $B^-(L^-_{diol})$. As was observed for L = glycol an increase of pH above 11 has no effect on $[B^-(L^-_{diol})]$ and $[B^-(L^-_{diol})_2]$.

Chemical shifts

With the aid of Table 2 it is obvious that each type of ester of boric acid and borate is characterized by a chemical shift range, viz. $\delta(B^0L) = +1$ to 0 ppm, $\delta(B^-L) = -11.5$ to -14.5 ppm and $\delta(B^-L_2) = -8$ to -10.5 ppm. For B^-L and B^-L_2 (L = diol) this was already reported by Henderson et al.[18] The chemical shifts of B^-L and B^-L_2 reported by these authors for L = glycol ($\delta = -13.4$ and -9.6 ppm, respectively) agree well with our values. The variation of chemical shifts within the given ranges can be explained using increments as will be shown in a forthcoming paper. Other chemical shift data of borate esters reported in the literature belong to acyclic borate esters ($B(OR)_4$: R = Me, ϕ; $\delta = -15.6$ to -16.3 ppm)[11] and cannot be used for comparison with our data. Chemical shifts of boric acid esters are only known for acyclic species ($B(OR)_3$: R = alkyl, ϕ; $\delta = 0.5$ to -3.3 ppm) and for boric acid esters with the residual hydroxyl group substituted by an alkoxy group ($\delta = +4.3$ to 0.8 ppm).[24] Our experimental shifts of +0.4 ppm are in the same range.

Table 2. ^{11}B chemical shifts[a] of esters of boric acid and borate

L	glycol	glycolic acid	oxalic acid	glyceric acid	
				αOHacid	diol
B^0L		+0.4[b]		+0.4[b]	
B^-L	-13.8	-11.9	-14.4	-12.8	-13.1
B^-L_2	-10.0	-8.4		-9.4	-8.7

[a] Relative to 0.1 M boric acid as external standard; D_2O; 20 °C.

[b] Estimated.

Association constants

The association constants as obtained from Fig. 4-7 are shown in Table 3. Boric acid esters proved to be more stable for L = α-hydroxycarboxylic acid than for L = diol, dicarboxylic acid. This is in agreement with results found in the literature (L = polyol,[21] L = α-hydroxycarboxylic acid[25]). Perhaps electronic effects and ring strain play a role. The association constants $K^{B^-}_{B^-L}$ and $K^{B^-L}_{B^-L_2}$ (L = glycol) agree with values obtained already by other workers using ^{11}B NMR or other techniques.[18] The association constants for L = glyceric acid bound as a diol, are larger than those for L = glycol as is to be expected from an extrapolation of published association constants of substituted glycols such as 1,2-propanediol,[18] 3-methoxy-1,2-propanediol[26] and 1-chloro-2,3-propanediol[27] ($K^{B^-}_{B^-L} = 2$–20; $K^{B^-L}_{B^-L_2} = 0.5$–2.5). $K^{B^-}_{B^-L}$ for L = carboxylic acid can be rewritten more realistically as

$$K^{B^0}_{B^-L} = [B^-L]/[B^0]*[L^-] = K^{B^-}_{B^-L} * K_a(\text{boric acid})/K_a(\text{carboxylic acid}) \qquad \text{(VII)}$$

according to the actual equilibrium:

$$B^0 + L^- \rightleftharpoons B^-L + H_2O$$

Table 3. Association constants of esters of boric acid and borate[a]

L	glycol	glycolic acid	oxalic acid[b]	glyceric acid	
				αOHacid	diol
$K^{B^0}_{B^0 L}$		1.0		~ 1	
$K^{B^-}_{B^- L}$	1.0	$1.4*10^5$	$1.7*10^8$	~ 10^5	6.2
$K^{B^- L}_{B^- L_2}$	0.16	20	< 0.5	~ 25	0.62
$K^{B^0}_{B^- L}$		1.2	2.9	~ 1	

[a] D_2O; 20 °C; $C_B = 0.1$ M; $C_L = 1.0$ M; I = 3.0.
[b] $C_L = 0.25$ M.

Values of $K^{B^0}_{B^0 L}$ calculated in this way are also included in Table 3. A comparison of $K^{B^0}_{B^0 L}$ with $K^{B^0}_{B^- L}$ (L = α-hydroxycarboxylic acid) shows that the affinity of boric acid is equal for L and L^-. A comparison with literature data[7,25,28] indicates that our $K^{B^0}_{B^- L}$ values are circa 10 times smaller. The literature method used, potentiometry, provides less direct information and thus one cannot be sure that the supposed number and type of compounds in the system is correct. The fact that $K^{B^- L}_{B^- L_2}$ for L = diol is smaller than for L = α-hydroxycarboxylic acid is also found by others (L = diol,[18] L = α-hydroxycarboxylic acid[28]) and is probably based on electronic effects.

"Charge Rule" for Predicting Optimal pH Stability

On the basis of the present results the following general rule of thumb may be formulated:

Esters of boric acid and borate in aqueous medium show the highest stability at that pH where the sum of the charges of the free esterifying species is equal to the charge of the ester

This "charge rule" will be illustrated below by some examples.
Esters of boric acid are most stable at low pH where dissociation of both B^0 and L hardly occurs:

$$B^0 + L \rightleftarrows B^0L + 2\ H_2O$$

Dissociation of boric acid favours formation of borate esters of 1,2-diols, i.e. a rather high pH (pH > pK_a (boric acid)) is required:

$$B^- + n\ L \rightleftarrows B^-L_n + 2\ n\ H_2O$$

With borate ester formation of α-hydroxycarboxylic acids and dicarboxylic acids pH dependent optima are involved. The borate diester of an α-hydroxycarboxylic acid shows maximal stability at pH = $pK_a(L)$ where the acid and its anion are present in equal amounts and boric acid is in its neutral form:

$$B^0 + L + L^- \rightleftarrows B^-L_2 + 3\ H_2O$$

The borate monoester, however, occurs preferentially at $pK_a(L) < pH < pK_a(B^0)$ where the carboxylic acid is ionized and boric acid is merely in its neutral form:

$$B^0 + L^- \rightleftharpoons B^-L + H_2O$$

A similar situation occurs with dicarboxylic acids at pH = $(pK_{a1} + pK_{a2})/2$. Finally, the pH dependent stability of borate esters of polyhydroxycarboxylic acids can be understood by combining the rules for diols and α-hydroxycarboxylic acids. Thus when the pH reaches $pK_a(B^0)$ borate esters of the α-hydroxycarboxylic acid type convert into borate esters of the diol type. With the aid of this "charge rule" it is possible to predict the species present in solution at a certain pH and one can avoid misinterpretations of the experimental results, especially in the case of polyhydroxy(poly)carboxylic acids.

EXPERIMENTAL

All ^{11}B NMR spectra were recorded at room temperature on a Nicolet NT-200 WB spectrometer at 64.19 MHz with a 0.1 M boric acid solution as external reference. The conditions for the four experiments were equal, viz. the total boron concentration C_B = 0.1 M, the total concentration of the dihydroxy compound C_L = 1.0 M (except for oxalic acid where C_L = 0.25 M) and the ionic strength I = 3.0 (NaCl). The samples were prepared by dissolution of the appropriate amounts of boric acid and organic compounds in D_2O. The pH was adjusted with 40% NaOD in D_2O (Merck) and measured with a calibrated MI 412 micro-combination pH probe from Microelectrodes, Inc. The total volume of each sample was 5 ml. Boric acid, glycol and oxalic acid were obtained from Baker and glycolic acid from Merck. Glyceric acid was obtained by ion exchange of calcium glycerate (Janssen Chimica) using Biorad AG 50W-X8 ion exchanger followed by freeze drying. The amount of crystal and absorbed water was determined by ^1H NMR.

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REFERENCES

1. J. Böeseken, Adv. Carbohydr. Chem. 4, 189 (1949).
2. R.J. Ferrier, Adv. Carbohydr. Chem. Biochem. 35, 31 (1978).
3. L. Vignon, Compt. Rend. 78, 148 (1874).
4. U. Weser, Struct. Bonding (Berlin) 2, 160 (1967).
5. R. Montgomery, Adv. Chem. Ser. 117, 197 (1973).
6. O-B-O angles are mean values calculated using crystal structures from the Cambridge Data File (until medio 1983); O-B-O angles range from 109° to 123° for boric acid esters and from 98° to 119° for borate esters.
7. K. Kustin and R. Pizer, J. Am. Chem. Soc. 91, 317 (1969).
8. W.R. Gilkerson, J. Chem. Phys. 27 (4), 914 (1957).
9. T. Yasunaga, N. Tatsumoto, and M. Miura, J. Chem. Phys. 43, 2735 (1965).
10. J.A. Peters and A.P.G. Kieboom, Recl. Trav. Chim. Pays-Bas 102, 381 (1983).
11. H. Nöth and B. Wrackmeyer, NMR Basic Princ. Prog. 14 (1978).
12. A.R. Siedle, Annu. Rep. NMR Spectrosc. 12, 177 (1982).
13. A.K. Covington and K.E. Newman, J. Inorg. Nucl. Chem. 35, 3257 (1973).
14. T.P. Onak, H. Landesman, R.E. Williams, and I. Shapiro, J. Phys. Chem. 63, 1533 (1959).
15. M.J. How, G.R. Kennedy, and E.F. Mooney, J. Chem. Soc., Chem. Commun. 267 (1969).
16. R.K. Momii and N.H. Nachtrieb, Inorg. Chem. 6, 1189 (1967).
17. H.D. Smith and R.J. Wiersema, Inorg. Chem. 11, 1152 (1972).
18. W.G. Henderson, M.J. How, G.R. Kennedy, and E.F. Mooney, Carbohydr. Res. 28, 1 (1973).
19. G.R. Kennedy and M.J. How, Carbohydr. Res. 28, 13 (1973).
20. Experimental data for L = glycol, pH > 6 are unpublished results from Mr. M. Makkee of this laboratory.
21. T.L. Paál, Acta Chim. Acad. Scient. Hung. 103, 181 (1980).

22. Handbook of Chemistry and Physics, CRC Press, West Palm Beach 52nd edn. (1972).

23. P.A. Sienkiewicz and D.C. Roberts, J. Inorg. Nucl. Chem. 42, 1559 (1980).

24. W.G. Henderson and E.F. Mooney, Annu. Rev. NMR Spectrosc. 2, 219 (1969).

25. V. Frei and A. Solcova, Coll. Czech. Chem. Commun. 30, 961 (1965).

26. G.L. Roy, A.L. Laferrieve, and J.D. Edwards, J. Inorg. Nucl. Chem. 4, 106 (1957).

27. T.L. Paál, Magyar Kemiai Folyoirat 34, 12 (1978).

28. N. Vermaas, Thesis, Delft University of Technology (1931).