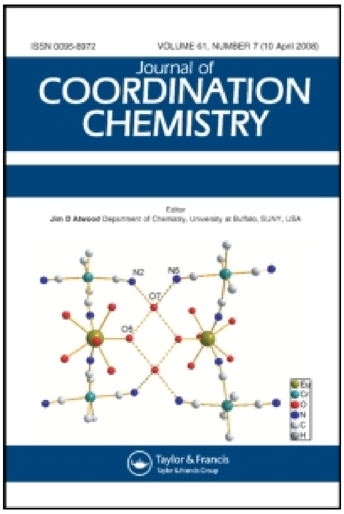

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REVIEW: UNIDENTATE COMPLEXES INVOLVING BORATE

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REVIEW

UNIDENTATE COMPLEXES INVOLVING BORATE

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Unidentate complexes of borate in aqueous solution may be anionic, cationic or neutral species. Stability constants published for each type of complex are reviewed. In addition, stability constants, log $K_{M,B}$, for monoboratolithium and monoboratopotassium complexes, 25°C, are calculated to be 0.64 and -0.18, respectively. Estimated values of stability constants (log $K_{M,B}$) for the monoborato-complexes for lead(II) (2.5), zinc(II) (2.3), cadmium(II) (1.6), aluminium(III) (4.5), cobalt(II) (1.2), nickel(II) (1.6), copper(II) (4.1) and iron(III) (5.5) are calculated from solubility data. It is shown that a linear free energy relationship exists between the dissociation constant of the ligand, pK_x, and the formation constant, log β_x of the unidentate complex involving boric acid and the ligand, *i.e.*, log β_x = (0.55 ± 0.04) pK_x-(2.71 ± 0.47) at 25°C. This relationship is independent of the charge on the ligand and is applicable to all unidentate borate complexes, including monoborato-complexes of metal ions.

KEYWORDS: boric acid, complexes, metal ions, anions, stability constants

INTRODUCTION

Complexation of boron (either as boric acid or the borate anion) in aqueous solution has been the subject of many studies. However, these have largely been confined to the two particular aspects, polydentate complexation of boron by polyhydroxy organic ligands and polyborate formation. An area which has received far less attention is where borate is involved in the formation of unidentate complexes. This includes both the formation of monoborato-complexes of metal ions and complexation of boric acid by anions of weak acids. Examples of both forms of unidentate complexation are known through their effects on rates of reaction,[1] the pK_a of boric acid,[2] and the solubilities of metal borates.[3]

Boric acid is a Lewis acid. It forms unidentate complexes with electron-donating ligands. The boron atom of the resulting complex will be coordinated by a trigonal pyramid structure involving three hydroxo groups and the ligand. The structure of this complex suggests that any interaction between the hydroxo groups and the unidentate ligand will be insignificant. This means that the boron atom in boric acid exhibits behaviour towards the ligand which is analogous to that of the hydrogen ion. In fact, a comparison of the formation constants for complexes involving boric acid and monovalent anions of weak acids and the corresponding dissociation constants of the acids showed a linear relationship.[1,4] Although this relationship has been applied only to complexes involving monovalent anionic ligands, it is possible that similar linear relationships will exist for groups of ligands with a different charge, including cationic ligands. It is the purpose of this paper to review the relevant data published on the stabilities of these complexes and to examine whether such linear relationships exist.

BORATE COMPLEXES WITH ANIONS

Boric acid is electron-deficient and is attracted to lone-pair electrons on anionic ligands, X^{m-}. Unidentate complex formation may be represented by equation(*1*), where { } represents activity.

$$B(OH)_3 + X^{m-} \leftrightarrow B(OH)_3X^{m-};\ \beta_x = \{B(OH)_3X^{m-}\}/\{B(OH)_3\}\{X^{m-}\} \qquad (1)$$

Equation (*1*) is analogous to the behaviour of the hydrogen ion with respect to interacting with the anion (equation *2*).

$$H^+ + X^{m-} \leftrightarrow HX^{(m-1)-};\ K_x = \{H^+\}\{X^-\}/\{HX^{(m-1)-}\} \qquad (2)$$

It should be noted that complex formation could be equally as well have been described in terms of equation (3), which describes the reaction in terms of the protonated ligand and the borate ion.

$$HX^{(m-1)-} + B(OH)_4^- \leftrightarrow B(OH)_3X^{m-} + H_2O;$$
$$B_x{}^* = \{B(OH)_3X^{m-}\}/\{HX^{(m-1)-}\}\{B(OH)_4^-\} \qquad (3)$$

However, expressing the reaction in this form would preclude direct comparison with the behaviour of the hydrogen ion (equation *2*).

The acid dissociation constants for a number of anions and the formation constants for the corresponding borate complexes, at 25°C, are summarised in Table 1. The data involving monovalent anions (m = 1) were those used to derive the linear free energy relationship reported above.

Unfortunately, the formation constant for only one divalent borate complex (m = 2) has been reported. The acid dissociation constant for this, the phthalate

Table 1 The acid dissociation constant (K_X) for acid, $HX^{(n-1)-}$, and the formation constant (β_X) for the unidentate borate complex, $B(OH)_3X^{n-}$, at 25°C.

Anion(X)	pK_X	log β_X	Reference
OH^-	15.74	4.76	1
OOH^-	11.65	3.73	1
OBr^-	8.66	1.26	1
OCl^-	7.54	0.56	1
CH_3COO^-	4.76	-0.43	4
F^-	3.17	-0.30	1
NO_2^-	3.15	-0.49	4
$C_6H_4(COOH)COO^-$	2.95	(-1.0)[a]	4
$C_6H_4(COO)_2{}^{2-}$	5.39	-0.07	4

[a] Data for hydrogenphthalatoborate complex is an approximation only and not used in the calculation of the free energy relationship.

anion, and the formation constant for the phthalatoborate complex are also given in Table 1. Interestingly, these data would be satisfied by the same free energy expression as that for the monovalent complexes. This fact suggests that the charge on the anion may not have a significant affect on the free energy relationship.

BORATE COMPLEXES WITH CATIONS AND NEUTRAL SPECIES

The formation of monoborato-complexes of metal ions may be represented by equation (*4*).

$$M^{n+} + B(OH)_4^- \leftrightarrow MB(OH)_4^{(n-1)+};\ K_{M,B} = \{MB(OH)_4^{(n-1)+}\}/\{M^{n+}\}\{B(OH)_4^-\} \quad (4)$$

Equation (*4*) is similar to equation (*3*) in that both $HX^{(m-1)-}$ and M^{n+} can be regarded as acting as ligands towards the borate ion. Since equation (*3*) can be rewritten in terms of equation (*1*), then equation (*4*) may be also rewritten in terms of complexation involving boric acid and the ligand, $MOH^{(n-1)+}$, and represented by equations (*5–7*).

$$M^{n+} + H_2O \leftrightarrow H^+ + MOH^{(n-1)+};\ K_x = \{H^+\}\{MOH^{(n-1)+}\}/\{M^{n+}\} \quad (5)$$

$$H^+ + B(OH)_4^- \leftrightarrow B(OH)_3 + H_2O;\ K_a = \{H^+\}\{B(OH)_4^-\}/\{B(OH)_3\} \quad (6)$$

$$MOH^{(n-1)+} + B(OH)_3 \leftrightarrow MB(OH)_4^{(n-1)+};$$
$$\beta_X = \{MB(OH)_4^{(n-1)+}\}/\{B(OH)_3\}\{MOH^{(n-1)+}\} \quad (7)$$

Expanding equation (*4*) in this manner means that the hydrated metal ion is represented as behaving like a weak acid, with the hydroxo-metal complex acting as the base. Therefore, equation(5) may be taken to be the equivalent of the reverse of equation(2). The value of K_x can be calculated from equation (*8*) using the stability constant for the hydroxo-metal complex, $K_{M,OH}$, and the dissociation constant of water, K_W.

$$pK_X = pK_W - \log K_{M,OH} \quad (8)$$

Values of $K_{M,OH}$ for most metal ions are well-characterised and may readily obtained from the literature.[5]

If the hydroxo-metal complex is taken to be the base then it would be expected to act as a ligand and to complex boric acid and equation(*7*) will be the equivalent of equation (*1*). Therefore, the formation constant for the borate complex, β_x may be calculated from equation (*9*) using $K_{M,B}$, K_a, and K_X.

$$\log \beta_X = \log K_{M,B} - pK_a + pK_X \quad (9)$$

Stability Constants for Known Monoborato-Complexes

Measurements of stability constants for monoborato-complexes of metal ions have been largely restricted to Group I and II metals. These measurements have arisen from attempts to model the dissociation constant of boric acid in solutions containing high concentrations of metal salts, such as sea-water. Values have been determined through measuring the effect of metal salts on the pK_a of a boric acid solution[6,7] or through effects on the pH of a borate solution.[8]

The stability constant for the monoborato-silver(I) complex has also been measured. This was determined by titrating a silver nitrate solution with boric acid and measuring the change in silver ion concentration with an ion selective electrode[9].

The stability constants, $K_{M,OH}$ and $K_{M,B}$, were used to calculate the acid dissociation constant of each metal ion and the corresponding formation constant of the monoborato-complex. These values are summarised in Table 2.

Calculated Stability Constants for Monoboratolithium and Monoboratopotassium Complexes

The stability constants for both monoboratolithium and monoboratopotassium complexes were calculated from the reported changes to the apparent dissociation constant for boric acid, $K_{a,M}*$, in solutions containing high concentrations of alkali metal salts.[2] The apparent dissociation constant is represented by equation (*10*), where [ ] represents concentration.

$$K_{a,M}* = \{H^+\}(\{B(OH)_4^-\} + [MB(OH)_4^0]) / [B(OH)_3] \qquad (10)$$

A comparison of $K_{a,M}*$ for a solution containing a metal ion, M^+, with that of a solution containing the same cocentration of sodium ions enables the stability constant, $K_{M,B}$, to be calculated as the ratio of $K_{Na,B}$ (equation *11*).

$$\frac{K_{a,M}*}{K_{a,Na}*} = \frac{\{B(OH)_4^-\} + [MB(OH)_4^0]}{\{B(OH)_4^-\} + [NaB(OH)_4^0]} = \frac{1 + K_{M,B}\gamma_1[M^+]}{1 + K_{Na,B}\gamma_1[Na^+]} \qquad (11)$$

The activity coefficients for neutral species were assumed to be unity. Those for monovalent anions, γ_1, were calculated from the ionic strength using the Davies equation (equation *12*).

$$\log \gamma_1 = -0.511\,[\sqrt{I}/(1 + \sqrt{I}) - 0.3I)] \qquad (12)$$

The apparent dissociation constants (pK_a) for boric acid, at 25°C, in 0.68 mol kg^{-1} solutions of sodium chloride and potassium chloride were found to be 8.853 and 8.996, respectively.[8] The specific gravity for both solutions was taken to be 1.03 kg L^{-1}.[10] The value of log $K_{Na,B}$ was 0.22. (see Table 2). The value for log $K_{K,B}$ was calculated to be − 0.18.

Table 2 Calculated values for the acid dissociation constant (K_X) for the hydrated metal ion, M^{n+}, and the formation constant (β_X) for the unidentate monoborato-metal complex, $MB(OH)_4^{(n-1)+}$, at 25°C.

Base (MOH)	log $K_{M,OH}$[a]	log $K_{M,B}$	pK_X	log β_X	Reference
$NaOH^0$	-0.2	0.22	14.2	5.2	7
$MgOH^+$	2.6	1.62	11.42	3.8	7
$CaOH^+$	1.3	1.80	12.7	5.3	7
$SrOH^+$	0.8	1.55	13.2	5.5	7
$BaOH^+$	0.6	1.49	13.4	5.7	7
$AgOH^0$	2.0	0.65[b]	12.0	3.5	9
$LiOH^0$	0.36	0.64	13.6	5.0	
KOH^0	-0.5	-0.18	14.5	5.1	

[a] Stability constants for $MOH^{(n-1)+}$ obtained from reference 5. [b] Calculated from log $K_{Ag,B}$ = 0.45 at I = 3.

It was reported from another study that the apparent dissociation constants for boric acid, at 25°C, in 2 mol L^{-1} solutions of lithium chloride, sodium chloride and potassium chloride were 5.0×10^{-9}, 2.2×10^{-9} and 0.9×10^{-9} mol L^{-1}, respectively.[2] A similar calculation using equation (*11*) gave the values of log $K_{Li,B}$ and log $K_{K,B}$ as 0.64 and -0.41, respectively. The small discrepancy between the value of log $K_{K,B}$ and that calculated above probably reflects the fact that the constant is small and the uncertainties involved in calculation of activity coefficients are relatively large. For this reason, the former value, which was measured at a lower potassium ion concentration, was taken to be more accurate.

The relative values of $K_{Li,B}$, $K_{Na,B}$ and $K_{K,B}$ reflect the fact that charge density on the lithium ion is largest and, as a consequence, it forms the most stable complex with the borate ion. Potassium will have the smallest charge density and will form the weakest complex. The formation constants for these complexes and the acid dissociation constants for the hydrated metal ions are summarised in Table 2.

Estimated Stability Constants for Monoborato-Complexes from Solubility Data

It was possible to obtain values for the stability constants of monoborato-complexes of a number of metal ions using solubility data reported by Shchigol'. This included solubility data for the borate salts of lead(II),[11] zinc(II) and cadmium(II),[12] aluminium(III),[13] cobalt(II) and nickel(II)[14] and copper(II).[15] The data were obtained by equilibrating metal borate salts with acid solutions or by precipitating metal borates and measuring the metal and borate contents of the resulting solutions. This allowed values for the solubility products to be calculated for a range of conditions. Variations in the value of each solubility product were taken to be the result of borato-metal complex formation.

Unfortunately, these systems were studied at 22.5°C. Although this temperature was close enough to allow comparison with systems at 25°C, the values calculated from this data were regarded as estimates only.

The solubility products of these metal borates were poorly defined. This necessitated estimating the value of each solubility product. This was achieved for a metal borate by calculating the apparent solubility product for each individual set of data and taking the value of the true solubility product to be slightly smaller than the lowest calculated value. Fortunately, calculations showed that the choice of solubility product made only a small difference to the value of the stability constant obtained for the borato-complex. Therefore, this approach was considered acceptable.

The data selected for these calculations had to meet the following criteria. First the solutions had to be of sufficient acidity to ensure that the concentration of $MOH^{(n-1)+}$ was small enough to be neglected in a calculation. Secondly, the total borate concentration was below 0.05 mol L^{-1} and the pH below 7 to preclude the possibility of significant polyborate formation[16]. It was also assumed that $MB(OH)_4^{(n-1)+}$ would be the predominant complex in solution.

The stability constant for each monoborato-complex was calculated in the following manner. The concentrations of total dissolved borate, T_B, and total dissolved metal, T_M, may be represented by equations (*13–14*).

$$T_B = [MB(OH)_4^{(n-1)+}] + [B(OH)_3] \qquad (13)$$

$$T_M = [MB(OH)_4^{(n-1)+}] + [M^{n+}] \qquad (14)$$

The pH of the solutions in which these experiments were caried out was low enough to ensure that the concentration of $B(OH)_4^-$ could be neglected.

The solubility product, K_S, for the metal borate may be calculated from equation (*15*).

$$K_s = \{M^{n+}\}\{B(OH)_4^-\}^n = K_a^n\{M^{n+}\}[B(OH)_3]^n / \{H^+\}^n \qquad (15)$$

Combining Equations (*13*), (*14*) and (*15*) gives equation (*16*).

$$T_B-[MB(OH)_4^{(n-1)+}] = \left[\frac{K_S\{H^+\}^n}{K_a^n\gamma_2(T_M-[MB(OH)_4^{(n-1)+}])}\right]^{1/n} \qquad (16)$$

Given that the concentration of the monoborato-complex must be in the range defined by equation (*17*), then the value for the concentration of $MB(OH)_4^{(n-1)+}$, which satisfies equation (*16*), may be readily computed.

$$0 \leq [MB(OH)_4^{(n-1)+}] \leq T_B \text{ and } \leq T_M \qquad (17)$$

The ionic strength was calculated from equation (*18*) and the activity coefficient for monovalent ions calculated from the Davies equation (equation *12*). The activity coefficients for divalent and trivalent ions were calculated by the extended Debye-Hückel equation, the parameters for which were given by Garrels and Christ.[17] These activity coefficients were included in the solution to equation (*16*).

$$I = 0.5(n^2[M^{n+}] + (n-1)^2[MB(OH)_4^{(n-1)+}] + [Na^+] + [NO_3^-] + [B(OH)_4^-]) \qquad (18)$$

In cases where the pH of the solutions were not specified then the hydrogen ion concentration was calculated from the sum of the charges (equation *19*).

$$n[M^{n+}] + (n-1)[MB(OH)_4^{(n-1)+}] + [Na^+] + [H^+] = [NO_3^-] + [B(OH)_4^-] + [OH^-] \qquad (19)$$

Combining equations (*6*), (*14*) and (*19*) gave the quadratic equation (*20*). Obtaining the roots of this quadratic equation enabled the hydrogen ion concentration to be calculated. This term could then be included in the solution of equation (*16*).

$$[H^+]^2 + ([M^{n+}] + (n-1)T_M + [Na^+] - [NO_3^-])[H^+] - \left[\frac{K_a[B(OH)_3] + K_W}{\gamma_1^2}\right] = 0 \qquad (20)$$

The solution of equation (*16*) enabled the concentrations of $B(OH)_3$, $MB(OH)_4^{(n-1)+}$, M^{n+}, and H^+ to be derived plus the relevant activity coefficients. These values allowed the stability constant of the monoborato-metal complex to be calculated using equation (*21*) which was derived from equations (*4*) and (*6*).

$$K_{M,B} = [H^+][MB(OH)_4^{(n-1)+}]\gamma_1\gamma_{n-1}/K_a[M^{n+}][B(OH)_3]\gamma_n \qquad (21)$$

The results of such a calculation are given in Table 3, where values for $K_{Pb,B}$ were calculated for a number of solutions. The solubility product was taken to be 5×10^{-13} mol^2 L^{-2}. This is smaller than the solubility product calculated by Shchigol'.[11] However, that calculation failed to take account of the effect of either $PbB(OH)_4^+$ or $Pb(OH)^+$ formation, thus giving rise to an over-estimation of the value of the solubility product.

Table 3 Estimated values for the stability constant ($K_{Pb,B}$) for the PbBOH)$_4^+$ complex, from the total concentration of dissolved lead (T_{Pb}) and dissolved boron (T_B) (solubility product of $Pb[B(OH)_4]_2$ taken to be 5×10^{-13} mol^2 L^{-2}).

T_{Pb} (10^{-2} mol L^{-1})	T_B (10^{-2} mol L^{-1})	$[PbB(OH)_4^+]$ (10^{-2} mol L^{-1})	pH	log $K_{Pb,B}$
0.21	2.14	0.12	6.44	1.8
0.46	2.17	0.14	6.24	2.0
0.85	2.25	0.23	6.14	2.4
1.55	2.47	0.45	5.96	2.9
2.39	3.00	0.98	6.20	3.0
2.96	3.08	1.06	6.32	2.5
				log $K_{Pb,B}$ = 2.5 ± 0.5

Shchigol' attempted to calculate log $K_{Pb,B}$ and derived the value of 5.2.[11] This was significantly larger than the value of 2.5 ± 0.5 obtained by the present calculation. However, an examination of Shchigol's calculation showed that it failed to take account of the redistribution of borate species in solution resulting from complex formation. This led to the calculation of a value more than two orders of magnitude too large.

Calculations similar to that for lead were performed for a number of metal-borate systems. Estimated values for the solubility products for the metal borates and calculated stability constants for monoborato-complexes are summarised in Table 4.

The standard deviation for the stability constant for each monoborato-complex is relatively large. This is probably a reflection of variation in the composition of the solid phase which caused a variation in the value of the solubility product and led to some uncertainty in the calculation of the stability constant. It was noted from the dissolution experiments that the ratio of the concentration of the total dissolved metal ion to that of the total dissolved boron varied in a manner which was inconsistent with the dissolution of a single solid phase. This suggested that the composition of the solid phase was being modified by the solution.

Shchigol' also calculated log $K_{Al,B}$ to be 7.5.[13] This value was obtained by examining the impact of the Al(III) ion on a solution containing Fe(III) ions and borate. $K_{Al,B}$ was calculated as a ratio of $K_{Fe,B}$. However, for reasons described below, the value obtained for $K_{Fe,B}$ was three orders of magnitude too large and, as a consequence, the value obtained for $K_{Al,B}$ was a significant over-estimation of the true value of 4.5 ± 0.4.

Values for the acid dissociation constant of each hydrated metal ion and the

Table 4 Estimated values for the solubility products of metal borates (K_s) and the corresponding stability constants (log $K_{M,B}$) for monoborato-complexes.

Metal Ion (M)	Solid Phase	Estimated K_s	log $K_{M,B}$	Source of Data
Pb^{2+}	$Pb[B(OH)_4]_2$	5×10^{-13}	2.5 ± 0.5	11
Zn^{2+}	$Zn[B(OH)_4]_2$	1×10^{-11}	2.3 ± 0.3	12
Cd^{2+}	$Cd[B(OH)_4]_2$	2×10^{-10}	1.6 ± 0.5	12
Al^{3+}	$Al[B(OH)_4]_3$	2×10^{-23}	4.5 ± 0.4	13
Co^{2+}	$Co[B(OH)_4]_2$	1×10^{-9}	1.2 ± 0.3	14
Ni^{2+}	$Ni[B(OH)_4]_2$	2×10^{-10}	1.6 ± 0.3	14
Cu^{2+}	$Cu[OH][B(OH)_4]$	5×10^{-19}	4.1 ± 0.5	15

stability constant of the $MB(OH)_4^{(n-1)+}$ complex were calculated from the values given in Table 4 and are summarised in Table 5.

Estimated Stability Constant for Monoborato-Iron(III) Complex

Shchigol' attempted to measure log $K_{Fe,B}$ by means of a spectroscopic method which yielded a value of 8.6.[18] The experiment involved adding boric acid solution to a solution of $Fe(NO_3)_3$ and measuring the optical density of the resulting solution using photometer with a green filter. However, the boric acid solution contained a high concentration of ammonium oxalate which itself formed a complex with the Fe(III) ion.[18] In addition, no account was taken of possible complex formation between boric acid and the oxalate anion. It was shown in the same paper that the stability constant (log K) for the oxalato-iron(III) complex, which was also measured by the same technique, was 8.4. The similarity of this value with that calculated for the monoborato-iron(III) complex suggests that oxalate may have interfered with the measurement of $K_{Fe,B}$.

This conclusion is further supported by the fact that it was reported that when $Fe(NO_3)_3$ was added to a borate solution which was free of oxalate, there was an initial increase in optical density.[13] This contrasts with the decrease in optical density brought about by adding a mixture of boric acid and ammonium oxalate to an $Fe(NO_3)_3$ solution.[18]

The value of $K_{Fe,B}$ can be estimated. Shchigol' examined mixtures of borate, $Fe(NO_3)_3$ and $Al(NO_3)_3$, which were free of oxalate, and determined that $K_{Fe,B}$ was greater than $K_{Al,B}$ by a factor of 12^{13}. Using the estimated value for $K_{Al,B}$, given in Table 4, log $K_{Fe,B}$ was calculated to be 5.5.

The acid dissociation constant of the Fe(III) ion and the formation constant for the monoborato-iron complex was calculated from this value and is given in Table 5.

LINEAR FREE ENERGY RELATIONSHIPS

Figure 1 shows a plot of formation constants for unidentate boron complexes (log β_x) and acid dissociation constants for the ligand (pK_x) using the data in Tables 1, 2 and 5. This shows that a single linear relationship appears to satisfy all data. Excluding the less reliable results given in Table 5 and for hydrogenphthalate, the

Table 5 Estimated values for the acid dissociation constant (K_x) for the hydrated metal ion, M^{n+}, and the formation constant (β_X) for the unidentate monoborato-metal complex, $(MB(OH)_4^{(n-1)+}$.

Base (MOH)	log $K_{M,OH}$[a]	log $K_{M,B}$	pK_X	log β_X
$PbOH^+$	6.3	2.5	7.7	1.0
$ZnOH^+$	5.0	2.3	9.0	2.1
$CdOH^+$	3.9	1.6	10.1	2.4
$AlOH^{2+}$	9.0	4.4	5.0	0.2
$CoOH^+$	4.3	1.2	9.7	1.7
$NiOH^+$	4.1	1.6	9.9	2.3
$CuOH^+$	6.3	4.1	7.7	2.6
$FeOH^{2+}$	11.8	5.5	2.2	-1.5

[a] Stability constants for $MOH^{(n-1)+}$ obtained from reference 5.

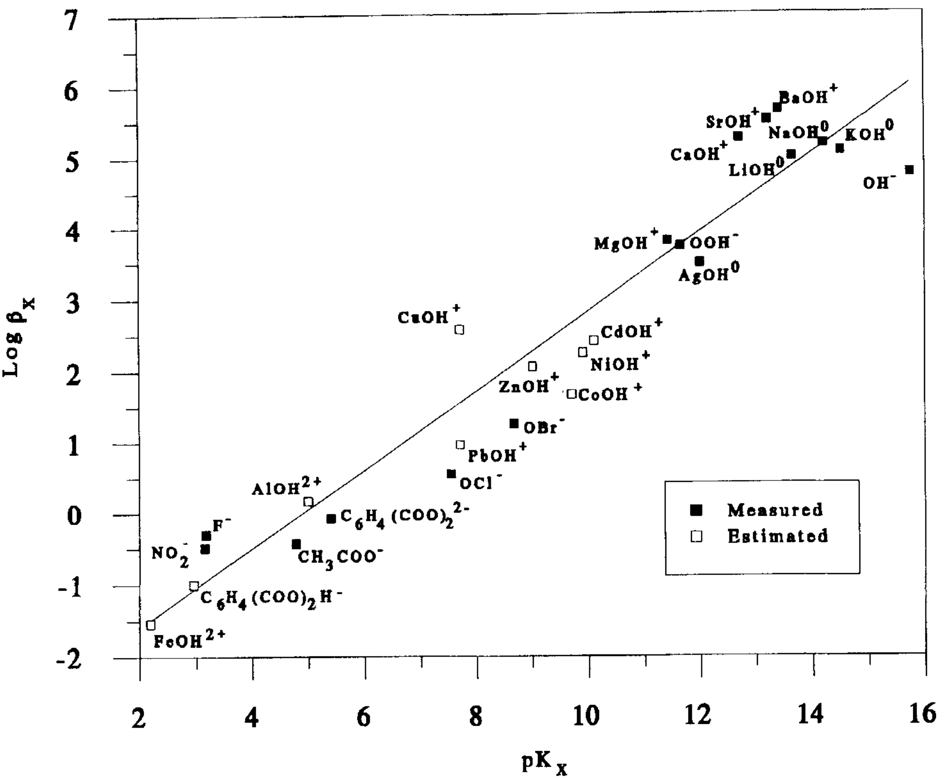

Figure 1 Linear free energy relationship between the stability constants (log β_X) and boric acid complexes and the acid dissociation constants (pK_X) of unidentate ligands. The line shows the least-squares best fit for log $\beta_X = (0.55 \pm 0.04)pK_X - (2.71 \pm 0.47)$ over the 16 measured points.

relationship may be expressed by equation (*22*) with a correlation coefficient of 0.92 (for 16 measured points).

$$\log\beta_X = (0.55 \pm 0.04)pK_X - (2.71 \pm 0.47) \qquad (22)$$

The fact that this expression may be applied to complexes with charges between +2 and −2 shows that the relationship is independent of the charge on the ligand. This implies that electrostatic attraction and repulsion of the charged hydrogen ion by the ligands is not an important factor. The reason for this is that in all but one case (F^-), both the hydrogen ion and boric acid utilise a lone-pair a electrons on an oxygen atom in bonding with the ligand. The charge on the rest of the ligand will only be significant in that it will affect the strength of the bond by altering the electron density at the oxygen atom.

This expression can best be explained in terms of changes of standard enthalpies and entropies. It was previously noted that the contribution of $T\Delta S$ to the free energy of reaction for the protonation of monovalent anions was fairly constant.[1] Changes in the free energy for the protonation of ligands were assumed to be the result of enthalpy differences. It was expected that the same argument could be applied to complexation of the anions by boric acid and that a similar trend would be observed because the anions would have been common to both systems.

Based on this argument, the difference between the entropy of reaction resulting from protonation of a ligand and that resulting from complexation with boric acid will be approximately constant and thus incorporated into the constant term in equation (*22*). This implies that much of the variation in TΔS values, particularly that arising from ligands with different charges, will be eliminated. This supposition is supported by values calculated from published data.[5,7] The difference between the entropy of reaction for the two systems involving the ligands OH^-, $MgOH^+$, $CaOH^+$, $SrOH^+$, $BaOH^+$ is in the range of 25–39 kJ mol^{-1}.

The constant term in equation (*22*) corresponds to an energy of 15 ± 3 kJ mol^{-1}. This is lower than the values calculated for the difference in entropies of reaction, a fact which suggests some contribution from enthalpy terms.

The gradient in equation (*22*) largely reflects the relative magnitudes of the enthalpies of the two systems and, in particular, the relative bond strengths. A ligand will contribute an electron pair to a bond with both the hydrogen ion and the boron atom. This will result in the completion of the first electron shell for the hydrogen and the second electron shell for boron. Hydrogen, being smaller than boron, will bind more strongly. The ratio of the strengths of the two bonds remain fairly constant and independent of the ligand.

Examples of this behaviour found in the literature have been largely confined to ligands which bind through an oxygen atom. However, similar behaviour was also observed for the fluoride. This suggests that the same linear relationship would be observed for ligands which bind through other atoms. For example, unidentate amino nitrogen ligands would form stable complexes. This suggestion is supported by the enhanced solubility of boric acid observed in the presence of ammonium salts.[3]

This study has demonstrated that boric acid will form unidentate complexes with anionic, cationic and neutral ligands. The stability of all these complexes may be predicted from the acid dissociation constants of the ligands by means of a single linear free energy relationship. This is particularly useful since many acid dissociation constants are known.

There are two areas where this approach will be particularly useful. Firstly, for complicated system where a range of hydroxo- and borato-complexes of metal ions exist. Such systems are very difficult to characterise. Since the free energy relationship is unaffected by the charge on the ligand, it will be possible to determine the predominant boron complexes in these systems. The second area where this approach will be useful is where reactions are studied in solutions containing borate. The reaction could potentially be modified by complex formation involving boron and the reactants. It now possible to predict whether such complex formation is likely to be significant and to also gain some insight into how such complexation would modify the reaction.

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