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# FORMATION OF NEUTRAL COMPLEXES OF BORIC ACID WITH 1,3-DIOLS IN ORGANIC SOLVENTS AND IN AQUEOUS SOLUTION

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**Abstract**—From solubility measurements in organic media and extraction experiments, the values of the stability constants of neutral 1 : 1 complexes (HBL) formed between boric acid (HB) and 1,3-diols (L) have been obtained in aqueous solution ($K_{c(w)}$) and in organic solvents ($K_{c(s)}$). The values of the partition coefficients of the diols ($P_L$) and the complexes ($P_{HBL}$) between water and the organic solvents have also been calculated. Generally, the addition of a diol to an aqueous solution of borax is accompanied by a decrease of pH due to the prevailing formation of borate species but, in the case of 2-methyl-2,4-pentanediol, the pH increased, in agreement with the formation of a single neutral complex. It is shown that a modification of a previous potentiometric procedure yields simultaneously the values of the stability constants of the neutral and anionic complexes in aqueous solution.

Complex formation between boric acid and polyols has been known for a long time. Whereas alcohols (ROH) react with boric acid (HB) to yield neutral esters like $B(OR)_3$, polyols (L) form chelates that generally involve two donating oxygen atoms.[1] The nature of these chelated complexes depends on the relative positions of the available hydroxyl groups of the ligand.

With carbohydrates and most polyols possessing 1,2-diol systems, the borate ion $[B(OH)_4]^-$ ($B^-$) forms anionic 1 : 1 ($BL^-$) and 1 : 2 ($BL_2^-$) species.[2] Their stability constants have been determined by potentiometry,[3–5] and $^{11}B$ NMR has provided much detail on their structures.[6–9] Because complex formation enhances the strength of boric acid, such reactions are useful for the titrimetric determination of boron.[10]

The reactions of 1,3-diols are not so well understood (Scheme 1). It was initially believed that only anionic 1 : 1 and 1 : 2 complexes similar to those of 1,2-diols were formed. These species have been studied by potentiometry[4] and characterized by $^{11}B$ NMR spectroscopy.[6] However, 1,3-diols also form neutral 1 : 1 complexes that allow the extraction of boric acid into non-aqueous phases. Solvent extraction of boric acid with 1,3-diols is often the first step of analytical methods[11–13] and of the industrial recovery of boron.[14] Neutral 1 : 1 complexes of 1,3-diols have been crystallized from water and analysed.[15] The relative stabilities of complexes of 1,2- and 1,3-diols have been investigated by Dale *et al.*[16,17] in various solvents. In anhydrous organic solvents, 2 : 3 complexes have been observed,[17] but they are readily hydrolysed to the monomeric 1 : 1 species by traces of water.

Little data can be found in the literature on the stability constants of boron complexes of diols in solvents other than water.[18,19] Dawber *et al.*[20,21] have presented $^{11}B$ NMR evidence that complexation in aqueous medium is not limited to vicinal hydroxyl groups, but may also involve those on alternate carbon atoms. A recent paper has reported mass spectroscopy experiments[22] showing a relationship between the mass spectrum patterns and the structures of borate complexes of α- and β-diols. Paál[23] and Kankare[24] have pointed out that the formation of neutral complexes should be considered besides the formation of anionic complexes, even with carbohydrates.

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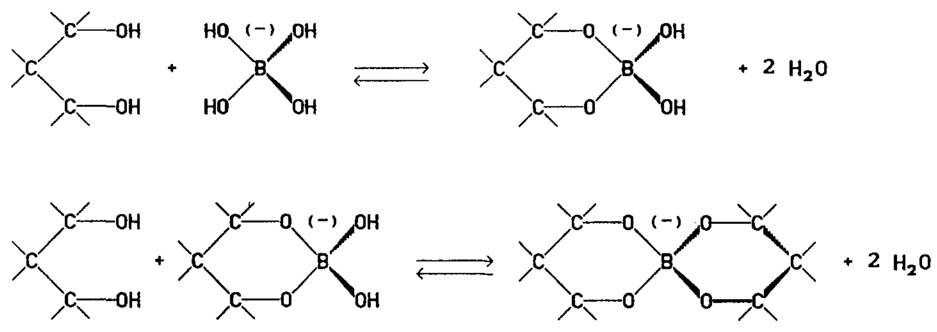
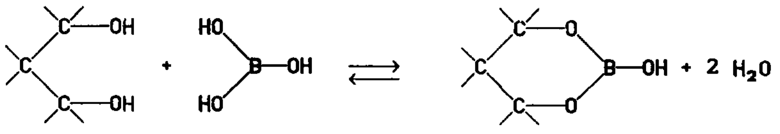


Formation of neutral complexes HBL of 1,3-diols



Scheme 1. Reactions of formation of 1 : 1 and 1 : 2 borate complexes.

This work was undertaken in order to determine the equilibrium constants of the reactions between boric acid and 1,3-diols in water and in organic solvents. Such diols are sometimes highly associated at high concentrations in chloroform,[25] but at low concentrations, the distribution data may be safely treated assuming monomeric species in both phases. On the basis of commercial availability, variable solubilities and physical states, we investigated the liquid diols 2-ethyl-1,3-hexanediol (EHD), 2-methyl-2,4-pentanediol (MPD) and 2,4-pentanediol (PD), and the solid diols 2,2,4-trimethyl-1,3-pentanediol (TMPD), 2,2-diethyl-1,3-propanediol (DEPD) and 2-n-butyl-2-ethyl-1,3-propanediol (BEPD). The formulae are given in Scheme 2.

## EXPERIMENTAL

All chemicals and solvents were of analytical grade and commercially available. All measurements were made at 25.0°C.

### *Potentiometry*

The method involved the measurement of pH of solutions of borax containing increasing concentrations of diols and was described elsewhere.[5] The ionic strength was adjusted (0.100 M) by addition of KCl.

### *Solubility measurements*

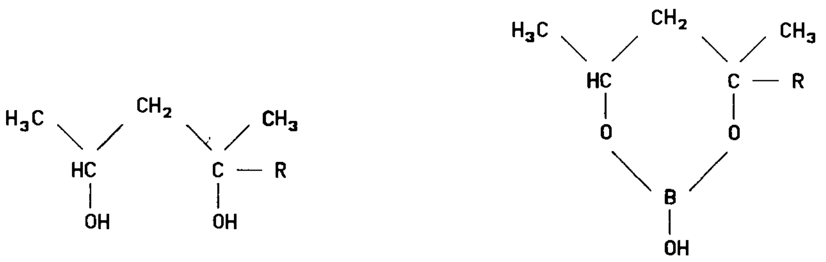
A weighed mass of boric acid (calculated in excess) was suspended in 25 cm$^3$ of solvent containing a known concentration of diol (0.3–0.7 M). The mixture was sufficiently stirred for 24 h until equilibration. After filtration to eliminate undissolved boric acid, the titration was performed as below.

### *Titration procedure*

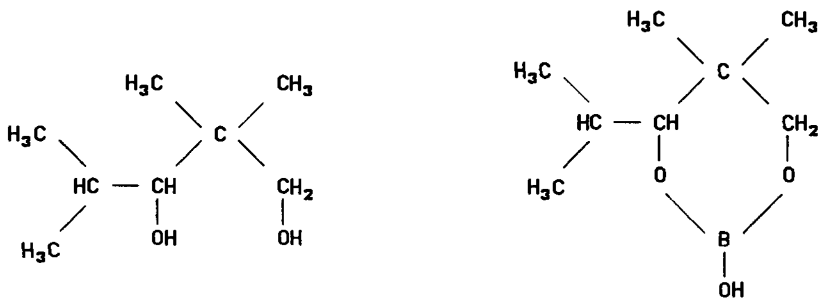
Aliquots (1.00 cm$^3$) of the solutions of boric acid were titrated with standard 0.100 M sodium hydroxide, using phenolphthalein as the indicator. For aqueous phases, the sample was diluted with water (20 cm$^3$) containing D-mannitol (1 g) in order to increase the strength of boric acid.[10] For the organic solutions that contained boric acid in complexed form, the presence of mannitol had the twofold effect of extracting boric acid in the aqueous phase and of displacing the diol from the complex.

**2,4-Pentanediol (PD)** R = H

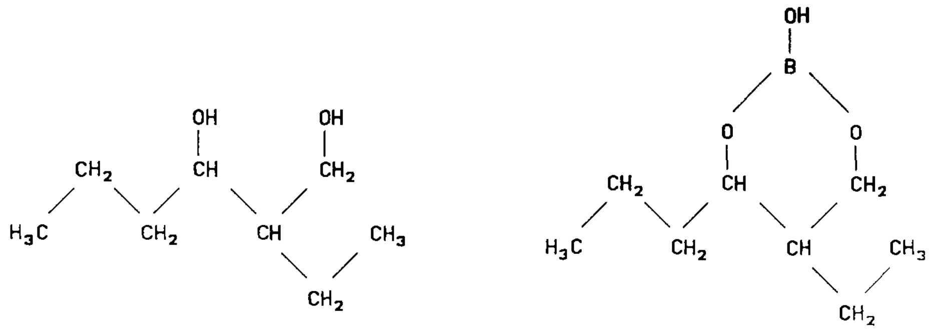
**2-Methyl-2,4-pentanediol (MPD)** R = $CH_3$



**2,2,4-Trimethyl-1,3-pentanediol (TMPD)**

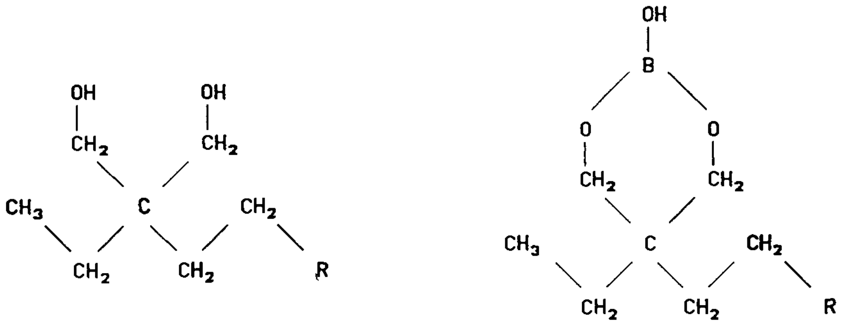


**2-Ethyl-1,3-hexanediol (EHD)**



**2,2-Diethyl-1,3-propanediol (DEPD)** R = H

**2-Butyl-2-ethyl-1,3-propanediol (BEPD)** R = $CH_2$-$CH_3$



Scheme 2. Structures of 1,3-diols and of their boric complexes.

It was generally necessary to add more mannitol (1–2 g) after the first appearance of the final purple colour to ensure that the extraction was complete. All titrations were carried out at least twice.

*Partition coefficients*

The partition coefficients of the diol and of the complex were calculated from extraction experiments. Typically, for the diol, two equal volumes (25 cm$^3$) of pure water and organic solvent containing the diol (concentration 0.6 M) were mixed with efficient stirring for 24 h. After separation with a funnel, the organic phase was recovered and boric acid (0.6 M) was added. The resulting suspension was stirred for 24 h, filtered and titrated as above.

For the complex, the extraction experiments involved an aqueous phase, containing a large excess of boric acid (1.6 M), and an equal volume of solvent (25 cm$^3$) containing the diol (0.6 M). After 24 h, both phases were separated, filtered and titrated as above.

## RESULTS

*Stability constants of the complexes in organic solvents*

Free boric acid is not appreciably soluble in most organic solvents. The distribution ratio of boric acid between chloroform and water has been reported[18] to be $4 \times 10^{-5}$. In every solvent used, the solubility of boric acid, initially lower than $2.5 \times 10^{-3}$ mol dm$^{-3}$, dramatically increased with the initial concentration $c_L$ of the diol (Fig. 1). The data agree with the formation of neutral 1 : 1 complexes HBL according to the equation:

$$\mathrm{HB\,(sol)} + \mathrm{L} \rightleftharpoons \mathrm{HBL}.$$

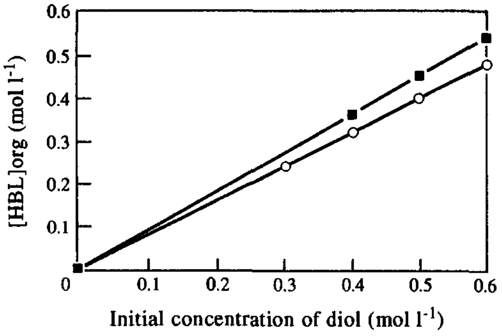


Fig. 1. Concentration of the neutral complex HBL in the organic phase *vs* the initial concentration $c_L$ of diol L; L = TMPD. The solvents are butyl ether (■) and carbon tetrachloride (○). Solid boric acid was present in excess, $c_{HB} = 0.6$ M.

A titration of the organic phase with sodium hydroxide gave the concentration of complex $[\mathrm{HBL}]_{(s)}$ and the concentration of the free diol $[\mathrm{L}]_{(s)}$ from the mass-balance relation:

$$[\mathrm{L}]_{(s)} = c_L - [\mathrm{HBL}]_{(s)}.$$

With the usual convention that activity of pure solids is unity, the corresponding complexation constant $K_{c(s)}$ was written as:

$$K_{c(s)} = [\mathrm{HBL}]_{(s)}/[\mathrm{L}]_{(s)} = [\mathrm{HBL}]_{(s)}/(c_L - [\mathrm{HBL}]_{(s)}).$$

It follows that $[\mathrm{HBL}]_{(s)}$ should be linearly related to $c_L$ by the relation:

$$[\mathrm{HBL}]_{(s)} = c_L \cdot K_{c(s)}/(1 + K_{c(s)}).$$

Plots of $[\mathrm{HBL}]_{(s)}$ *vs* $c_L$ yield straight lines that demonstrate the 1 : 1 stoichiometry. Examples for the complex of TMPD in two solvents are shown in Fig. 1. The values of $K_{c(s)}$ are related to the slope $p$ by the relation:

$$K_{c(s)} = p/(1-p).$$

*Partition coefficient of the diol* $\mathrm{P}_L$

The partition coefficient is related to the concentrations of the diol in both phases at equilibrium (equal volumes were used):

$$P_L = c_{L(s)}/c_{L(w)}.$$

The solubility method described above was used for the determination of the concentration of diol in the organic phase. After separation of the phases, solid boric acid in excess was added to the organic phase, so that the diol equilibrated with the complex:

$$c_{L(s)} = [\mathrm{HBL}]_{(s)} + [\mathrm{L}]_{(s)}.$$

Using the known value of $K_{c(s)}$, the concentration $[\mathrm{L}]_{(s)}$ was calculated from the concentration $[\mathrm{HBL}]_{(s)}$ obtained by titration of the organic phase:

$$c_{L(s)} = [\mathrm{HBL}]_{(s)}(1 + 1/K_{c(s)}).$$

The concentration $[\mathrm{L}]_{(w)} = c_{L(w)}$ of the diol in the aqueous phase was obtained by difference, knowing $c_{L(i)}$, the initial concentration of diol.

$$[\mathrm{L}]_{(w)} = c_{L(i)} - c_{L(s)}.$$

The results for the six diols in various solvents are presented in Tables 1–6. Both PD and MPD (the pentane-2,4-diols) are more soluble in water than in the organic phases. The other diols, especially BEPD, are more soluble in organic solvents, especially chloroform.

Table 1. Stability constants of the complex HBL in organic solvents ($K_{c(s)}$) and in aqueous solution ($K_{c(w)}$), and partition coefficients of L and HBL (L = TMPD, $T = 298$ K)

| Solvent | $K_{c(s)}$ | $P_L$ | $P_{HBL}$ | $K_{c(w)}$ |
|---|---|---|---|---|
| $CCl_4$ | 4.55 | 3.1 | 34.0 | 0.53 |
| $CHCl_3$ | 17.8 | 5.45 | 202.0 | 0.55 |
| BuOBu | 10.7 | 3.6 | 60.4 | 0.74 |
| $C_6H_6$ | 7.9 | 3.45 | 44.4 | 0.73 |
| $o$-$C_6H_4Cl_2$ | 9.3 | 3.15 | 62.5 | 0.57 |
| DIBK | 11.6 | 3.8 | 80.0 | 0.70 |

In Tables 1–6, BuOBu is butyl ether, DIBK is di-isobutylketone, $C_{30}H_{62}$ is squalane, $C_6H_{12}$ is cyclohexane, $C_6H_5$—$C_6H_{13}$ is n-hexylbenzene. Other solvents are represented by their formulae. Accuracy: $K_{c(s)} \pm 2\%$, $P_L \pm 4\%$, $P_{HBL} \pm 10\%$, $K_{c(w)}$ values $\pm 0.2$. In principle, all values of $K_{c(w)}$ for a given diol should be equal, since they do not depend on the solvent used in the extraction of boric acid.

Table 2. Stability constants of the complex HBL in organic solvents ($K_{c(s)}$) and in aqueous solution ($K_{c(w)}$), and partition coefficients of L and HBL (L = BEPD, $T = 298$ K)

| Solvent | $K_{c(s)}$ | $P_L$ | $P_{HBL}$ | $K_{c(w)}$ |
|---|---|---|---|---|
| $CHCl_3$ | 7.0 | 6.6 | 25.0 | 2.3 |
| $C_6H_6$ | 2.9 | 26.5 | 40.5 | 2.4 |
| BuOBu | 2.55 | 25.7 | 28.5 | 3.0 |
| $CCl_4$ | 2.2 | 26.0 | 35.4 | 2.2 |
| DIBK | 2.45 | 26.6 | 39.7 | 2.2 |

Table 3. Stability constants of the complex HBL in organic solvents ($K_{c(s)}$) and in aqueous solution ($K_{c(w)}$), and partition coefficients of L and HBL (L = DEPD, $T = 298$ K)

| Solvent | $K_{c(s)}$ | $P_L$ | $P_{HBL}$ | $K_{c(w)}$ |
|---|---|---|---|---|
| $CHCl_3$ | 9.20 | 2.13 | 28.2 | 0.79 |
| DIBK | 3.65 | 1.62 | 9.1 | 0.77 |

Table 4. Stability constants of the complex HBL in organic solvents ($K_{c(s)}$) and in aqueous solution ($K_{c(w)}$), and partition coefficients of L and HBL (L = EHD, $T = 298$ K)

| Solvent | $K_{c(s)}$ | $P_L$ | $P_{HBL}$ | $K_{c(w)}$ |
|---|---|---|---|---|
| $CHCl_3$ | 15.6 | 7.75 | 207 | 0.73 |
| $C_6H_5Cl$ | 6.1 | 5.35 | 70.0 | 0.64 |
| $C_6H_6$ | 6.35 | 5.22 | 69.7 | 0.61 |
| $C_6H_5CH_3$ | 5.25 | 3.92 | 41.5 | 0.65 |
| $CCl_4$ | 4.0 | 3.10 | 26.8 | 0.70 |
| BuOBu | 7.8 | 2.70 | 41.0 | 0.69 |
| DIBK | 8.7 | 3.50 | 55.0 | 0.65 |
| $o$-$C_6H_4Cl_2$ | 8.3 | 3.60 | 56.0 | 0.66 |
| $C_6H_5$—$C_6H_{13}$ | 5.3 | 1.60 | 14.1 | 0.64 |
| $C_6H_{12}$ | 2.9 | 2.84 | 14.4 | 0.69 |
| $C_{12}H_{26}$ | 5.3 | 0.67 | 6.4 | 0.66 |
| $C_7H_{16}$ | 3.35 | 1.27 | 7.7 | 0.66 |
| Decaline | 2.95 | 1.55 | 8.7 | 0.61 |
| $C_{30}H_{62}$ | 2.5 | 0.60 | 3.3 | 0.60 |

Table 5. Stability constants of the complex HBL in organic solvents ($K_{c(s)}$) and in aqueous solution ($K_{c(w)}$), and partition coefficients of L and HBL (L = MPD, $T = 298$ K)

| Solvent | $K_{c(s)}$ | $P_L$ | $P_{HBL}$ | $K_{c(w)}$ |
|---|---|---|---|---|
| $CHCl_3$ | 203[a] | 0.50 | 50.7 | 2.30 |
| $CH_2Cl_2$ | 127[a] | 0.47 | 31.6 | 2.30 |
| $CCl_4$ | 67 | 0.031 | 1.25 | 2.28 |
| BuOBu | 38 | 0.086 | 1.82 | 2.23 |
| $C_6H_6$ | 84 | 0.088 | 3.98 | 2.27 |
| DIBK | 27 | 0.23 | 2.62 | 2.30 |
| $C_6H_5Cl$ | 63 | 0.05 | — | — |
| $C_6H_5CH_3$ | 52 | 0.06 | — | — |
| $C_6H_{12}$ | 1.0 | 0.08 | — | — |
| $C_7H_{16}$ | 0.5 | 0.03 | — | — |
| $o$-$C_6H_4Cl_2$ | 106 | 0.078 | 3.94 | 2.31 |

[a] Determined by a reversed calculation, starting from $K_{c(w)} = 2.30$ (mean value found in other solvents).

### *Partition coefficient of the complex and stability constant of the complex in the aqueous phase by the extraction method*

The partition coefficient of the complex is defined by the relation:

$$P_{HBL} = [HBL]_{(s)}/[HBL]_{(w)}.$$

$[HBL]_{(s)}$ was obtained directly by titration of the organic phase, but the determination of $P_{HBL}$ required the indirect calculation of $[HBL]_{(w)}$. With

Table 6. Stability constants of the complex HBL in organic solvents ($K_{c(s)}$) and in aqueous solution ($K_{c(w)}$), and partition coefficients of L and HBL (L = PD, $T = 298$ K)

| Solvent | $K_{c(s)}$ | $P_L$ | $P_{HBL}$ | $K_{c(w)}$ |
|---|---|---|---|---|
| $CHCl_3$ | 26.1 | 0.082 | 3.40 | 0.80 |
| $CH_2Cl_2$ | 26.9 | 0.072 | 3.12 | 0.83 |
| $CCl_4$ | 2.7 | 0.021 | 0.12 | 0.82 |
| BuOBu | 4.1 | 0.048 | 0.32 | 0.80 |
| $C_6H_6$ | 5.2 | 0.046 | 0.45 | 0.74 |
| DIBK | 5.5 | 0.067 | 0.65 | 0.83 |

equal volumes of both phases, the mass-balance equation can be written as:

$$[HBL]_{(w)} = c_L - [HBL]_{(s)} - [L]_{(s)} - [L]_{(w)}.$$

With boric acid in excess ($[HB]_1 = 1.6$ M), i.e. in the presence of solid, $[L]_{(s)}$ is obtained from the known value of $K_{c(s)}$:

$$[L]_{(s)} = [HBL]_{(s)}/K_{c(s)}$$

and $[L]_{(w)}$ is obtained from the known value of $P_L$:

$$[L]_{(w)} = [L]_{(s)}/P_L.$$

$[HBL]_{(w)}$ is then calculated from $[HBL]_{(s)}$:

$$[HBL]_{(w)} = c_L - [HBL]_{(s)} - [HBL]_{(s)}/K_{c(s)} - [HBL]_{(s)}/(K_{c(s)} \cdot P_L)$$

$$P_{HBL} = 1/(c_L/[HBL]_{(s)} - 1 - 1/K_{c(s)} - 1/(K_{c(s)} \cdot P_L)).$$

Since the complexation of a diol with boric acid enhances its solubility in organic solvents, $P_{HBL}$ is always larger than $P_L$ (Tables 1–6).

### *Stability constants* $K_{c(w)}$ *of the complexes* HBL *in the aqueous phase*

$K_{c(w)}$ is obtained from the results of the extraction experiments:

$$K_{c(w)} = [HBL]_{(w)} \cdot [HB]_{(w)}^{-1} \cdot [L]_{(w)}^{-1}$$

$$[HBL]_{(w)} = [HBL]_{(s)}/P_{HBL}$$

$$[L]_{(w)} = [HBL]_{(s)}/(K_{c(s)} \cdot P_L).$$

A titration of the aqueous phase gives the overall concentration of complexed and uncomplexed boric acid. Thus, the concentration of free boric acid in the aqueous phase is:

$$[HB]_{(w)} = C_{HB(w)} - [HBL]_{(w)} = c_{HB(w)} - [HBL]_{(s)}/P_{HBL}.$$

The value of the stability constant $K_{c(w)}$ is eventually obtained:

$$K_{c(w)} = (1/P_{HBL})/(c_{HB(w)} - [HBL]_{(s)}/P_{HBL}) \cdot (1/K_{c(s)} \cdot P_L)$$

$$K_{c(w)} = K_{c(s)} \cdot P_L/(P_{HBL} \cdot c_{HB(w)} - [HBL]_{(s)}).$$

Obtaining a constant value of $K_{c(w)}$ for a given diol is a good criterion for the consistency of the results found in different solvents. The agreement for all the investigated diols is shown in Table 7.

### *Potentiometric method for the determination of the stability constants*

When a diol that forms anionic 1 : *n* complexes is added to an aqueous solution of borax (an equimolar mixture of boric acid and sodium borate), a decrease of pH is generally observed,[2–5] according to reaction (1):

$$HB + nL \rightleftharpoons BL_n^- + H^+ \quad (n = 1 \text{ or } 2). \quad (1)$$

This is indeed the case for five diols, but, on the contrary, MPD increases the pH of a solution of borax (Table 8). This result may be attributed to the formation of the neutral complex instead of the anionic species. The corresponding uptake of protons is due to reaction (2):

$$B^- + L + H^+ \rightleftharpoons HBL. \quad (2)$$

It may be considered that for many other 1,3-diols, the variations of acidity due to the addition of diol are the sum of opposite reactions (1) and (2) that must both be taken into account. The actual

Table 7. Stability constants of boron complexes of diols in aqueous medium at 298 K

| Diol | $\beta_1^a$ | $\beta_2^a$ | $K_{c(w)}^a$ | $K_{c(w)}^b$ |
|---|---|---|---|---|
| TMPD | 1.78 | 15.1 | 0.54 | 0.60 |
| DEPD | 10.0 | 15.8 | 0.76 | 0.78 |
| EHD | 1.99 | <0.06 | 0.66 | 0.65 |
| PD | 3.16 | <0.03 | 0.87 | 0.80 |
| MPD | <0.01 | <0.01 | 2.29 | 2.30 |
| BEPD[c] | 7.76 | 437 | 2.24 | 2.40 |

$\beta_1 = [BL^-] \cdot [B^-]^{-1} \cdot [L]^{-1}$;
$\beta_2 = [BL_2^-] \cdot [B^-]^{-1} \cdot [L]^{-2}$;
$K_{c(w)} = [HBL] \cdot [HB]^{-1} \cdot [L]^{-1}$.

[a] Potentiometry, constant ionic strength (KCl, 0.1 M), accuracy $\beta_1 \pm 2\%$ ; $\beta_2 \pm 2\%$ ; $K_{c(w)} \pm 2\%$.

[b] Extraction method, mean of values for various organic solvents (Tables 1–6), accuracy ±0.2.

[c] The concentration of diol was <0.04 M, owing to its low solubility in water.

Table 8. Determination of the stability constants of the boron complexes of 2-methyl-2,4-pentanediol (MPD) at 298 K

| Mass of diol (g) | $c_L$ (mol dm$^{-3}$) | pH$_{1/2}$ | p$K'_a$ (calc.) |
|---|---|---|---|
| MPD | | | |
| 0.000 | 0.0000 | 8.96 | 8.96 |
| 0.500 | 0.0423 | 9.01 | 9.00 |
| 1.010 | 0.0855 | 9.04 | 9.04 |
| 2.010 | 0.1701 | 9.10 | 9.10 |
| 3.010 | 0.2547 | 9.15 | 9.16 |
| 4.010 | 0.3393 | 9.21 | 9.21 |
| 5.010 | 0.4239 | 9.25 | 9.25 |
| 6.010 | 0.5085 | 9.30 | 9.30 |
| 7.010 | 0.5932 | 9.34 | 9.33 |
| 8.010 | 0.6778 | 9.38 | 9.37 |

Volume of solution 100 cm$^3$. Constant ionic strength (KCl, 0.1 M). pH$_{1/2}$ is the pH of a solution of borax ($c_B = c_{HB} = 2.6 \times 10^{-3}$ M) in the presence of MPD at concentration $c_L$. p$K'_a$ is calculated using eq. (7) with parameters: $M = 118.18$ g mol$^{-1}$, p$K_a = 8.96$, $\beta_1 = \beta_2 = 0$, $K_{c(w)} = 2.29$.

direction of the variation of pH depends on the prevailing reaction.

In the absence of diol, the pH of a solution of borax has a value pH$_{1/2}$ equal to the p$K_a$ of boric acid. At constant ionic strength (KCl, 0.1 M), the acidity constant may involve concentrations instead of activities:

$$K_a = [B^-] \cdot [H^+]/[HB]. \quad (3)$$

When a 1,3-diol L reacts simultaneously with boric acid and borate ion:

$$B^- + nL \rightleftharpoons BL_n^-$$

with

$$\beta_n = [BL_n^-] \cdot [B^-]^{-1} \cdot [L]_n^-, \quad n = 1 \text{ or } 2;$$

$$HB + L \rightleftharpoons HBL$$

with

$$K_{c(w)} = [HBL] \cdot [HB]^{-1} \cdot [L]^{-1},$$

the analytical concentrations of borate ion ($c_B$) and boric acid ($c_{HB}$) are given by eqs (4) and (5);

$$c_B = [B^-] + [BL^-] + [BL_2^-]$$
$$= [B^-](1 + \beta_1[L] + \beta_2[L]^2) \quad (4)$$

$$c_{HB} = [HB] + [HBL] = [HB](1 + K_{c(w)}[L]). \quad (5)$$

As borax corresponds to half-neutralized boric acid, $c_B = c_{HB}$ and pH$_{1/2}$ = p$K'_a$, the conditional acidity constant in the presence of diol is:

$$[H^+]_{1/2} = K'_a = [H^+] \cdot c_B/c_{HB}. \quad (6)$$

Combination of eqs (4)–(6) gives eq. (7), which relates the conditional acidity constant $K'_a$ to the concentration of free diol [L]:

$$K'_a = K_a \cdot (1 + \beta_1[L] + \beta_2[L]^2)/(1 + K_{c(w)}[L]). \quad (7)$$

In our experiments, the diol was in large excess over borax and thus $[L] \simeq c_L$. Therefore, the variations of pH$_{1/2}$ *vs* $c_L$ were monitored and were treated using a laboratory-made BASIC routine, to obtain the values of $\beta_1$, $\beta_2$ and $K_{c(w)}$ (Table 7). The values found for $K_{c(w)}$ agree nicely with those calculated by the extraction method.

## DISCUSSION

Quantitative equilibrium data are reported for the formation of neutral 1 : 1 complexes of boric acid with various 1,3-diols in aqueous and organic solutions. In agreement with the extraction behaviour of such complexes, their stability constants are larger in organic solvents than in aqueous solution (Tables 1–6). Moreover, the partition coefficients of the complexes $P_{HBL}$ are generally favourable to the organic phase, even for diols highly soluble in water ($P_L < 1$) like MPD and PD.

The nature of the solvent strongly influences the formation of the neutral complex. For example, the extraction of boric acid by several diols is 10-fold lower in hexane than in chloroform.[19] In this work, we found that saturated hydrocarbons like heptane, cyclohexane, dodecane, decaline and squalane are poor solvents of diols L and complexes HBL. This is shown in the case of EHD by the low values for $P_L$ and $P_{HBL}$, whereas the stability constants of the complex are only slightly lower than in other solvents (Table 4). In the case of the water-soluble diol MPD (Table 5), the $P_L$ values are similar in alkanes and aromatic solvents, but the values of $K_{c(s)}$ reported in heptane and cyclohexane are much lower than in any other solvent.

Aromatic hydrocarbons are good solvents of the diols and the complexes. However, in agreement with the above paragraph, a significant decrease of $P_{HBL}$ is observed when substituting benzene by aliphatic side chains. Data for EHD (Table 4) show a decrease of the value of $P_{HBL}$ from benzene (69.7) to toluene (41.5) and hexylbenzene (14.1).

Chlorinated solvents like chloroform and dichloromethane readily dissolve the diols and allow the formation of very stable complexes. This probably accounts for their frequent use in extraction studies,[11–14,18,19] although the theoretical grounds for the general use of chloroform were not stated in the literature. In the case of BEPD, chloroform is not the best solvent for L and HBL, but affords the highest value for $K_{c(s)}$. Dichlorination of benzene also enhances the values of $K_{c(s)}$ and $P_{HBL}$ for the complexes of TMPD, EHD and MPD, although the effect is not so clear with chlorobenzene. In contrast, carbon tetrachloride does not stabilize the complexes in a particular way.

Oxygenated solvents like diisobutylketone (DIBK) and butyl ether (BuOBu) are generally associated with high values of $K_{c(s)}$ and $P_{HBL}$ and are possible substitutes for toxic solvents like aromatics and chlorohydrocarbons. One may also note that for MPD and PD (Tables 5 and 6), $CHCl_3$ and $CH_2Cl_2$ allow outstanding stabilization of the complexes, which is not so obvious with TMPD, for example. A complete interpretation of the relative stability in various solvents of the boric complex of a given diol should take into account the structure of the diol and the way in which the solvent solvates both the diol and the complex. The formation of hydrogen bonds between the solvent and the diol or the complex has been suggested.[19] Our results also suggest that polarity may be an important factor.

In the aqueous phase, all diols, except MPD, form anionic complexes (Table 7). The $BL^-$ species are of low stability ($\beta_1 \leqslant 10$) with respect to complexes of 1,2-diols and other polyols like carbohydrates.[3–5,7–9,21] Three diols, TMPD, BEPD and DEPD, also afford 1 : 2 anionic *spiro* complexes $BL_2^-$, that of BEPD having noticeable stability ($\beta_2 = 437$). A possible structural reason for the absence of 1 : 2 complexes ($\beta_2 < 0.01$) with other diols is the lack of substituents on the central carbon atom. For comparison, Paál[23] reported $\beta_1 = 1.38$ and $K_{c(w)} = 0.54$ ($I = 0.01$ M) for the complex of 1,3-butanediol, whereas Egneus and Uppström[19] reported $K_{c(w)} = 0.59$ ($I = 0.5$ M) for the complex of 2,2-diphenyl-1,3-propanediol. These $K_{c(w)}$ values are close to the mean value ($K_{c(w)} \simeq 0.7$) obtained in this work for four diols, but not MPD and BEPD.

We have mentioned that MPD, which does not form anionic complexes $BL_n^-$, decreases the conditional acidity constant $K'_a$ of boric acid, contrary to all other diols and polyols. However, the homologous diol PD behaves differently and forms a $BL^-$ complex, confirming an $^{11}B$ NMR study by Sinton,[26] who detected a second species at [L] > 2 M, assumed to be the anionic 1 : 2 complex, but no neutral complex of PD. The introduction of a methyl group at C(2) or C(3) in the PD molecule was also reported to increase the extraction ability.[19] These results may indicate a high sensitivity of the complex-forming reaction towards the substitution of the ligand near the site of chelation.

Moreover, this work demonstrates that the variations of $pK'_a$ *vs* $c_L$ may be complicated when the formation of complexes of borate ion and boric acid occurs simultaneously. This phenomenon also occurs with ligands like alditols, for which the formation of neutral complexes is generally overlooked, because the proportions of the anionic complexes are generally large, compared to that of the neutral species, which can hardly be detected. However, Kankare[24] reported that a satisfactory description of the potentiometric data obtained for the D-mannitol–boric acid system required the assumption of the existence of 2 : 1 and 1 : 2 neutral complexes in addition to the well-established 1 : 1 and 1 : 2 anionic complexes, and Paál determined the stability constants of the neutral HBL complexes of several hexitols (D-mannitol, D-glucitol and galactitol) by an extraction study.[23] A similar competition probably occurs with the diol complexes of substituted boronic acids,[27] except 1,3-propanediol, which gives only anionic complexes with methylboronic acid[28] and boric acid,[29] and does not extract boric acid in chloroform.[19]

It is often assumed[18,25] that a large partition coefficient $P_L$ is necessary for a diol to be an efficient extracting agent for boric acid. Nevertheless, some derivatives of PD,[19] very soluble in water, are also good extracting agents. Our results show that this may be due to the HBL complex being favoured with respect to the unextractable anionic chelates.

## CONCLUSION

Equilibrium constants relevant to the chelation of boric acid into organic solvents by various 1,3-diols have been determined from solubility and extraction experiments. Experimental data correlate nicely with the formation, in both phases, of 1 : 1 neutral complexes formulated as HBL, besides anionic 1 : 1 and 1 : 2 borate complexes formed only in the aqueous phase. The stability constants $K_{c(w)}$ of species HBL in aqueous solution were determined by two independent methods that gave values in good agreement. Contrary to PD, MPD is unable to form anionic chelates and yields only the neutral HBL complex, which may explain its unexpectedly high extraction ability.

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