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Properties of the Borate Ion in Dilute Aqueous Solutions

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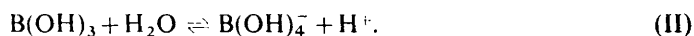
In this study the viscosity B_η coefficient and the ionic partial molar volume of the borate ion in aqueous solutions have been determined at 25 and 45 °C. These properties, together with data reported for the borate mobility, the borate-cation interactions and the formation entropy of the borate ion in aqueous solutions, indicate that $\text{B}(\text{OH})_4^-$ is a "structure-maker", but its behaviour resembles neither that of a typical strongly hydrated ion (*e.g.*, Li^+) nor that of hydrophobic ions.

The partial molar volume and the hydrodynamic radius of the borate ion are close to those corresponding to a rigid sphere having the borate ion crystal radius and bearing a single charge. However, due to its tetrahedrally disposed OH groups it interacts strongly with water molecules but without substantially modifying the bonding pattern present in the solvent.

The chemistry of aqueous borate solutions is characterized by the existence of a series of polyborate anionic species in solution and by the fact that the acid undergoes hydration before ionization. We are particularly interested in the physicochemical aspects of dilute borate aqueous solutions as employed in heavy water pressurized reactors, where its protolytic and adsorptive behaviour are of great importance.

The literature shows that different authors interpret the available experimental evidence as an indication that the borate ion is either a "structure-breaker" or a "structure-maker". This discrepancy in the interpretation of the borate-water interactions in dilute aqueous solution prompted us to measure and analyse various properties of the borate ion which give information on the borate-water interactions.

In aqueous solutions of alkali metal borates various anionic species can exist depending on the concentration and the pH of the solution; the transformation of one species into another involves aggregation of boric acid and borate ions together with protolytic processes. These equilibria have been carefully studied, using potentiometric techniques, by two groups of researchers.^{1, 2} The fact that in dilute aqueous solutions and in the absence of excess boric acid the monomeric borate ion is the predominant anionic species was confirmed by cryoscopic measurements,^{3, 4} as well as by spectroscopic^{5, 6} and conductivity⁷ studies. Furthermore, the spectroscopic evidence demonstrates that the monomeric borate ion has tetrahedral symmetry and is generally considered to be $\text{B}(\text{OH})_4^-$. The observed large low-field chemical shift of ^{11}B which is observed when boric acid dissociates⁸ is due to the fact that upon ionization the acid undergoes a change from planar sp^2 hybridization to the tetrahedral sp^3 hybridization of the borate ion. Thus the ionization of boric acid does not proceed directly by proton donation to a solvent molecule. The ionization process may be depicted by one of the following two processes which cannot be distinguished thermodynamically because they are coupled to the water autoprotolytic equilibrium



Process (I) was observed to be the kinetically relevant process for the ionization of boric acid by Kajimoto *et al.*,⁹ who employed a T-jump technique to follow the fast kinetics of ionization of the acid. The fact that the ionization of boric acid proceeds indirectly is also confirmed by the direct determination of the volume of ionization from studies of the pressure coefficient of the dissociation constant. The values obtained for $\Delta V_{\text{ion}}^\circ$ corresponding to reaction (II) were $-32.1 \text{ cm}^3 \text{ mol}^{-1}$ at 22°C ¹⁰ and $-30.5 \text{ cm}^3 \text{ mol}^{-1}$ at 25°C .¹¹ These values are much more negative than those observed for the dissociation of weak acids by direct proton transfer to a water molecule.¹²

Ward and Millero,¹³ from their apparent molar volume determinations for aqueous sodium borate solutions, and Pitzer and Mayorga,¹⁴ in their assessment of the osmotic and activity coefficients of (1-1) electrolyte solutions, concluded that the borate ion behaves like a "structure-breaking" ion.¹⁵

Our recent study of the conductivities of lithium and sodium borates⁷ in dilute aqueous solutions suggests that the borate ion is a "structure-maker" when its ionic mobility and its ion-pairing behaviours are considered. The same conclusion may be obtained from the following: (i) The shift of the pK of boric acid induced by the alkali metal chlorides;¹⁶ LiCl significantly increases the apparent dissociation constant of boric acid, while CsCl makes B(OH)₃ a weaker acid. (ii) The sodium and lithium borates show the same relative ion-pairing⁷ and solubility¹⁷ pattern as the fluorides or the hydroxides.^{18, 19} These observations may be interpreted in terms of attractive Gurney cospheres surrounding the lithium and the borate ions. This implies that the borate ion cannot be a "structure-breaker" because this would add a repulsive contribution to its coulombic interaction with lithium and sodium ions and an attractive contribution to its interaction with the other alkali metal ions.

EXPERIMENTAL

The preparation of the alkali metal borate solutions as well as the details of the determination of the borate ion mobilities are reported elsewhere.⁷ In the present work we have measured the viscosity and density of lithium and sodium borate aqueous solutions as a function of concentration at 25 and 45°C . In all circumstances extreme precautions were taken to avoid CO₂ contamination of the borate solutions.

The viscosity and density measurements were carried in order to gain information about the water-borate-ion interactions through the B_η coefficient and the partial molar volume at infinite dilution of the electrolytes, respectively. Consequently, no especial effort was devoted to the study of the concentration dependence of the partial molar volume which for the studied concentration range was within the experimental uncertainty of the piknometric technique which we have employed ($\pm 0.5 \text{ cm}^3 \text{ mol}^{-1}$). The concentration range was purposely restricted to <0.05 molar in order to avoid contributions from polyborate ions.

For a binary electrolyte in dilute solutions, the solution density, ρ , is related to that of the pure solvent (ρ°) by:

$$\rho = \rho^\circ + \frac{M_2 - \bar{V}_2^\circ \rho^\circ}{1000} c \quad (1)$$

where M_2 and \bar{V}_2° are the molecular weight and the infinite dilution partial molar volume of the solute, respectively.

The viscosity of the solutions was measured with Cannon-Fenske viscometers having flow-times of the order of 1000 s at 25°C . In order to attain the maximum possible precision, the volume of liquid in the viscometers was kept constant during each concentration run, which were started with the calibration of the viscometer using pure water with subsequent addition of stock borate solution. These additions were performed by withdrawing from the viscometers controlled amounts of liquid and then replenishing the viscometer with the same volume of borate stock solution. Since small differences in volume could not be

avoided, the flow-time was corrected using a previous calibration which showed a change of 0.1 s for every 10 mg difference in the amount of water. The reproducibility attained was 0.1–0.2 s.

The concentration dependence of the viscosity of electrolyte solution is given by the Jones–Dole equation which may be written:

$$Y \equiv \frac{\eta - \eta^\circ}{\eta^\circ \sqrt{c}} = A + B_\eta \sqrt{c}. \quad (2)$$

According to eqn (2), Y varies linearly with the square root of c ; the experimental data fall on a straight line from whose ordinate the value of A could be determined. It agreed within experimental error with the theoretical value of the limiting slope.²⁰ The values of B_η were determined to within 2 % from eqn (2).

Hydrolysis, as described by reaction (I), affects the values of the measured properties and it was necessary to take it into account in order to obtain the true values for the borates. All the additive properties of the solutions (P^{obs}) have been corrected for the hydrolysis making

$$P^{\text{obs}} = (1 - \beta)P(\text{borate}) + \beta[P(\text{hydroxide}) + P(\text{boric acid})] \quad (3)$$

where $P(i)$ is the value of the property for component i and β is the degree of hydrolysis which was calculated from the equilibrium constants obtained by Mesmer *et al.*²

RESULTS

Table 1 summarizes the results for both alkali metal borates, for boric acid and for the borate ion.

TABLE 1.—PROPERTIES OF BORIC ACID, LITHIUM AND SODIUM BORATES AND BORATE ION IN AQUEOUS SOLUTIONS

$T/^\circ\text{C}$	species	B_η /dm ³ mol ^{−1}	\bar{V}_i° /cm ³ mol ^{−1}	$\lambda_i^{\circ a}$ /S cm ² mol ^{−1}	r_s^b /Å
15	B(OH) ₄ [−]	—	—	27.7 ₄	2.60
25	B(OH) ₃	0.091	39.2	—	—
	LiB(OH) ₄	0.387	23.7	—	—
	NaB(OH) ₄	0.316	23.2	—	—
	B(OH) ₄ [−]	0.233	29.2	35.2 ₇	2.61
45	B(OH) ₃	0.104	41.5	—	—
	NaB(OH) ₄	0.320	25.7	—	—
	B(OH) ₄ [−]	0.234	30.8	52.0 ₀	2.65

^a Values taken from ref. (7). ^b r_s = hydrodynamic or Stokes' radius.

The value obtained for the partial molar volume of boric acid at both temperatures agrees with the values reported by Ward and Millero¹³ and by Ellis.²¹ However, the value for the partial molar volume of sodium borate differs by 2.4 cm³ mol^{−1} from that reported in the literature,¹³ which appears not to have been corrected by hydrolysis. The discrepancy, however, is larger than may be accounted for by hydrolysis.

The differences in B_η and the partial molar volumes of the lithium and sodium borates at 25°C agree, within experimental error, with the differences of the corresponding properties observed for other lithium and sodium salts and reported in the literature. From the values in table 1 it is possible to calculate the volume of ionization of boric acid according to reaction (II), the values, at 25 and 45°C, being −32.8 and −33.9 cm³ mol^{−1}, respectively, in good agreement with the values obtained from the pressure dependence of the dissociation constant of boric acid (*cf.* Introduction).

The ionic contribution to the B_η coefficients were obtained by subtracting the values of the cationic coefficients reported by Kaminsky.²² For the partial molar volume, the (absolute) cationic contributions were obtained from data in the literature^{23, 24} considering the absolute volume of the H⁺ ion to be -4.7 and -5.0 cm³ mol^{−1} at 25 and 45°C, respectively.

In order to calculate the crystallographic radius of the B(OH)₄[−] ion we have considered it a tetrahedral ion, as illustrated in fig. 1. From the values of the bond lengths and angles^{25, 26} a radius of 2.44 Å was calculated corresponding to a crystal molar volume for the borate ion of 36.63 Å³.

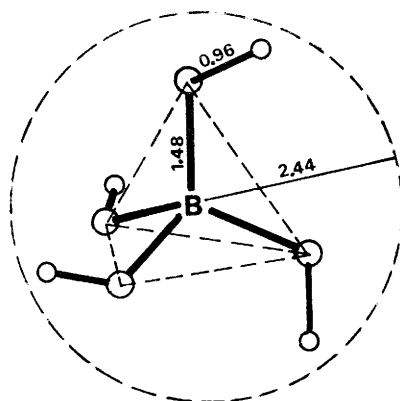


FIG. 1.—Crystal radius of borate ion. Distances are given in Å. The dashed circle is the crystal radius.

DISCUSSION

Table 1 shows that the value of the mobility of the borate ion is close to that of the highly hydrated Li⁺ ion. Since the temperature dependence of the ionic mobility may be employed to obtain information on the type of ion-solvent interactions,²⁷ the temperature coefficient of $\ln(\lambda_i^\circ \eta^\circ)$ for B(OH)₄[−] is compared with those of other monovalent ions at 25°C in table 2.

TABLE 2.—TEMPERATURE COEFFICIENT OF THE WALDEN PRODUCT FOR DIFFERENT MONOVALENT IONS AT 25°C

	$\frac{d\ln(\lambda_i^\circ \eta^\circ)}{dT}$ /10 ⁴ K ^{−1}	r_s /Å	r_{cryst} /Å	ref.
Li ⁺	8.8	2.38	0.60	19
Cs ⁺	−40.0	1.19	1.69	28
B(OH) ₄ [−]	−5.7	2.61	2.44	7
ClO ₄ [−]	−45.7	1.37	2.3	29
NMe ₄ ⁺	−12	2.07	3.47	28
NEt ₄ ⁺	0.1	2.86	4.00	28
N(EtOH) ₄ ⁺	−0.6	3.41	4.6	29
Cl [−]	−25.2	1.21	1.81	29

Table 2 shows that the borate ion has a moderately negative temperature coefficient for its Walden product and that there is little difference between its crystallographic and Stokes' radii. For typical "structure-breaking" ions, either cations or anions, the value of $\text{dln}(\lambda_i^\circ \eta^\circ)/\text{dT}$ is more negative than $-1.0 \times 10^{-3} \text{ K}^{-1}$ and the Stokes' radius is notably smaller than the crystallographic one. Even NMe_4^+ has a more negative temperature coefficient of the Walden product than the borate ion; the temperature coefficient of the latter is intermediate between that of NMe_4^+ and those of NEt_4^+ or N(EtOH)_4^+ ions, but for all these tetra-alkylammonium ions the crystallographic radii are seen to be much bigger than their hydrodynamic size. On the other hand, B(OH)_4^- does not behave as a strongly hydrated ion like Li^+ because in this case one would expect a hydrodynamic radius larger than the crystallographic one.

A similar conclusion is drawn from the value of the borate partial molar volume at infinite dilution, which can be accounted for by the sum of the crystallographic molar volume and the electrostrictive contribution. The latter was calculated employing the semi-empirical expression²⁴

$$\bar{V}_{\text{elect}}^\circ(i) = \frac{Bz_i^2}{r_i}. \quad (4)$$

The value of the constant B depends to a certain extent on the choice of a particular treatment of the volume data; however, for an ion of the size of B(OH)_4^- an average value of $-4.5 \pm 0.7 \text{ cm}^3 \text{ mol}^{-1}$ is obtained. Thus,

$$\bar{V}^\circ[\text{B(OH)}_4^-] - (\bar{V}_{\text{cryst}}^\circ + \bar{V}_{\text{elect}}^\circ) = -2.9 \text{ cm}^3 \text{ mol}^{-1}$$

and the borate ion appears to have an ionic partial molar volume which is close to that expected for a rigid sphere having its crystallographic size and bearing a single charge.

The value of B_η for B(OH)_4^- (cf. table 1) corresponds to that of a typical "structure-making" ion. Since the B_η coefficient is known to be related to the entropy of hydration of ions, it seemed interesting to calculate this thermodynamic property for the borate ion. We have also calculated the entropy of hydration of the ions BF_4^- and H_2PO_4^- , whose sizes are similar to that of borate (2.33 and 2.50 Å, respectively) and whose interactions with water may be usefully compared with those of B(OH)_4^- . The entropies of formation of the aqueous ions (1 molar standard state) have been taken from Circular 500 of NBS. For the borate ion the value in Circular 500 was corrected to that corresponding to B(OH)_4^- , since the value reported is the entropy of formation of the H_2BO_3 ion. The entropies of the gaseous ions (1 atm standard state) were calculated by the standard methods employing the spectroscopic data reported in the literature.³⁰ Table 3 summarizes the results of the calculations. The data in table 3 show that B(OH)_4^- and H_2PO_4^- have a large negative S_{hydr}° which implies that they are both "structure-makers". The similarity of the interactions of these two ions with water is further supported by the large value of $B_\eta = 0.34 \text{ dm}^3 \text{ mol}^{-1}$ of H_2PO_4^-

TABLE 3.—STANDARD ENTROPY OF HYDRATION OF RELEVANT ANIONS

	r_{cryst} /Å	S_{aq}°	S_{g}° /J K ⁻¹ mol ⁻¹	$-S_{\text{hydr}}^\circ$
BF_4^-	2.33	192.5	265.7	73.22
B(OH)_4^-	2.44	123.0	266.9	143.9
H_2PO_4^-	2.50	110.9	272.0	161.1

and by the fact that its Stokes' radius, 2.85 Å, is close to the crystallographic radius.³¹ On the other hand, BF₄⁻ behaves very differently, being a typical "structure-breaker". This general picture is supported by spectroscopic studies which indicate that borate-water interactions are stronger than those of XO₄⁻ oxyanions with water⁶ and that the BF₄⁻ - -H₂O interactions are much weaker than for the oxyanions.³²

A better way of comparing ion-water interactions in terms of ionic partial molar volumes, ionic B_η coefficients and entropies of hydration is to subtract from these quantities the contributions which do not reflect the ion-solvent specific interactions. For the two first properties we adopt the criteria proposed by Bramhall³³ that the contributions of the crystallographic hard spheres should be subtracted from the observed values. This is

$$10^3 \alpha = \bar{V}^\circ(i) - \bar{V}_{\text{cryst}}^*$$

and

$$\Delta B_\eta = B_\eta - 0.0025 \bar{V}_{\text{cryst}}^\circ.$$

For the entropy of hydration it is convenient to compare the cosphere contributions (S_{cos}°) with the hydration entropies, as suggested by Friedman and Krishnan.³⁴ These quantities are plotted for various univalent ions in fig. 2. It may be seen once more that the borate ion, like H₂PO₄⁻, is clearly a "structure-maker" but not in the same sense as Li⁺ is. They do not appear to alter the water structure in their immediate neighbourhood to a larger extent than that expected for a rigid sphere having one charge and their crystal radii. This is certainly related to the presence of surface OH⁻ groups in these ions and explains the attraction observed between the cospheres of Li⁺ and B(OH)₄⁻ ions. The lithium ion would approach the anion without perceiving a water structure very different from that in pure water and probably with a

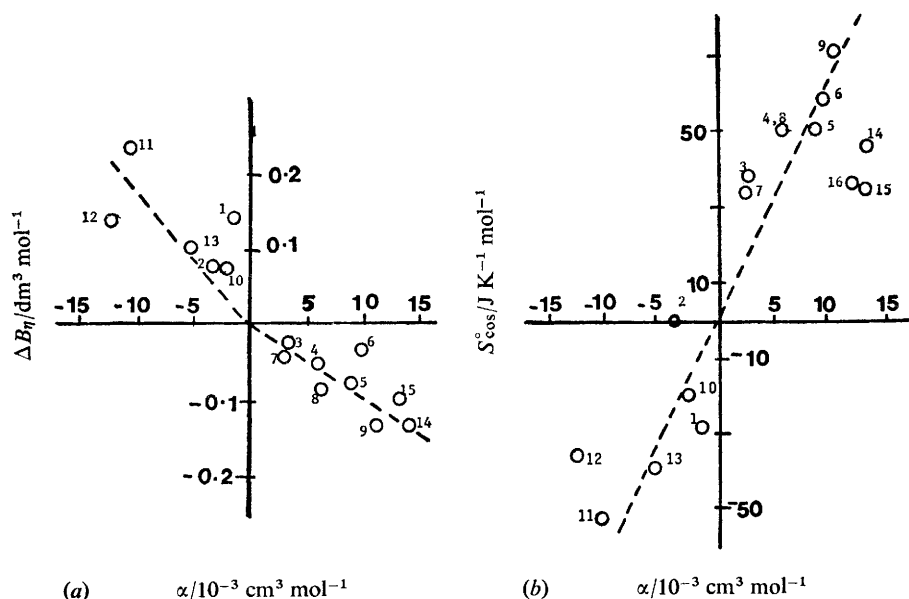
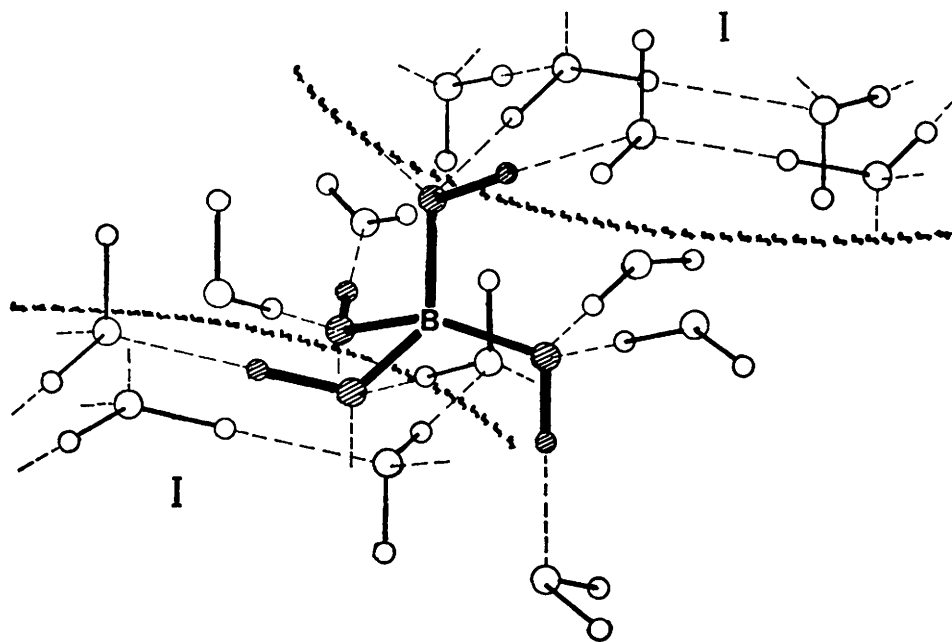


FIG. 2.—(a) ΔB_η (dm³ mol⁻¹) against α (cm³ mol⁻¹). (b) S_{cos}° (J K⁻¹ mol⁻¹) against α (cm³ mol⁻¹). Monovalent ions represented: 1 : Li⁺; 2 : Na⁺; 3 : K⁺; 4 : Rb⁺; 5 : Cs⁺; 6 : NH₄⁺; 7 : Cl⁻; 8 : Br⁻; 9 : I⁻; 10 : F⁻; 11 : H₂PO₄⁻; 12 : B(OH)₄⁻; 13 : OH⁻; 14 : ClO₄⁻; 15 : NO₃⁻; 16 : BF₄⁻.

* Following Bramhall,³³ $\bar{V}^\circ(i)$ has been taken in this expression as the conventional ionic partial molar volume [i.e., $\bar{V}^\circ(\text{H}^+) = 0.0$ cm³ mol⁻¹].



more favourable dipole moment orientation. This point is schematically illustrated in fig. 3 where it is shown that two OH groups of the borate ion can simultaneously occupy positions in lattice-like [ice-like regions (I) in fig. 3] regions of extensive hydrogen bonding which occur due to random fluctuations of the hydrogen-bonding structure of liquid water.

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