

Determination of the Acidity Constant of Boric Acid in Synthetic Sea Water Media

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The acidity constant of boric acid has been determined by potentiometric titrations in synthetic sea water covering a salinity range of 20–40 ‰ and a temperature range of 5–30°C. The activity scale is chosen so that the activity coefficient approaches unity when the concentrations of H^+ , OH^- , $B(OH)_3$ and $B(OH)_4^-$ approach zero in synthetic sea water of a certain salinity. The concentration unit is M_w , mol per kg solution.

This work is a determination of the acidity constant of boric acid (the stability constant for hydrolysis of boric acid) as defined by

$$K_B = [H^+][B(OH)_4^-]/[B(OH)_3] \quad (1)$$

in activity scales based on sea water of different salinities. These values should be used when correcting measured total alkalinity to carbonate alkalinity if the pH-alkalinity method is used for determination of the concentrations of the carbonate species in a sea water sample with our pH-scale¹ and dissociation constants of carbonic acid.^{2,3}

The total alkalinity of a sea water sample, not being polluted or anoxic, and neglecting trace phosphate and organic carboxylates, can be expressed in equilibrium concentrations by

$$A_t = [B(OH)_4^-] + 2[CO_3^{2-}] + [HCO_3^-] + [OH^-] - [H^+] \quad (2)$$

The carbonate alkalinity, denoted A_c and used in the expressions for calculation of the concentrations of the carbonate species, is defined by

$$A_c = 2[CO_3^{2-}] + [HCO_3^-] \quad (3)$$

Thus $[B(OH)_4^-]$ and $([OH^-] - [H^+])$ must be subtracted from A_t to evaluate A_c for a sample. The term $([OH^-] - [H^+])$ can be neglected for most sea water samples. The term $[B(OH)_4^-]$ can be expressed in K_B and B_t , defined by

$$B_t = [B(OH)_3] + [B(OH)_4^-] \quad (4)$$

by the equation

$$[\text{B}(\text{OH})_4^-] = B_t K_B / (K_B + [\text{H}^+]) \quad (5)$$

B_t can usually be calculated from the chlorinity by the constant ratio $B_t(\text{mol/kg})/\text{Cl}(\text{‰}) = 2.13 \times 10^{-5}$.

The activity scales based on sea water used in our definitions of constants and pH are treated in detail by Sillén⁴ and discussed by the present author in papers on the carbonate system.^{2,3}

Previously, Buch⁵ and Lyman⁶ have determined the acidity constant of boric acid in sea water at various salinities and temperatures. However, they used different activity scales for H^+ and the borate species. This is discussed in detail elsewhere.³

SYMBOLS AND UNITS

The concentration unit used in the present work is $M_w = \text{mol per kg solution}$, a pressure and temperature independent concentration unit suggested by Dyrssen and Sillén.⁷ Concentrations of buret solutions are given in $M = \text{mol per litre of solution}$.

Most of the notations used in the text are listed below:

- A_c carbonate alkalinity defined by eqn. (3).
- A_t total alkalinity defined by eqn. (2).
- B total concentration of boric acid in equilibrium solutions.
- B_0 value of B in starting equilibrium solutions.
- B_t total concentration of boric acid defined by eqn. (4).
- $C_{\text{Na}}, C_{\text{Mg}}, C_{\text{Ca}}, C_{\text{Cl}}, C_{\text{SO}_4}$, total concentrations of Na^+ , Mg^{2+} , Ca^{2+} , Cl^- , and SO_4^{2-} in equilibrium solutions.
- E measured emf.
- E_0 a constant in $E = E_0 + (RT \ln 10/F) \log h$.
- H excess hydrogen ion concentration.
- H_0 value of H in starting equilibrium solution.
- H_T excess hydrogen ion concentration over H_2O in buret solutions ($-H_T$ is the titre of sodium hydroxide).
- h free concentration of H^+ , $h = [\text{H}^+]$.
- K_B acidity constant of boric acid defined by eqn. (1).
- K_w the ionic product of water.
- S equilibrium solution.
- S_0 starting equilibrium solution.
- T_1, T_2 buret solutions.
- $\beta_{-10}, \beta_{-11}, \beta_{-13}$, stability constants defined under Calculations.
- $\sigma, \sigma(\text{H})$ standard deviations defined in Ref. 18.

EXPERIMENTAL

Chemicals and solutions. The *synthetic sea-water media* were prepared (mainly following Sillén^{4,8}) with composition of Na^+ , Mg^{2+} , Ca^{2+} , Cl^- , and SO_4^{2-} as previously described.³ Stock solutions of *boric acid* in synthetic sea water were prepared by weighing in sodium chloride, sodium sulphate, and stock solutions of magnesium- and calcium

chlorides, and adding distilled water to about 95 % of the final weight of the solution. After deaeration to remove carbon dioxide, a weighed amount of dried boric acid (Merck Suprapur[®]) was added followed by deaerated distilled water to the final weight of the solution.

Hydrochloric acid (Merck Titrisol[®]) was added to each weighed amount of equilibrium solution before titration started.

The *sodium hydroxide* was prepared from 50 % NaOH and standardized against potassium hydrogen phthalate.

Solutions of synthetic sea water with the double concentrations of all ions (except sodium ions; see T₂ below) were prepared and added from a second buret to keep the ionic strength and main composition of the equilibrium solutions constant. The *hydrogen gas* was purified in a Deoxo[®] (Engelhard Ind. AB) cartridge.

Apparatus. The *titration vessel* was a five-necked glass vessel. The *voltmeter* for measuring the emf of the cell was a Solartron digital voltmeter, model 1867, with 10 μ V resolution and free from measurable drift.

The *hydrogen electrodes* were prepared according to Bates.⁹ The *reference electrodes* were Ag,AgCl-electrodes (prepared according to Brown¹⁰) in a saltbridge solution of synthetic sea water saturated with AgCl. The design of the *saltbridge* has been described previously by the author.²

A paraffin oil bath *thermostat* was used which could be adjusted to the temperature desired within 0.05°C.

The equilibrium solution was stirred by a stream of hydrogen gas. The hydrogen gas from the tank was washed in three bottles containing H₂SO₄, NaOH, and synthetic sea water, and the stream was divided into two; one for the hydrogen electrode and one for stirring the solution.

THE EMF MEASUREMENTS

The experimental investigation of the hydrolysis of boric acid in sea water was carried out as potentiometric titrations. In each titration the analytical hydrogen excess H in the equilibrium solution S was varied by adding sodium hydroxide (solution T₁) from a buret. The concentrations of the medium ions in S were kept practically constant by adding equal volumes from T₁ and a buret solution T₂ described below. The total boron concentration was altered by dilution from 10 mM_w in the starting solution S₀ to about 8.8 mM_w in the final solution. The compositions of the solutions can be represented by the following equations:

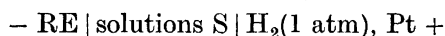
$$S = H \frac{M_w}{M_w} H^+, C_{Na} \frac{M_w}{M_w} Na^+, C_{Mg} \frac{M_w}{M_w} Mg^{2+}, C_{Ca} \frac{M_w}{M_w} Ca^{2+}, C_{Cl} \frac{M_w}{M_w} Cl^-, C_{SO_4} \frac{M_w}{M_w} SO_4^{2-}, B \frac{M_w}{M_w} B(OH)_3$$

$$T_1 = -H_T \frac{M_w}{M_w} NaOH$$

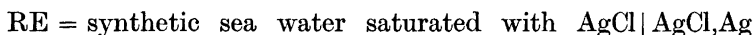
$$T_2 = (2C_{Na} + H_T) \frac{M_w}{M_w} Na^+, 2C_{Mg} \frac{M_w}{M_w} Mg^{2+}, 2C_{Ca} \frac{M_w}{M_w} Ca^{2+}, 2C_{Cl} \frac{M_w}{M_w} Cl^-, 2C_{SO_4} \frac{M_w}{M_w} SO_4^{2-}$$

The starting solution contained an excess of H⁺ (over H₂O and B(OH)₃). Gran¹¹ extrapolation can be performed using titration points with excess of H⁺ to give preliminary values of E_0 , the constant in Nernst's equation (6).

The titrations were followed by measuring the emf, E , of the cell



where RE is a reference half cell of the composition



The emf of this cell, in the range of $\log h$ investigated, can be written

$$E = E_0 + (RT \ln 10/F) \log h \quad (6)$$

since the liquid junction potential is negligible if the test and reference solutions are based on the same ionic medium and the junction is well defined.¹² Thus the hydrogen ion concentration at equilibrium, h , can be evaluated from eqn. (6). After an addition of the buret solutions, the emf values became constant in 10 to 20 min. Back titrations were not performed since the reversibility of the borate equilibria has been previously demonstrated by Ingri.¹³

CALCULATIONS AND RESULTS

For each titration, about 30 (V_T, E)-values ("titration points") were collected in the $\log h$ range $-2.7 > \log h > -9.5$. These primary data were processed with an IBM 360/65 computer, using a Fortran version of the generalised least squares program LETAGROP, with procedures ETITR written by Sillén *et al.*^{14,15} In the LETAGROP calculations no other species were assumed to be present in the solution than H^+ , OH^- , $B(OH)_3$, $B(OH)_4^-$, and $B_3O_3(OH)_4^-$. Each titration was executed separately. With H^+ and $B(OH)_3$ as components, the stability constants can be written

$$\beta_{-10} = K_w = [H^+][OH^-] \quad (7)$$

$$\beta_{-11} = K_B = [B(OH)_4^-]/h^{-1}[B(OH)_3] \quad (8)$$

and

$$\beta_{-13} = [B_3O_3(OH)_4^-]/h^{-1}[B(OH)_3]^3 \quad (9)$$

(Adding $3H_2O$, the species $B_3O_3(OH)_4^-$ can be written $(B(OH)_3)_3OH^-$; the $-1,3$ -complex of $B(OH)_3$ with H^+ .) In the executions the constant β_{-11} , and the "analytical parameters" E_0 , H_0 , and B_0 were adjusted. The values of K_w and β_{-13} were held fixed. Values for K_w were taken from Ref. 2 and the value of β_{-13} was chosen as 10^{-6} in all titrations. This was based on a rough mean obtained from preliminary calculations. The reasons for including the $-1,3$ -complex in the calculations is discussed elsewhere.¹⁶

Changes in the liquid junction potential have been neglected because of the low values of h and $[OH^-]$ in the titrations. Experiments described in a previous paper² gave evidence for protolytic impurities present in all solutions on the concentration level $2 \times 10^{-5} M_w$. However, their inclusion in the LETAGROP calculations only very slightly influenced the error squares sum and pK_B ; they were therefore omitted.

During the titration the concentration of $MgOH^+$ increases, but no correction was made because $Mg(OH)_2$ is not precipitated and $[Mg^{2+}]$ and thus $[OH^-]/[MgOH^+]$ will be practically constant. $MgOH^+$ may therefore be included as a medium effect in K_w and is considered in the choice of activity scale. This is fully discussed in a subsequent paper.¹⁷ The error squares sum minimized was $U = \sum (H_{calc} - H_{tot})^2$, defined in Ref. 15. The quantity $(H_{calc} - H_{tot})/B_{tot}$, the "error" in H_{tot} divided by B_{tot} in each titration point, showed a random scattering of numerically small values around zero.

Table 1. Values from the output of LETAGROP executions of $-\log \beta_{-11}$, the standard deviation given as 3σ (as defined in Ref. 18), and the standard deviation in H , $\sigma(H)$ (defined in Ref. 18), for the titrations performed in this work.

Temperature °C	Salinity ‰	$-\log \beta_{-11} =$ pK_B	3σ	$\sigma(H)$ $\times 10^3(\text{mM})$
25	35	8.611 ^a	0.003	5.15
25	35	8.611 ^a	0.002	4.25
15	35	8.728	0.008	14.7
15	35	8.731	0.004	8.3
5	35	8.857 ^b	0.003	6.91
5	35	8.862 ^b	0.004	5.97
25	30	8.638	0.003	4.20
25	20	8.716	0.004	6.89

^a Frydman *et al.*¹⁹ found $pK_B = 8.63 \pm 0.03$ in a synthetic sea water medium similar to that used in this work.

^b Frydman *et al.*¹⁹ found $pK_B = 8.86 \pm 0.02$.

In Table 1 values of $\log \beta_{-11} = pK_B$ with standard deviation (given as 3σ) and the standard deviation in H , $\sigma(H)$, as defined in Ref. 18, are listed for eight titrations. The values for 35 ‰ were plotted against $1/T$ and a linear regression of the pK_B -values against $1/T$ was performed assuming that ΔH° for the hydrolysis of boric acid is constant over the temperature range studied. The equation for the regression line is

$$pK_B = 1026/T + 5.170 \quad (10)$$

A procedure to interpolate values of pK_B in the temperature range 5° to 30°C and salinity range 20 to 40 ‰ is described in Ref. 16.

DISCUSSION

The values of pK_B for 35 ‰ given in tables of Buch,⁵ Lyman,⁶ and this work are listed in Table 2 for temperatures between 5 and 30°C. Larger differences between the values for 5 and 30°C are observed for the constants determined in this work than for the constants from the other authors. The

Table 2. Values of pK_B in sea water as tabulated by Buch,⁵ Lyman,⁶ and this work form for 35 ‰ salinity.

Author	Temp. °C					$pK_B(5^\circ) -$ $pK_B(30^\circ)$	
	5	10	15	20	25		30
Buch	8.85	8.81	8.75	8.72	8.68	8.65	0.20
Lyman	8.89	8.84	8.79	8.75	8.70	8.66	0.23
This work	8.86	8.79	8.73	8.67	8.61	8.55	0.31

different pH-scales used may explain this observation. The differences between values of pH in the scales according to Sørensen (used by Buch) and NBS (used by Lyman) are approximately constant with temperature. The pH scale used in this work is in very close agreement with an activity scale for H^+ where activity can be replaced by the total concentration of H^+ , both free and bound to sulfate in the sea water medium. On this scale the variation of pH with temperature seems to be greater than the temperature variation of pH on other scales. The difference of pK -values between high and low salinities is greater for boric acid than for carbonic acid. This indicates that the medium ions form somewhat stronger complexes with $B(OH)_4^-$ than with HCO_3^- . In Ref. 17 comparisons are made between values of the acidity constant of boric acid determined in synthetic sea water and sodium chloride media of corresponding ionic strength. A special investigation of the weak complexing between Ca^{2+} and $B(OH)_4^-$ in 3 M $NaClO_4$ has been carried out by Frydman *et al.*¹⁹

A calculation of the distribution of boron between the different species proposed by Ingri using HALTAFALL^{20,21} was performed for the total boron concentration of 0.00042 M found in sea water of 35 ‰ salinity. The stability constants valid for 3 M $NaClO_4$ were used. The polynuclear species contributed to less than 0.001 ‰ of the total boron content. It might be safe to state that no other species are formed in the hydrolysis of boric acid in sea water than the borate ion $B(OH)_4^-$ and its complexes with the medium ions.

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