Experimental evaluation of the isotopic exchange equilibrium
\[ ^{10}\text{B(OH)}_3 + ^{11}\text{B(OH)}_4^- = ^{11}\text{B(OH)}_3 + ^{10}\text{B(OH)}_4^- \] in aqueous solution

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Abstract

The precision of spectrophotometric measurements of indicator absorbance ratios is sufficient to allow evaluation of small isotopically induced differences in the dissociation constant of boric acid \((K_B)\). The quotient of \(^{11}K_B\) and \(^{10}K_B\), obtained using isotopically \(\geq 99\%\) pure borate/boric acid buffers, provides an equilibrium constant for the reaction \(^{10}\text{B(OH)}_3 + ^{11}\text{B(OH)}_4^- \rightleftharpoons ^{11}\text{B(OH)}_3 + ^{10}\text{B(OH)}_4^-\) which heretofore had not been experimentally determined. Previous theoretical and semi-empirical evaluations of this equilibrium, which is important for assessments of the paleo-pH of seawater and the paleo-\(p\text{CO}_2\) of the atmosphere, have yielded constants, \(^{11}K_B\) \(= ^{10}K_B/^{11}K_B\), that have ranged between \(1.0194\) and approximately \(1.033\). The experimentally determined value \(^{11}K_B\) \(= 1.0285 \pm 0.0016\) (mean \(\pm 95\%\) confidence interval) obtained at \(25^\circ C\) and 0.63 molal \((\text{mol} \cdot \text{kg}^{-1} \cdot \text{H}_2\text{O})\) ionic strength is in much better agreement with recent theoretical assessments of \(^{11}K_B\) that have ranged between 1.026 and 1.033, than the much-cited original estimate \((1.0194)\) of Kakihana et al. (1977) \([\text{Fundamental studies on the ion-exchange separation of boron isotopes. Bulletin of Chemical Society of Japan 50, 158–163}]\). Since the activity quotient for the fractionation reaction is almost equal to unity, it is expected that the \(^{11}K_B\) value obtained in this study will be applicable over a wide range of solution compositions and ionic strengths.

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1. Introduction

The boron isotopic composition of marine carbonates constitutes a promising tracer of the paleo-pH of seawater and the paleo-\(p\text{CO}_2\) of the atmosphere (Hemming and Hanson, 1992; Spivack et al., 1993; Sanyal et al., 1995; Palmer et al., 1998;
Pearson and Palmer, 2000). Accurate characterization of the aqueous equilibrium quotient appropriate to Eq. (1) is a keystone in the foundation of paleo-pH and paleo-\(\rho\)CO\(_2\) reconstruction (Hemming and Hanson, 1992):

\[
^{10}\text{B(OH)}_3 + ^{11}\text{B(OH)}_3 \\
\rightleftharpoons ^{11}\text{B(OH)}_3 + ^{10}\text{B(OH)}_3.
\] (1)

Despite the significance of this equilibrium, it has been noted (Pagani et al., 2005; Zeebe, 2005; Liu and Tossell, 2005) that there have been no direct experimental determinations of the key equilibrium quotient \((^{11-10}K_B)\) appropriate to Eq. (1):

\[
^{11-10}K_B = [^{11}\text{B(OH)}_3][^{10}\text{B(OH)}_3] \\
/[^{10}\text{B(OH)}_3][^{11}\text{B(OH)}_3].
\] (2)

The earliest estimate for \(^{11-10}K_B\) (\(^{11-10}K_B = 1.0194\) at 25°C) is that of Kakihana et al. (1977). Although the value is widely cited, recent assessments indicate that \(^{11-10}K_B\) may be significantly larger: \(^{11-10}K_B = 1.033\) (Palmer et al., 1987); \(^{11-10}K_B = 1.0260\) (Oi, 2000a; Oi and Yanase, 2001); \(^{11-10}K_B = 1.0267\) (Pagani et al., 2005); \(^{11-10}K_B \geq 1.030\) (Zeebe, 2005) and \(^{11-10}K_B = 1.0263\) (Liu and Tossell, 2005).

In the present work, we have used precise procedures for spectrophotometric measurement of solution pH (Byrne, 1987) to measure differences in the dissociation constants of \(^{11}\text{B(OH)}_3\) and \(^{10}\text{B(OH)}_3\). Thousands of at-sea measurements of seawater pH (Clayton and Byrne, 1993; Clayton et al., 1995; Byrne et al., 1999) demonstrate that spectrophotometric pH measurements obtained via absorbance ratios are precise to ±0.0004 units or better. Solution pH measurements precise to within ±0.0004, in conjunction with appropriately designed comparisons of borate/boric acid buffering characteristics, can be used to resolve much of the controversy surrounding indirect assessments of \(^{11-10}K_B\). Herein we present both the basis for spectrophotometric measurements of \(^{11-10}K_B\) and the first direct measurements of this important equilibrium quotient.

2. Theory

Subsequent to the addition of boric acid (\(\text{B(OH)}_3\)) to a solution containing dissolved KCl, the charge balance relationship for the solution can be written as

\[
[K^+] + [Na^+] + [H^+] = [Cl^-] + [B(OH)_4^-] \\
+ [OH^-] + [HI^-] + 2[I^-].
\] (3)

Since \([K^+] = [Cl^-]\), and total indicator concentration \(I_T = [HI^-] + [I^-]\), Eq. (3) can be rewritten as

\[
[Na^+] + [H^+] = [B(OH)_4^-] + [OH^-] + [I^-] + I_T.
\] (4)

The dissolved concentration of borate ion ([\(\text{B(OH)}_4^-\)]) can be written as

\[
[B(OH)_4^-] = B_T/(1 + [H^+]/K_B),
\] (5)

where \(B_T\) is the total dissolved boron concentration ([\(\text{B(OH)}_3\)]) and the \(\text{B(OH)}_3\) dissociation constant is written as

\[
K_B = [B(OH)_4^-][H^+]/[\text{B(OH)}_3].
\] (6)

The hydroxide concentration in solution can be written in terms of the \(\text{H}_2\text{O}\) hydrolysis constant \((K_w)\)

\[
[\text{OH}^-] = K_w [H^+]^{-1}
\] (7)

and the concentration of indicator in anionic form is written in analogy to Eq. (6) as

\[
[I^-] = I_T/(1 + [H^+]/K_I),
\] (8)

where

\[
K_I = [I^-][H^+][\text{HI}^-]^{-1}.
\] (9)

Under our experimental conditions, concentrations of the \(\text{H}_2\text{I}\) indicator species are insignificant. Consequently, combining Eqs. (4), (5), (7), and (8), the dissociation constant of boric acid can be written as

\[
K_B = [H^+][(][Na^+] + [H^+] - K_w[H^+]^{-1} - [I^-] - I_T) \\
/((B_T - [Na^+]) - [H^+] \\
+ K_w[H^+]^{-1} + [I^-] + I_T)).
\] (10)

The \(pK_B\) of boric acid (\(pK_B = -\log K_B\)) can then be written in the following form:

\[
pK_B = pH - \log \chi,
\] (11)

where

\[
\chi = ([Na^+] + [H^+] - K_w[H^+]^{-1} - [I^-] - I_T) \\
/((B_T - [Na^+]) - [H^+] \\
+ K_w[H^+]^{-1} + [I^-] + I_T)
\] (12)

Eq. (11) can be applied to solutions containing pure \(^{10}\text{B}\) and pure \(^{11}\text{B}\) buffers (\(\text{B(OH)}_3\))\(^{10}\) (\(\text{B(OH)}_4^-\)). Measurements using \(^{10}\text{B}\) and \(^{11}\text{B}\) can be combined
to provide equilibrium data as follows:

\[ p^{11}K_B - p^{10}K_B = 11(pH) - 10(pH) \]

\[ - \log(11/10). \]  

(13)

The left side of Eq. (13) is equal to

\[ \log(11K_B/10K_B) = \log(11-10K_B) \]  

(14)

and provides the equilibrium constant appropriate to Eq. (1). The right-hand side of Eq. (13) is composed of two terms. The term written as \( 11(pH) - 10(pH) = \Delta pH \) is the difference in the spectrophotometrically measured pH of the \( 11B \) and \( 10B \) buffer solutions. Spectrophotometric pH can be determined with sulfonephthalein indicators using an equation of the following form (Byrne, 1987):

\[ pH = pK_I + \log((R - e_1)/(e_2 - Re_3)), \]

(15)

where \( pK_I = -\log K_I \) is defined by Eq. (9), \( R \) is an absorbance ratio, and \( e_i \) are molar absorptivity coefficient ratios. Since \( pK_I \) is invariant at constant temperature, ionic strength and solution composition, the \( \Delta pH \) term in Eq. (13) can be written as

\[ 11(pH) - 10(pH) = \log((11R - e_1)/(e_2 - 11Re_3)) \]

\[ - \log((10R - e_1)/(e_2 - 10Re_3)), \]

(16)

where \( 11R \) and \( 10R \) are absorbance ratios measured in \( 11B \) and \( 10B \) buffers. The final term in Eq. (13) is essentially zero if \([Na^+] > [B_3[H^]\] - \[K_0[H^]+[I^-] + I_T \] and \([B_4-[Na^+]] > [B_3[H^]+K_0[H^]+[I^-] + I_T \]. Under our experimental conditions, wherein \([Na^+] \approx 0.02 \text{ mol kg}^{-1} \text{ H}_2\text{O}, B_T \approx 0.05 \text{ mol kg}^{-1} \text{ H}_2\text{O, } pH \approx 8.6, I_T \approx 3 \times 10^{-6} \text{ mol kg}^{-1} \text{ H}_2\text{O and } \Delta pH \leq 0.03, \) the term \( \log(11/10) \) is smaller than 0.0001. In this case, log \( (11-10K_B) \) can be determined solely through observations of changes in sulfonephthalein indicator absorbance ratios \( (11R \text{ and } 10R) \):

\[ \log(11-10K_B) = \log((11R - e_1)/(e_2 - 11Re_3)) \]

\[ - \log((10R - e_1)/(e_2 - 10Re_3)), \]

(17)

3. Materials and procedures

Boric acid as \( 10B(OH)_3 \) (99 atom% \( 10B \)) and \( 11B(OH)_3 \) (99 atom% \( 11B \)), KCl (99.99% purity), 1.0 M NaOH, and pH indicator thymol blue were obtained from Sigma-Aldrich. The boric acid and KCl were dried in a dessicator containing \( P_2O_5 \) for 3 days before use. Equimolar \( 10B(OH)_3 \) and \( 11B(OH)_3 \) solutions (0.05 mol kg\(^{-1}\) \text{ H}_2\text{O}) were prepared in 0.6 mol kg\(^{-1}\) \text{ H}_2\text{O} KCl. Approximately 25 g of each solution were then weighed into 10 cm spectrophotometric cells. Equal amounts of 1.0 M NaOH, approximately 0.5 g, were then added (by weight) to each cell. These procedures resulted in two solutions that were equimolar in \( Na^+ \), and whose concentration of \( 10B \) and \( 11B \) were identical. For all solutions, \( B_T \approx 0.05 \text{ mol kg}^{-1} \text{ H}_2\text{O, } [Na^+] \approx 0.02 \text{ mol kg}^{-1} \text{ H}_2\text{O, and } pH \approx 8.6. \)

The pH of the \( 10B(OH)_3/10B(OH)_4^- \) and \( 11B(OH)_3/11B(OH)_4^- \) buffers, prepared as described above, were measured via the spectrophotometric procedures described in Zhang and Byrne (1996). Absorbance measurements were obtained using an HP 8453 spectrophotometer. The temperature of the solution was controlled \( (25 \pm 0.1 \text{ C}) \) and the salinity dependence of the HSO\(_4^-\) standard given in DOE (1994). It should be noted, once again, that the \( pK_I \) of thymol blue is of no importance in \( \Delta pH \) determinations since \( pK_I \) is constant at constant temperature, ionic strength and medium composition.

4. Results and discussion

The results of four experiments, each containing five paired mixtures of \( 10B(OH)_3/10B(OH)_4^- \) and \( 11B(OH)_3/11B(OH)_4^- \), are shown in Table 1. The standard deviation of the \( \Delta pH \) measurements in Table 1 was 0.0015. The average difference in pH
between the isotopic mixtures was
\[ \Delta p_{\mathrm{H}} = 0.0122 \pm 0.0007 \]  
(mean $\pm$ 95% confidence interval). \( \cdotp \) (20)

This result, in conjunction with Eqs. (13) and (14) indicates that the equilibrium constant appropriate to Eq. (1) is
\[ {^{11-10}K_B} = 1.0285 \pm 0.0016 \]  
(mean $\pm$ 95% confidence interval). \( \cdotp \) (21)

This value is significantly larger than the estimates of Kakihana et al. (1977) and Sanchez-Valle et al. (2005), \( {^{11-10}K_B} = 1.0194 \) and \( {^{11-10}K_B} = 1.0176 \), which were obtained using spectral methods, but is in generally good agreement with a variety of theoretical predictions (Zeebe, 2005; Liu and Tossell, 2005; Palmer et al., 1987; Oi, 2000a; Oi and Yanase, 2001) and empirical estimates (Pagani et al., 2005), which range between 1.026 and 1.033.

The pH precisions shown in Table 1 (\( \Delta p_{\mathrm{H}} \) standard deviation = 0.0015) are slightly inferior to those that we have achieved at sea in measurements of seawater, which is a somewhat more poorly buffered medium than the experimental solutions composed in the present investigation. We strongly suspect that the precision of our pH measurements, and therefore the accuracy of our \( \Delta p_{\mathrm{H}} \) and \( {^{11-10}K_B} \) measurements is amenable to improvement. In this regard, two key improvements are recommended. Use of a double beam spectrometer should significantly reduce potential absorbance drifts that can occur between measurements of \( ^{10}\mathrm{B} \) and \( ^{11}\mathrm{B} \) buffers. Secondly, it would be beneficial to compose all solutions under an atmosphere free of CO\(_2\). With such changes, and others, we suspect that the standard deviation of Table 1 \( \Delta p_{\mathrm{H}} \) measurements can be reduced to $\pm$0.0005 or better.

It should be noted that the equilibrium observations in this study were obtained at buffer intensities that are substantially higher than those needed for stable spectrophotometric pH measurements. If the total boron concentrations in our experiments were reduced by a factor of 10, the resulting buffer intensities would still substantially exceed those of seawater. As such, toward the goal of eliminating the potential influence of polyborate formation on fractionation, it would be useful to employ the procedures outlined in this work over a range of boron concentrations. The equilibrium data for polyborates in 1 molal KCl at 25°C presented by Baes and Mesmer (1976) indicate that polyborate species represented approximately 5.3% of the total

<table>
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<th>Experiment</th>
<th>( ^{10}\mathrm{pH} (^{10}\mathrm{B(OH)}_3 + \mathrm{NaOH}) )</th>
<th>( ^{11}\mathrm{pH} (^{11}\mathrm{B(OH)}_3 + \mathrm{NaOH}) )</th>
<th>( ^{11}\mathrm{pH} - ^{10}\mathrm{pH} )</th>
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Average: \( \Delta p_{\mathrm{H}} = 0.0122 \pm 0.0007 \) (mean $\pm$ 95% confidence interval).
boron in our experiments. Of this total, $B_3O_4(OH)_4$ accounted for approximately 4.6% of the total boron and the remainder (0.7%) was the dimer, $B_2O(OH)_5^-$. A 10-fold reduction in the total boron concentration would reduce the trimer concentration by a factor of approximately 100 and the dimer by a factor of 10. Measurements over a range of concentrations would allow extrapolation of the equilibrium isotopic exchange constant ($11^{-10}K_B$) to total boron levels that exist in seawater and other natural aqueous solutions. Although it is desirable to minimize polyborate formation, there are reasons to expect that the influence of polyborate formation on $11^{-10}K_B$ will be small even at boron concentrations above those utilized in the present work. The calculations of Oi (2000b) indicate that boron fractionations into four co-ordinate $B(OH)_4^-$ and the four co-ordinate sites of $B_3O_4(OH)_4$ are very similar, 1.026 and 1.030, respectively (Table 2 of Oi, 2000b).

Finally, although the equilibrium characterizations in this study were obtained in a simple synthetic solution, it should be noted that insofar as the activity quotient for reaction (1) is very close to unity, the $11^{-10}K_B$ value obtained in this work should be applicable over a wide range of solution compositions and ionic strength. Using the procedures described in this work, this expectation can be directly examined in synthetic solutions that closely mimic the natural composition of seawater.

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