



Controls on the pH of hyper-saline lakes – A lesson from the Dead Sea



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ABSTRACT

The pH of aqueous environments is determined by the dominant buffer systems of the water, defined operationally as total alkalinity (TA). The major buffer systems in the modern ocean are carbonic and boric acids of which the species bicarbonate, carbonate and borate make up about 77%, 19% and 4% of the TA, respectively. During the course of seawater evaporation (e.g. lagoons) the residual brine loses considerable portion of the dissolved inorganic carbon (DIC) and carbonate alkalinity (CA) already at the early stages of evaporation. DIC and CA decrease due to massive precipitation of CaCO_3 , while total boron (TB) increases conservatively, turning borate to the dominant alkalinity species in marine derived brines. In the present work we assess the apparent dissociation constant value of boric acid (K'_b) in saline and hypersaline waters, using the Dead Sea (DS) as a case study. We explain the DS low pH (~ 6.3) and the effect of the boric and carbonic acid $\text{p}K'$ -s on the behavior of the brine's buffer system, including the pH increase that results from brine dilution.

The K'_b in DS was estimated from TB, TA, DIC and pH data measured in this study and early empirical data on artificial DS brines containing just carbonic acid. The K'_b value was corroborated by Pitzer ion interaction model calculations using PHREEQC thermodynamic code applied to the chemical composition of the DS. Our results show that K'_b increases considerably with the brine's ionic strength, reaching in the DS to a factor of 100 higher than in "mean" seawater. Based on theoretical calculations and analyses of other natural brines it is suggested that brines' composition is a major factor in determining the K'_b value and in turn the pH of such brines. We show that the higher the proportion of divalent cations in the brine the higher the dissociation constants of the weak acids (presumably due to formation of complexes). The low pH of the Dead Sea is accordingly explained by its extremely high ionic strength ($\text{TDS} = 348 \text{ g/L}$) and the dominance of the divalent cation, Mg^{2+} . Other natural hyper-saline brines with high concentration of divalent cations such as Kunteyi Lake in China and Don-Juan Pond in Antarctica follow the same general pattern. In contrast, the high pH of soda lakes results not only from their high TA but also by the dominance of the monovalent cation, Na^+ . Our study emphasizes the strong control of brine composition on $\text{p}K'_b$ and pH. These factors should be taken into consideration when reconstructing past and present environmental evaporitic environments.

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1. Introduction

The pH of aqueous environments is determined by the dominant buffer systems of the water. Operationally, the acid-neutralizing capacity is defined by the total alkalinity (TA) which is deter-

mined by potentiometric titration with strong acid (Emerson and Hedges, 2008; Stumm and Morgan, 1996; Zeebe and Wolf-Gladrow, 2001). In many natural waters, particularly groundwater, this term is associated solely with carbonic acid deprotonated species. However, other dissolved weak acid species, such as boric acid, silicic acid and dissolved organic acids may also contribute to TA. For example, in seawater, boric acid makes up $\sim 4\%$ of the total alkalinity (TA), and, neglecting H^+ and OH^- , TA is the sum of equivalents of the deprotonated species of carbonic and boric acids:

$$\begin{aligned} \text{TA} &\approx [\text{B}(\text{OH})_4^-] + [\text{HCO}_3^-] + 2 \cdot [\text{CO}_3^{2-}] \\ &= \text{TB} \cdot \alpha_B + \text{DIC} \cdot (\alpha_1 + 2 \cdot \alpha_2) \end{aligned} \quad (1)$$

Abbreviations: DSB, Dead Sea brine; TA, total alkalinity; CA, carbonate alkalinity; BA, borate alkalinity; DIC, dissolved inorganic carbon; TB, total boron; β , buffer intensity.

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where square brackets denote concentrations in mmol kg^{-1} , α_B is the molar fraction of B(OH)_4^- out of total B (TB), and α_1 and α_2 are the molar fractions of HCO_3^- and CO_3^{2-} , respectively, out of total dissolved inorganic carbon (DIC). TB and DIC are the sum of the following:

$$\text{TB} = [\text{B(OH)}_4^-] + [\text{B(OH)}_3] \quad (2)$$

$$\text{DIC} = [\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (3)$$

where

$$[\text{H}_2\text{CO}_3^*] = [\text{CO}_{2(\text{aq})}] + [\text{H}_2\text{CO}_3]$$

Carbonic acid is the major buffer in seawater, whereby the carbonate alkalinity (CA, the last term in the right part of Eq. (1)) comprises $\sim 96\%$ of TA, while borate alkalinity (BA, the first term in the right part of Eq. (1)) comprises just $\sim 4\%$. However, beyond a degree of evaporation of ~ 6 times seawater, 70% of the original CA is lost due to precipitation of aragonite (Lazar and Erez, 1992; Lazar et al., 1983). This implies that BA becomes a major buffer in marine derived brines.

The modern Dead Sea (DS) is a hypersaline lake characterized by high divalent cations, calcium and magnesium concentrations, low Na/Cl ratio and relatively low sulfate and DIC (Neev and Emery, 1967; Zak, 1967). Its present composition evolved by evaporation of seawater that entered the DS rift valley in the late Miocene – early Pliocene (the Sedom Lagoon) and underwent salt precipitation and water–rock interactions. Among the latter, dolomitization is most important since it introduced Ca to the brine, thereby allowing the precipitation of gypsum that removed much of the sulfate which remained from the evaporitic stage. Dolomitization also allowed the brine to attain its low Mg/Ca ratio relative to evaporated seawater. Freshwater inflows continuously supplied the basin with bicarbonate and sulfate, and as a result, during glacial periods which were characterized by positive water balance, the Ca-rich brine deposited alternating sequences of layered aragonite and gypsum, along with detrital material (e.g. Neev and Emery, 1967; Neugebauer et al., 2014; Stein, 2001; Stein et al., 1997; Zak, 1967). A detailed description of its geochemical evolution can be found in Starinsky (1974), Gavrieli and Stein (2006), Katz and Starinsky (2008).

The pH of the current DS (during 2013; total dissolved solids, $\text{TDS} = 348 \text{ gL}^{-1}$, density 1.242 kgL^{-1}) is 6.27 ± 0.03 (Golan et al., 2014). During dilution with distilled water the pH of the brine rises (Amit and Bentor, 1971; Ben-Yaakov and Sass, 1977; Golan et al., 2014) whereas it decreases during evaporation (Stiller et al., 1985). Similar decrease in pH with increasing ionic strength was observed in other natural brines (e.g. Lazar and Erez, 1992; Rieke and Chilingar, 1962; Zheng and Liu, 2009). Sass and Ben-Yaakov (1977) showed that the apparent dissociation constants (K' , in which H^+ is expressed in activity, a_{H^+} , and the other species in concentrations) of the carbonate species in the DS brine (DSB) and synthetic DSB are higher than their values in mean seawater. They suggested K'_1 and K'_2 , values (defined in Eq. (4) and Eq. (5)) of $10^{-5.09}$ and $10^{-6.23}$, respectively for the DSB at $\text{TDS} = 330 \text{ gL}^{-1}$, significantly higher than the mean seawater values of $10^{-6.0}$ and $10^{-9.1}$, respectively (Mehrbach et al., 1973).

$$K'_1 = \frac{[\text{HCO}_3^-] \cdot a_{\text{H}^+}}{[\text{H}_2\text{CO}_3^*]} \quad (4)$$

$$K'_2 = \frac{[\text{CO}_3^{2-}] \cdot a_{\text{H}^+}}{[\text{HCO}_3^-]} \quad (5)$$

Accordingly, at a given pH, the relative abundance of HCO_3^- and CO_3^{2-} in the high ionic strength (I) DSB is higher than in seawater by factors of ~ 10 and ~ 1000 , respectively. The relatively

high CO_3^{2-} concentration, as dictated by the low $\text{p}K'$ -s ($= -\log K'$) of the carbonate species in the DSB, explain also the precipitation of aragonite from the DSB at its rather low pH (Sass and Ben-Yaakov, 1977). These observations are supported by studies on other natural and synthetic brines, which also exhibit decreasing $\text{p}K'$ s with increasing ionic strength (e.g., Dickson, 1990; Felmy and Weare, 1986; Hansson, 1973; He and Morse, 1993; Hershey et al., 1986; Rogers and van den Berg, 1988).

Early studies indicated that the TA of the DSB is not comprised solely of the carbonate system (Barkan et al., 2001; Luz et al., 1997; Neev and Emery, 1967; Stiller et al., 1985). Based on the relatively high TB concentrations it was suggested that borate (B(OH)_4^- , the boric acid species, Eq. (6)), is the major weak acid in the DSB (Luz et al., 1997; Schoenfeld and Held, 1965; Stiller et al., 1985; Vengosh et al., 1991). The present study evaluates quantitatively the apparent dissociation constant (H^+ in activity, other species in concentrations) of boric acid (K'_B) in the DSB and its role in determining the brine's low pH:

$$K'_B = \frac{[\text{B(OH)}_4^-] \cdot a_{\text{H}^+}}{[\text{B(OH)}_3]} \quad (6)$$

The $\text{p}K'_B$ derived in this study along with the latest chemical data is then used to explain some of the phenomenon recorded previously in the lake. Finally, we show that the ionic composition, and not only the ionic strength, determines the pH of the DSB and other natural brines by controlling the $\text{p}K'$ values of both the DIC and TB systems.

2. Methods

2.1. Sampling: location and procedures

DSB was collected by Niskin bottles near the center of the lake (sampling site EG-320). The brine was analyzed for density, major ionic composition, DIC, pH, TB and TA. Density was measured with accuracy of $\pm 0.0005 \text{ g cm}^{-3}$ (PAAR, DMA 35). Samples for chemical analyses of major ions were collected in pre-weighed 50 ml plastic vials. The samples were weighed again in the laboratory and diluted with double distilled water before analysis in order to dissolve salts that may have precipitated in the bottle after collection. Major cations were analyzed with ICP-AES (Perkin Elmer, Optima 3300), the sum of Br^- and Cl^- was determined by potentiometric titration with AgNO_3 and B and Br^- were analyzed by ICP-MS (Perkin Elmer, NexION 300D). Electrical charge balance did not exceed 2%. DIC was determined in a vacuum extraction line followed by manometric procedure (Barkan et al., 2001). The line was calibrated using a certified reference material obtained from Andrew Dickson (UCSD; Batch # 123). Total alkalinity was determined by titration with 0.01 N HCl, calibrated with laboratory internal standard and $< 0.2\%$ imprecision. pH was measured with a combination electrode (Orion 81-03) calibrated against a cell of hydrogen and chloride ion selective electrodes (Golan et al., 2014).

2.2. PCO_2 measurements

DSB collected on July 2014 from a depth of 100 m was measured for partial pressure of carbon dioxide (PCO_2) by equilibrating with 10% volumetric headspace filled with 99.999% N_2 . The single point batch samples were prepared for analyses in 150 ml syringes. During the following week, the headspaces of the individual syringes were measured one at a time with increasing time steps, until values stabilized, thereby indicating attainment of equilibrium. The gas sample from the headspace was injected into a gas chromatograph (Varian, Micro-GC 490) equipped with a plot-U column and a thermal conductivity detector. The precision

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