



The stoichiometric dissociation constants of carbonic acid in seawater brines from 298 to 267 K

Stathys Papadimitriou^{a,*}, Socratis Loucaides^b, Victoire M.C. Rérolle^{b,1}, Paul Kennedy^a, Eric P. Achterberg^{c,2}, Andrew G. Dickson^d, Matthew Mowlem^b, Hilary Kennedy^a

^a Ocean Sciences, College of Natural Sciences, Bangor University, Menai Bridge, Anglesey LL59 5AB, UK

^b National Oceanography Centre, Southampton SO14 3ZH, UK

^c University of Southampton, National Oceanography Centre, Southampton SO14 3ZH, UK

^d Marine Physical Laboratory, Scripps Institution of Oceanography, University of California, San Diego, 9500 Gilman Drive, La Jolla, CA 92093-0244, USA

Received 21 April 2017; accepted in revised form 21 September 2017; Available online 28 September 2017

Abstract

The stoichiometric dissociation constants of carbonic acid (K_{1C}^* and K_{2C}^*) were determined by measurement of all four measurable parameters of the carbonate system (total alkalinity, total dissolved inorganic carbon, pH on the total proton scale, and CO_2 fugacity) in natural seawater and seawater-derived brines, with a major ion composition equivalent to that of Reference Seawater, to practical salinity (S_p) 100 and from 25 °C to the freezing point of these solutions and –6 °C temperature minimum. These values, reported in the total proton scale, provide the first such determinations at below-zero temperatures and for $S_p > 50$. The temperature (T , in Kelvin) and S_p dependence of the current pK_{1C}^* and pK_{2C}^* (as negative common logarithms) within the salinity and temperature ranges of this study ($33 \leq S_p \leq 100$, $-6 \text{ °C} \leq t \leq 25 \text{ °C}$) is described by the following best-fit equations: $pK_{1C}^* = -176.48 + 6.14528 S_p^{0.5} - 0.127714 S_p + 7.396 \times 10^{-5} S_p^2 + (9914.37 - 622.886 S_p^{0.5} + 29.714 S_p) T^{-1} + (26.05129 - 0.666812 S_p^{0.5}) \ln T$ ($\sigma = 0.011$, $n = 62$), and $pK_{2C}^* = -323.52692 + 27.557655 S_p^{0.5} + 0.154922 S_p - 2.48396 \times 10^{-4} S_p^2 + (14763.287 - 1014.819 S_p^{0.5} - 14.35223 S_p) T^{-1} + (50.385807 - 4.4630415 S_p^{0.5}) \ln T$ ($\sigma = 0.020$, $n = 62$). These functions are suitable for application to investigations of the carbonate system of internal sea ice brines with a conservative major ion composition relative to that of Reference Seawater and within the temperature and salinity ranges of this study.

© 2017 Elsevier Ltd. All rights reserved.

Keywords: Carbonic acid; Dissociation constants; Below-zero temperature; Brines; Sea ice

1. INTRODUCTION

The investigation of the carbonate system in aquatic environments is essential in the understanding and monitor-

ing of the carbon cycle in the hydrosphere. Such investigations have intensified in the marine environment because of the crucial role the ocean plays in the absorption and storage of the anthropogenic CO_2 emitted to the atmosphere during the Industrial era (Takahashi et al., 1997; Sabine et al., 2004). Through this process, the ocean is a major repository of anthropogenic CO_2 (Takahashi, 2004), with consequent chemical and ecosystem functioning effects from the acidification of surface oceanic waters (decreased oceanic pH relative to pre-industrial era values) (Caldeira and Wickett, 2003; Feely et al., 2004; Takahashi et al.,

* Corresponding author.

E-mail address: s.papadimitriou@bangor.ac.uk (S. Papadimitriou).

¹ Present address: FLUIDION SAS, 75001 Paris, France.

² Present address: GEOMAR, Helmholtz Centre for Ocean Research, 24148 Kiel, Germany.

2014; Gattuso et al., 2015). The acidification effect on the oceanic carbonate system by atmospheric CO₂ absorption (Takahashi, 2004; Sabine et al., 2004) has been observed in surface coastal and pelagic waters (Takahashi et al., 2014), including large areas of the Arctic Ocean (Feely et al., 2008; Yamamoto-Kawai et al., 2009; Cai et al., 2010; Semiletov et al., 2016).

One of the challenges that remain in the high latitude (polar) oceans of the Earth's cryosphere is reliable determination of the carbonate system in the brine-ice system in the extensive seasonal sea ice cover of these environments (Brown et al., 2014; Miller et al., 2015; Papadimitriou et al., 2016). Early investigations in the composition and activity of the ice-associated (sympagic) microbial community in sea ice have uncovered the role of this multi-phase system on the surface of high latitude oceans as a habitat akin to other large-scale biomes, such as the deserts and tundra (Fritsen et al., 1994; Gleitz et al., 1995; Arrigo et al., 1997; Thomas and Dieckmann, 2002; Kennedy et al., 2002). Subsequent investigations have revealed a complex internal carbon cycle driven not only by the sympagic autotrophic and heterotrophic microbial communities, but also by two other major chemical reactions in the surface ocean, CO₂ gas exchange and hydrated CaCO₃ authigenesis (Papadimitriou et al., 2004; Delille et al., 2007; Dieckmann et al., 2008; Munro et al., 2010; Papadimitriou et al., 2012; Fischer et al., 2013). The internal carbon cycling in sea ice is complemented by measurable CO₂ fluxes to and from the atmosphere as a function of ice temperature (Delille et al., 2014) and to the underlying ocean by gravity drainage of the internal brines (Rysgaard et al., 2007; Rysgaard et al., 2011). These past investigations have culminated in a keen interest in the carbonate system of sea ice brines (Brown et al., 2014; Miller et al., 2015), the residual internal solution where all biogeochemical reactions occur either in isolation from, or in direct exchange with, the adjacent seawater column and the atmosphere depending on the temperature- and salinity-dependent permeability of the medium (Golden et al., 1998). Sea ice brines are derived from the frozen surface seawater by physical concentration of the dissolved sea solutes following their expulsion from the ice crystal matrix. Along with degassed components, the brines can become trapped in pockets and channels in the sea ice structure. As a result of internal thermal equilibrium in sea ice along temperature gradients extending seasonally slightly above or far below the freezing point of seawater (−1.92 °C at 0 dbar pressure and salinity 35; UNESCO, 1983), the salinity of internal brines can vary from the hypersaline to values in excess of 100 below −6 °C, and the concentration of brine solutes can likewise vary (Gleitz et al., 1995; Miller et al., 2011a, 2011b; Papadimitriou et al., 2012; Geilfus et al., 2012a).

The carbonate system in the marine environment is defined by pressure, temperature, salinity, the total concentration of boron and the dissociation constant of boric acid, the total concentrations of sulfate and fluoride, along with the equilibrium constants for the formation of the bisulfate ion and HF, respectively, the dissociation constants of carbonic acid, the value of two of its four measurable parameters [total alkalinity (A_T), total dissolved inorganic

carbon (C_T), pH, and the fugacity of CO₂ (*f*CO₂)] and, lastly, the weak acid-base systems in the dissolved macro-nutrient and metabolite pools (phosphate, silicate, ammonium, sulphide) and their respective dissociation constants (Millero, 1995; Dickson et al., 2007). To date, all relevant dissociation constants have been adequately constrained empirically as a function of temperature and salinity for above-zero temperatures and practical salinity (S_P) up to 50 (Millero, 1995, and references therein). Great investigative effort has been invested in the experimental determination of the first and second stoichiometric (concentration-based) dissociation constants of carbonic acid in seawater and solutions derived from seawater by dilution or evaporation, both in natural and artificial media with the mean stoichiometric composition of seawater (Hansson, 1973; Mehrbach et al., 1973; Goyet and Poisson, 1989; Roy et al., 1993; Mohica-Prieto and Millero, 2002; Millero et al., 2006). The determination of the carbonate system in the complex and sparsely accessible sea ice system is currently limited to direct measurements of A_T and C_T (Miller et al., 2015) and is further compounded by the large uncertainty in the values of the relevant acid-base dissociation constants as they are currently estimated via extrapolation of the existing different salinity-temperature functions to the physical sea ice conditions (temperature < 0 °C, S_P > 50) (Brown et al., 2014). Direct in-situ measurements of *f*CO₂ in the sea ice system are still rare either in bulk sea ice (Miller et al., 2011a, 2011b; Geilfus et al., 2012b) or in brines, which are, moreover, subject to the sparse spatial resolution afforded by brine collection in boreholes through the ice surface (Delille et al., 2007; Geilfus et al., 2012a; Delille et al., 2014). In addition, direct brine pH measurement has not been possible so far at below-zero temperatures and high salinities as a result of sampling and analytical difficulties in this complex system. As a first step towards the implementation of direct pH measurement in sea ice brines, the pH of Tris buffers (Papadimitriou et al., 2016) and the p(K₂e₂) of the pH-indicator dye *meta*-Cresol Purple (Loucaides et al., 2017) have recently been characterized electrometrically with the Harned cell and spectrophotometrically, respectively, to S_P = 100 and −6 °C. Sea ice geochemists, therefore, have so far relied on indirect determination of brine *f*CO₂ and pH from the solution of the system of equations that describe the acid-base equilibria of the oceanic carbonate system using temperature, salinity, nutrient concentrations (if available), and the direct measurements of A_T and C_T as input parameters, with the caveats of extrapolation mentioned above (Brown et al., 2014).

Here, we present measurements that allowed the determination of the dissociation constants of carbonic acid in seawater and seawater-derived brines at below-zero temperatures to the freezing point of these solutions up to S_P = 100 and a temperature minimum of −6 °C. The S_P and temperature ranges of this study were set because the ionic composition and inter-ionic ratios in surface oceanic water are conserved in the natural sea ice brines over these temperature and salinity ranges. More concentrated, cooler sea ice brines (S_P > 100 and *t* < −6 °C) become supersaturated with respect to a suite of hydrated solid phases,

Download English Version:

<https://daneshyari.com/en/article/5783154>

Download Persian Version:

<https://daneshyari.com/article/5783154>

[Daneshyari.com](https://daneshyari.com)