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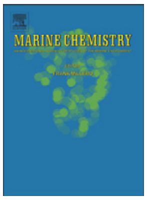

The effect of mirabilite precipitation on the absolute and practical salinities of sea ice brines

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ABSTRACT

The sea ice cover of high latitude oceans contains concentrated brines which are the site of in-situ chemical and biological reactions. The brines become supersaturated with respect to mirabilite ($Na_2SO_4 \cdot 10H_2O$) below −6.4 °C, and the associated removal of Na^+ and SO_4^{2-} from the brine results in considerable non-conservative changes to its composition. The changes are reflected in the brine salinity, which is a fundamental physico-chemical parameter in the sea ice brine system. Here, measurements of electrical conductivity and brine composition in synthetic sea ice brines between −1.8 and −20.6 °C, obtained during a comprehensive investigation of the brine-mirabilite equilibrium at below-zero temperatures reported elsewhere, are combined with modelled estimates to assess the behaviour of the absolute (S_A) and practical (S_P) salinities of sea ice brines. Results display substantial divergence of S_P from S_A below −6.4 °C, reaching a 7.2% difference at −22.8 °C. This is shown to create inaccuracies when S_P is assumed to be equivalent to S_A, firstly by misrepresenting the conditions inhabited by sea ice biota, whilst also creating errors in the calculation of physical sea ice parameters. Our measured and modelled data are used to refine the $S_A - T$ relationship for sea ice brines, implicit of mirabilite precipitation, which is crucial in estimating brine properties in absence of salinity data. Furthermore, because S_P is the parameter measured in field studies, we provide an $S_P - T$ relationship for sea ice brines to −22.8 °C, which aids in explaining the trends observed in available $S_P - T$ data from sea ice brines in the Southern Ocean, demonstrating the importance of the mirabilite-brine equilibrium in natural sea ice. Finally, we initiate the development of a conversion factor for the estimation of S_A from S_P measurement in sea ice brines, and produce an equation that can calculate S_A from modelled brine density. This work ultimately highlights careful consideration of salinity concepts when applied to the sea ice system.

1. Introduction

The Na–K–Mg–Ca–Cl–SO_4–H_2O system describes 99.4% of the major dissolved ions in Standard Seawater by weight (Millero et al., 2008), and these ions have long been known to display constant ratios to one another throughout the world ocean (Forchhammer, 1865; Dittmar et al., 1873). This conservative behaviour gave rise to the concept of salinity, which was originally defined as a measure of the mass of dissolved salts per unit mass of seawater and is now termed absolute salinity (S_A) (Lewis, 1980). Accurate and rapid determination of salinity is paramount in the calculation of seawater density (Millero et al., 2008; Pawlowicz, 2015), therefore, since the advent of salinity as a concept, the method of its measurement has evolved to its present form of determination from measurement of electrical conductivity (Fofonoff, 1985; Lewis, 1980). The combined contribution of charged dissolved species to the total electrical conductivity of a solution is a conservative property and its measurement is converted to 'practical' salinity (S_P) by the Practical Salinity Scale 1978 (PSS-78). According to the PSS-78 definition (Perkin and Lewis, 1980), the S_P of a solution is derived from the ratio (R_{15}) of the total electrical conductivity of the solution to that of a solution of potassium chloride (KCl) in pure water with a KCl mass fraction of 32.4356 g when both solutions are at 15 °C on the IPTS-68 scale, and zero gauge pressure (Fofonoff, 1985; Lewis, 1980; Millero et al., 2008). Practical salinity is dimensionless, and when $R_{15} = 1$, $S_P = 35$. The reproducibility of conductivity measurements is good enough for deep sea research where S_P accuracies within ±0.006 (King et al., 2001) are required, and is now the dominant method for salinity measurement in both oceanography at sea and in the laboratory. Measurement of S_P also allows for precise calculation of S_A based on the most recent accurate chemical analysis defining $S_A = 35.16504\ g\ kg_{solution}^{-1}$ in Standard Seawater with $S_P = 35$ (Millero et al., 2008), with $S_A/S_P = 1.004715 \pm 0.0005$ (Jackett et al., 2006; Pawlowicz, 2012; Millero et al., 2008; Millero and Huang, 2009). This relationship is valid for practical salinities between 2 and 42, which is the working salinity range of the PSS-78 (Lewis, 1980; Pawlowicz, 2012).

The electrical conductivity of a solution is a function of its temperature, the total amount of charged species dissolved in it, and their interionic ratios (Weeks, 2010). Deviations from the constant stoichiometric ratios of Standard Seawater (Table 1) will occur as a result of any

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Table 1
A comparison of the compositions of Simplified (DOE, 1994) and Standard (Millero et al., 2008) Seawater. The remaining ions in Standard Seawater that are not tabulated include: Sr^{2+}, HCO_3^- Br^-, CO_3^{2-}, $B(OH)_4^-$, F^-, OH^-, $B(OH)_3$ and CO_2.

Solute	$S_P = 35$	
	Simplified Seawater	Standard Seawater
	g kg_{sol}^{-1}	
Na^+	10.7848	10.7815
K^+	0.3992	0.3991
Mg^{2+}	1.2840	1.2837
Ca^{2+}	0.4152	0.4121
Cl^-	19.4715	19.3527
SO_4^{2-}	2.7128	2.7124
H_2O	964.93	964.83
Remaining ions	N/A	0.2285

process that leads to non-conservative behaviour of the major ions, with the formation of seawater-derived brines in evaporative or cryospheric environments providing apt examples (McCaffrey et al., 1987; Marion et al., 1999; Grasby et al., 2013; Butler et al., 2016). Amongst the best studied cryospheric environments on Earth is the sea ice cover of high latitude oceans, which extends over approximately 20 million km^2 seasonally (Dieckmann and Hellmer, 2010), covering ~5% of the Earth's surface. Sea ice undergoes large changes in temperature, chemical composition, and structure throughout its seasonal cycle (Gleitz et al., 1995), which are reflected in the labyrinth of inclusions within the ice that contain rejected liquid brine at local ice-brine (thermal) equilibrium (Weeks and Ackley, 1986; Petrich and Eicken, 2010; Light et al., 2003; Golden et al., 2007). At the low temperature (−1.8 to ~−35 °C; Miller et al., 2011) and hypersaline conditions (up to ~220 g $kg_{solution}^{-1}$; Ewert and Deming, 2013) of sea ice brines, a suite of dissolved salts reach saturation with respect to their, typically hydrated, solid phases, which precipitate. The current understanding of solid-solution equilibria in sea ice states the following sequence of precipitates from sea ice brine as it cools to its eutectic: ikaite ($CaCO_3 \cdot 6H_2O$) at temperatures less than −2 °C (depending on brine pCO_2; Papadimitriou et al., 2013), mirabilite ($Na_2SO_4 \cdot 10H_2O$) at −6.4 °C (Butler et al., 2016), hydrohalite ($NaCl \cdot 2H_2O$) at −22.9 °C (Marion et al., 1999; Butler and Kennedy, 2015), sylvite (KCl) at −33 °C, and $MgCl_2 \cdot 12H_2O$ at −36.2 °C (Gitterman, 1937; Nelson and Thompson, 1954). In addition to this sequence, gypsum ($CaSO_4 \cdot 2H_2O$) may also precipitate (Gitterman, 1937; Marion et al., 1999), though estimates for the temperature region of its precipitation are conflicting, and range from −3 °C (Geilfus et al., 2013) to −22.2 °C (Marion et al., 1999).

Salt precipitation in sea ice can result in substantial non-conservative changes in the ionic composition of the brine; recent measurements indicate that mirabilite precipitation results in a reduction of the total concentrations of Na^+ and SO_4^{2-} by up to 13% and 92%, respectively, by −20.6 °C (Butler et al., 2016). The changes are particularly significant given that these ions contribute approximately 38% to S_A (Table 1) and 30% to the total electrical conductivity of the solution.

Salt precipitation in sea ice is confined to the brine inclusions that permeate its structure, ranging in diameter from 10 μm to 10 mm depending on the ice temperature (Light et al., 2003). The physical and chemical properties of the brine define the conditions inhabited by the sympagic (within ice) community, which is comprised of bacteria, microalgae, viruses, fungi, protozoans, and small metazoans (Horner et al., 1992; Thomas and Dieckmann, 2002; Ewert and Deming, 2013). Microscopic biota potentially covers between 6% and 41% of the brine channel surface area at −2 °C (Krembs et al., 2000), while salt precipitates at colder temperatures may provide additional solid surfaces with which microorganisms can interact (Ewert and Deming, 2013). The salinity of the brine within the inclusions is temperature-dependent (Assur, 1960) and represents one of the major constraints on resident sea ice organisms because it affects the function of proteins and the surrounding osmotic conditions (Ewert and Deming, 2013). Brine salinities in sea ice extend from diluted seawater during ice melt with salinities <30 g $kg_{solution}^{-1}$, to salinities exceeding ~220 g $kg_{solution}^{-1}$ during winter months when the ice is at its coldest. For this reason, an accurate representation of brine salinity is required for determining the physicochemical conditions of the internal sea ice habitat (Thomas et al., 2010; Ewert and Deming, 2013).

Sea ice salinity is most often measured as a bulk property, determined as S_P in melted sea ice samples. Measurements of bulk sea ice S_P are then used to estimate the physical parameters of the ice pack, such as brine volume fraction and porosity (Cox and Weeks, 1988; Gleitz et al., 1995; Petrich and Eicken, 2010). In such instances, the salinity of the internal brines can be estimated as S_A from the ice temperature via available liquidus equations (Assur, 1960; Cox and Weeks, 1986; Notz and Worster, 2009), assuming local ice-brine equilibrium, i.e., $T_{ice} = T_{fr}$, where $T_{fr} =$ the freezing point of internal sea ice brine. These equations describe ice, water and salt mass balance as a function of temperature and are based on dissolved salt analysis provided in the seminal work on seawater freezing by Nelson and Thompson (1954). The accuracy of the original measurements, with respect to mirabilite precipitation in particular, has recently been evaluated from a comprehensive assessment of mirabilite solubility in equilibrium sea ice brines (Butler et al., 2016). Discrepancies include indications for mirabilite-brine disequilibrium in the freezing experiments of Nelson and Thompson, and a warmer onset temperature of mirabilite precipitation (−6.4 °C) than previously thought (−8.2 °C). These discrepancies will be reflected in the liquidus ($S_A - T_{fr}$) equations for the ice-brine equilibrium (Assur, 1960; Cox and Weeks, 1986; Notz and Worster, 2009). In light of these recent developments, there is scope for refinement of the $S_A - T_{fr}$ relationship. In addition, while the liquidus equation in sea ice yields the S_A of the internal brines from ice temperature measurements, S_P is the property that is directly measured in sea ice brines as afforded by the available oceanographic instruments and protocols. Such brine samples are typically obtained by centrifugation or by drilling bore holes through the surface to varying depth in the ice (sackhole brines), and represent conditions that extend well into the temperature-salinity region of salt precipitation (Krembs et al., 2000; Papadimitriou et al., 2004; Munro et al., 2010; Norman et al., 2011; Garrison et al., 2003). Universally in sea ice research, the difference between brine S_A (from the liquidus equation) and S_P (as typically measured directly) is assumed to be insignificant or is ignored (Munro et al., 2010; Garrison et al., 2003; Norman et al., 2011). Therefore, there is also a pressing need for rigorous evaluation of the relevance of S_P measurements and of the S_A and S_P relationship in non-conservative sea ice brines.

Here, we examine the effect of salt precipitation on the practical and absolute salinities of synthetic sea ice brines at thermal equilibrium between −1.8 and −20.6 °C using laboratory measurements of S_A and S_P during an extensive investigation of the mirabilite-brine equilibrium at below-zero temperatures reported in Butler et al. (2016). In addition, we use the FREZCHEM thermodynamic code and equations for the electrical conductivity of individual ions (McCleskey et al., 2012) to model S_A and S_P in our experimental conditions. The FREZCHEM code has been developed for the study of cold aqueous geochemistry (Marion and Kargel, 2008) and has been used in the investigation of physical-chemical processes in sea ice (Marion et al., 1999; Grasby et al., 2013; Geilfus et al., 2013; Papadimitriou et al., 2013), and is particularly accurate in computing ice-brine-mirabilite equilibria in sea ice brines (Butler et al., 2016). Lastly, measured and modelled data are compared to $S_P - T$ data of natural sea ice brines from the Southern Ocean (Gleitz et al., 1995; Norman et al., 2011). Together the data are used; to assess and refine the existing $S_A - T_{fr}$ relationship compared to several empirical liquidus equations currently in use; to define a novel $S_P - T_{fr}$ relationship for sea ice brines implicit of mirabilite precipitation; to develop a conversion factor that can account for the changing S_A to S_P ratio in sea ice brines affected by mirabilite precipitation; and to produce an empirical equation for the estimation of S_A from sea ice brine density.