

# Temperature coefficient of seawater pH as a function of temperature, pH, DIC and salinity

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## Abstract

pH is a measure of the hydrogen ion activity in a solution, which is a function of temperature. Under normal seawater conditions, it is well constrained. Nowadays, with an increasing interest in complex environments (e.g., sea ice), a better understanding of the temperature change on pH under extreme conditions is needed. The objective of this paper was to investigate the temperature coefficient of the seawater pH ( $\Delta\text{pH}/\Delta T$ ) over a wide range of temperature, pH, dissolved inorganic carbon (DIC) and salinity by a method of continuous pH measurement with the temperature change, and to verify the application of CO2SYS for pH conversion under extreme conditions (on the National Bureau of Standards (NBS) scale and the total proton scale). Both experimental results and CO2SYS calculations showed that  $\Delta\text{pH}/\Delta T$  was slightly affected by temperature over the range of 0°C to 40°C and by pH (at 25°C) from 7.8 to 8.5. However, when pH was out of this range,  $\Delta\text{pH}/\Delta T$  varied greatly with pH value. According to the experimental results, changes in DIC from 1 mmol/kg to 5 mmol/kg and salinity from 20 to 105 had no significant effect on  $\Delta\text{pH}/\Delta T$ . CO2SYS calculations showed a slight increase in  $\Delta\text{pH}/\Delta T$  with DIC on both the NBS scale and the total proton scale; and underestimated  $\Delta\text{pH}/\Delta T$  at high salinity (i.e., beyond the oceanographic range) on the NBS scale. Nevertheless, CO2SYS is still suitable for pH conversion even under extreme conditions by simply setting the input values of DIC and salinity in CO2SYS within the oceanographic range (e.g., DIC=2 mmol/kg and S=35).

**Key words:** temperature coefficient, pH measurement, CO2SYS, sea ice, ocean acidification

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## 1 Introduction

The rapid increase of atmospheric CO<sub>2</sub>, especially over the past decades, has resulted in increased CO<sub>2</sub> uptake by the oceans. As a result, signs of ocean acidification (OA, decrease in seawater pH) have been detected in many regions, particularly at high latitudes (Fabry et al., 2009). The severity of OA has been projected to increase drastically in the foreseeable future (Feely et al., 2009; Steinacher et al., 2009), raising major concerns over the condition of marine ecosystems (Doney et al., 2009; Orr et al., 2005). So far, the evidence of OA is primarily indicated by the decreasing saturation of calcite or aragonite (Feely et al., 2009; Yamamoto-Kawai et al., 2009). Quantitative assessment of immediate changes in seawater pH has been challenging due to the uncertainties associated with detecting small changes. For instance, since the beginning of the industrial era, the pH of surface seawater has decreased by 0.05–0.10 or at a rate of  $-0.0014$  to  $-0.0024$  per year (IPCC, 2014). Detecting such small changes in seawater pH, even on the decadal to centennial scales, requires meticulous efforts to eliminate the bias associated with pH measurements and the conversion at different temperatures.

The pH of seawater is typically measured by potentiometric or spectrophotometric techniques (Marion et al., 2011). Both methods are subject to measurement bias, with the temperature being one of the common causes. As pH is temperature dependent, the pH measurement is preferentially done at the *in situ* tem-

perature. However, this is not always practical; as such, pH is often measured at a temperature (e.g., 25°C) different from the *in situ* temperature (Dickson et al., 2007), which further requires a conversion. Besides, when pH is determined by a glass electrode, the temperature difference between samples and electrode calibration might lead to uncertainty in pH determination due to the liquid junction potential; this error is considered to increase as the temperature difference between samples and electrode calibration widens and cannot be eliminated by automatic temperature compensation using a temperature probe (Barron et al., 2005). Therefore, it is recommended that the pH measurement and electrode calibration are carried out at the same temperature (Dickson et al., 2007).

The effect of temperature on seawater pH has been extensively studied. Gieskes (1969) determined the temperature coefficient of seawater pH ( $\Delta\text{pH}/\Delta T$ ) on the National Bureau of Standards (NBS) scale experimentally by measuring the pH difference between two temperatures and derived  $\Delta\text{pH}/\Delta T = (-0.0114 \pm 0.0010) \text{ } ^\circ\text{C}^{-1}$  at 1 atm pressure. Within the range of oceanographic interest, this relationship was considered to be independent of pH, salinity (S) and temperature (T). Ben-Yaakov (1970), however, calculated that  $\Delta\text{pH}/\Delta T$  (also on the NBS scale) is a function of salinity, pH, and alkalinity; and suggested that the averaged  $\Delta\text{pH}/\Delta T$  proposed by Gieskes (1969) should be avoided for precision calculations. With the development of equilibrium constants of the carbonate system in seawater, Millero (1979)

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presented an empirical polynomial equation (polynomial in temperature, independent of salinity) for converting pH (on both the NBS scale and total proton scale) measured at 25°C to an *in situ* temperature based on the thermodynamic calculations under the conditions of  $T=0\text{--}40^\circ\text{C}$ ,  $S=30\text{--}40$  and  $\text{pH}_{25}=7.6\text{--}8.2$ . Hunter (1998) determined the temperature dependence of pH (on the total proton scale) using the updated equilibrium constants of the  $\text{CO}_2$  system in seawater and found that neither salinity nor alkalinity affects the temperature-dependence of pH over the oceanographic range. In a more recent study, Lui and Chen (2017) used 816 sets of data of the surface seawaters from six stations in the global oceans and proposed that pH at the *in situ* temperature and 25°C can be converted into each other using only temperature, with a coefficient of  $-0.015$  l on the total proton scale. However, these studies were mainly restricted to the conditions within the oceanographic range. The impacts of low temperature, high pH, dissolved inorganic carbon (DIC) and salinity (e.g., under the condition of sea ice brine) on  $\Delta\text{pH}/\Delta T$  are poorly known.

The carbonate system of sea ice is of great interest given its role in the  $\text{CO}_2$  cycle in the polar regions. Until recently, Papadimitriou et al. (2016) determined the pH of tris buffers at sub-zero temperatures and hypersaline conditions, so that the accurate measurement of pH in sea ice brine is possible. Nevertheless, the pH measurement of the sea ice brine has always exerted difficulties due to the harsh physical environment. As a result, it is practically measured at room temperature (e.g., 25°C) and converted to the *in situ* temperature. However, the accuracy of pH conversion under extreme conditions (i.e., high salinities and sub-zero temperatures) so far has received little attention.

In this study, continuous pH measurement with the temperature change was applied to determine  $\Delta\text{pH}/\Delta T$ . The effects of temperature, pH, DIC and salinity on  $\Delta\text{pH}/\Delta T$  over a wide oceanographic range and beyond were investigated, particularly for the conditions representative for sea ice brine. In addition, the calculation results from CO2SYS on both the NBS scale and the total proton scale were compared with the experimental data to verify the suitability of CO2SYS for pH conversion even under extreme conditions.

## 2 Materials and methods

### 2.1 pH electrode calibration

Twelve glass electrodes without the built-in temperature sensor (Metrohm 6.025 3.100, Metrohm Company) were tested on their response time and drift. Four best electrodes were selected for the experiment, which had fast response time (within seconds) and small drift (less than 0.01 pH/h) with a response slope >98% of the ideal Nernst slope and a mv reading close to 0 at  $\text{pH}=7$  (25°C). For each experiment, two randomly selected pH electrodes out of four were applied, which were calibrated using two NBS buffers (Radiometer analytical, IUPAC standard): one electrode was calibrated at 25°C (pH buffers: 7.000 and 10.012; referred to as  $\text{pH}_{25}$ ), and the other one was calibrated at 0°C (pH buffers: 7.118 and 10.317; referred to as  $\text{pH}_0$ ). Although there exists systematic uncertainty in pH measurement on the NBS scale due to the liquid junction difference between NBS buffers and seawater samples (Kadis and Leito, 2010), the offset of the measured pH from the true pH value should be constant with the temperature change at the same salinity (Easley and Byrne, 2012). Thus, it does not affect the determination of  $\Delta\text{pH}/\Delta T$  under each given condition.

### 2.2 Solution preparation

The artificial seawater was prepared based on the recipe from

Millero (2006) with slight modifications. Solutions with salinities different from 35 were prepared with the salts proportionally to those in the standard salinity of 35. For example, the amount of each salt needed at  $S=70$  was twice as much as that at  $S=35$ . The desired pH (7.5 to 10.0) at 25°C was adjusted by adding either HCl or NaOH solutions using a titration system (TA20 plus, SI Analytics), with a maximum variation within 0.05. Solutions with different DIC concentrations ranging from 1 mmol/kg to 5 mmol/kg were prepared by varying the amount of  $\text{NaHCO}_3$  added to the artificial seawater at  $S=35$ , with other salts kept unchanged. Salts used in this study were obtained from Merck (EM-SURE® ACS, ISO, Reag, Ph Eur) except for  $\text{SrCl}_2$  and  $\text{H}_3\text{BO}_3$ , from Carl Roth (p.a., ACS, ISO).

### 2.3 Experimental setup

A closed system was employed in which pH electrodes could monitor the change of solution pH as a function of temperature. A 350 mL Savilex reaction vessel placed in a double-walled water jacket was filled with artificial seawater. The reaction vessel was accommodated with two electrodes and a Metrohm temperature probe (Pt 1000, calibrated against the ice-water medium of temperature 0°C, with a precision of 0.1°C). The temperature was controlled by means of a refrigerated circulating water bath (Haake F6), with antifreeze added. The solution was first cooled down to sub-zero temperatures (above freezing point) and then heated to the final temperature (e.g., 25°C) at a rate of around 0.3°C/min. The solution was stirred at a constant rate of 250 r/min using an agitator equipped with an impeller. pH values from two individual pH electrodes were recorded every 10 s by a computer.  $\Delta\text{pH}/\Delta T$  was derived from the slope of the pH (obtained from the mean of  $\text{pH}_0$  and  $\text{pH}_{25}$ ) vs. temperature over a certain temperature range (e.g., 25°C).

### 2.4 Effect of different parameters on $\Delta\text{pH}/\Delta T$

Four parameters were investigated on  $\Delta\text{pH}/\Delta T$ : (1) temperature (0°C to 40°C) at the experimental condition of  $\text{pH}=8.0$ , DIC concentration=2 mmol/kg and  $S=35$ , with  $\Delta\text{pH}/\Delta T$  derived over a temperature span of every 5°C; (2) pH (7.5 to 10.0) at the experimental condition of DIC concentration=2 mmol/kg and  $S=35$ , with  $\Delta\text{pH}/\Delta T$  derived over a temperature span from 0°C to 25°C; (3) DIC (1 mmol/kg to 5 mmol/kg) at the experimental condition of  $\text{pH}=8.0$  and  $S=35$ , with  $\Delta\text{pH}/\Delta T$  derived over a temperature span from 0°C to 25°C; and (4)  $S$  (20 to 105) at the experimental condition of  $\text{pH}=8.0$ , with  $\Delta\text{pH}/\Delta T$  derived over a temperature span from subzero (i.e.,  $-1^\circ\text{C}$  at  $S=20$  and  $S=35$ ;  $-2^\circ\text{C}$  at  $S=70$ ;  $-3^\circ\text{C}$  at  $S=105$ ) to 25°C.

### 2.5 CO2SYS calculation

$\Delta\text{pH}/\Delta T$  under different conditions was also calculated by the CO2SYS program (version 2.1) on both the NBS scale and the total proton scale (Pierrot et al., 2006). In order to convert pH at different temperatures by the CO2SYS program, an additional known carbonate system parameter (i.e., DIC, alkalinity or  $p\text{CO}_2$ ) is needed. In this study, DIC was chosen as the input parameter. The equilibrium constants for the carbonate system were from Mehrbach et al. (1973) refit by Dickson and Millero (1987), and the equilibrium constant for  $\text{KHSO}_4$  was from Dickson (1990), and the  $[\text{B}]_T$  value was from Uppström (1974). The input values of "Pressure", "Total P" and "Total Si" were set at 0. The input values of salinity, DIC and pH were selected in accordance with the experimental conditions. The temperature in the "input condition" was set at 25°C, while the temperature in the "output condition" was set consistent with the experimental temperature range

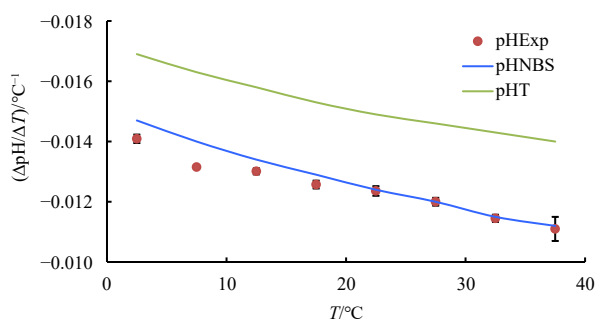
with a step of 1°C.  $\Delta\text{pH}/\Delta T$  was derived from the slope of the calculated pH against temperature. When calculating the temperature effect on  $\Delta\text{pH}/\Delta T$ ,  $\Delta\text{pH}/\Delta T$  was averaged at every 5°C span from temperature 0°C to 40°C; while calculating the pH, DIC and salinity effects on  $\Delta\text{pH}/\Delta T$ ,  $\Delta\text{pH}/\Delta T$  was averaged over the same temperature range as applied in the experiment.

### 3 Results and discussion

#### 3.1 Temperature effect on $\Delta\text{pH}/\Delta T$

The observed difference between  $\text{pH}_{25}$  and  $\text{pH}_0$  (pH electrodes calibrated at 25°C and 0°C, respectively) at temperature from 0°C to 40°C, and at the experimental condition of  $S=35$ , DIC concentration=2 mmol/kg and  $\text{pH}=8.0$  (25°C) is shown in Fig. S1 (green line). Although the difference becomes large at high temperatures, its maximum difference is  $\leq 0.02$ . These results indicate that the uncertainty in pH determination introduced by the difference in calibrating temperature and sample temperature as large as 40°C is acceptable for pH measurement on the NBS scale. As NBS buffers might freeze at sub-zero temperatures, this demonstrates that calibrations performed at temperatures above the freezing point of the NBS buffers could reliably be applied to measurements at sub-zero temperatures. The mean pH value (Fig. S1, blue line), as calculated by averaging  $\text{pH}_{25}$  and  $\text{pH}_0$ , decreases with temperature from 8.32 to 7.82 with a coefficient of determination  $R^2 \geq 0.999$ .

The change in  $\Delta\text{pH}/\Delta T$  at every 5°C span of temperature from 0°C to 40°C and at the experimental condition of  $S=35$ , DIC concentration=2 mmol/kg and  $\text{pH}=8.0$  is shown in Fig. 1. Even though pH decreases linearly with temperature over the whole temperature range (0–40°C, Fig. S1), both experimental results and CO2SYS calculations (pH on the NBS scale) reveal that at a smaller temperature span (i.e., 5°C),  $\Delta\text{pH}/\Delta T$  is slightly different and decreases with increasing temperature, with a maximum variation of 0.003 over the temperature range from 0°C to 40°C. There seems to be a small offset of  $\Delta\text{pH}/\Delta T$  between the measured and calculated ones (on the NBS scale) at temperatures lower than 20°C in Fig. 1, which might be due to the slow response of pH electrodes at low temperatures. However, the difference is small, less than 0.001. The calculations based on the total proton scale show the same trend but with a constant difference ( $-0.0028 \pm 0.0002$ ) from the experimental results due to the different definitions of the pH scale. Therefore, using a fixed temperature coefficient might not be proper to convert pH at differ-



**Fig. 1.** Temperature coefficient of seawater pH ( $\Delta\text{pH}/\Delta T$ ) at every 5°C span from temperature 0°C to 40°C and at the experimental condition of salinity=35, DIC concentration=2 mmol/kg and  $\text{pH}=8.0$  (25°C): experimental results are labelled by red dots; lines are derived from CO2SYS calculation based on the NBS scale (blue) and the total proton scale (green), respectively.

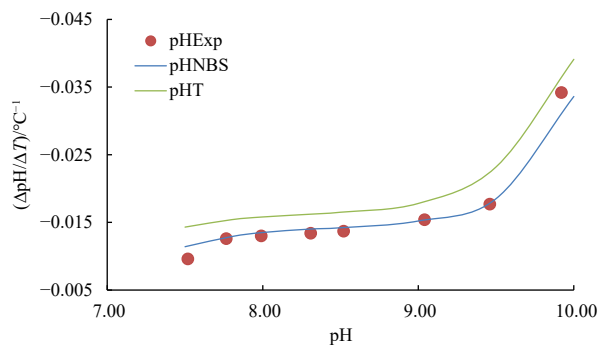
ent temperatures. Instead, one can conveniently use CO2SYS for pH conversion at any given temperature from 0°C to 40°C with the pH scale chosen consistent with the analytical one.

It is necessary to point out that  $\Delta\text{pH}/\Delta T$  determined over the whole experimental temperature range is a linear approximation to a nonlinear phenomenon, which might suffer from a small error as it is temperature-related. However, it should not affect the comparison of  $\Delta\text{pH}/\Delta T$  (over the same or nearly the same temperature span, e.g., 25°C) under the particular experimental condition (e.g., pH, DIC or salinity) in the following discussion.

#### 3.2 pH effect on $\Delta\text{pH}/\Delta T$

The difference between  $\text{pH}_{25}$  and  $\text{pH}_0$  under different pH conditions at temperature from 0°C to 25°C is shown in Fig. S2a–h (green lines). At  $\text{pH} \leq 9.0$ , the difference in measured pH becomes large at high temperatures. At  $\text{pH}=9.5$ , the pH difference decreases with temperature; while at  $\text{pH}=10.0$ , the pH difference first decreases with temperature then increases. Those different trends are probably due to the pH electrodes selected randomly for the experiment. Nevertheless, the maximum differences in the measured pH are within 0.02 under all tested pH conditions. Blue lines show the continuous change of pH with temperature from 0°C to 25°C; it decreases with the temperature under all tested pH conditions from 7.5 to 10.0. The linearity of the pH change with temperature is better at high pH ( $\text{pH} > 8.0$ , with a  $R^2 \geq 0.999$ ) than at low pH ( $\text{pH} < 8.0$ , with a  $R^2 \geq 0.99$  but  $\leq 0.999$ ).

The change in  $\Delta\text{pH}/\Delta T$  over the 25°C span at different pH from 7.5 to 10.0 and at the experimental condition of  $S=35$  and DIC concentration=2 mmol/kg is shown in Fig. 2. The experimental results and CO2SYS calculations (pH on the NBS scale) agree very well (with a small difference at  $\text{pH}=7.5$  and 10), both showing that  $\Delta\text{pH}/\Delta T$  increases with pH. The calculations based on the total proton scale also show the same trend. At pH from 7.8 to 8.5, which covers the oceanographic pH range, the difference in  $\Delta\text{pH}/\Delta T$  is relatively small, with an average measured  $\Delta\text{pH}/\Delta T$  of  $(-0.0132 \pm 0.0005)^\circ\text{C}^{-1}$ . Hence,  $\Delta\text{pH}/\Delta T$  can be considered to be independent of pH within the oceanographic range. Outside this pH range, the change in  $\Delta\text{pH}/\Delta T$  with pH becomes larger. Especially at high pH (i.e.,  $\text{pH} \geq 9.5$ ), the increase is dramatic; the calculated  $\Delta\text{pH}/\Delta T$  reaches  $-0.0336^\circ\text{C}^{-1}$  at  $\text{pH}=10$ , almost three times larger than those at pH within the oceanographic range. This suggests that in an environment with high pH, such



**Fig. 2.** Temperature coefficient of seawater pH ( $\Delta\text{pH}/\Delta T$ ) at different pH (25°C) from 7.5 to 10.0 and at the experimental condition of  $S=35$ , DIC concentration=2 mmol/kg; experimental results are labelled by red dots; lines are derived from CO2SYS calculation based on the NBS scale (blue) and the total proton scale (green), respectively. The uncertainty in  $\Delta\text{pH}/\Delta T$  for each experimental data point is within  $\pm 0.0002^\circ\text{C}^{-1}$ .

as the seawater experiencing an intense algal bloom (Middelboe and Hansen, 2007; Van Alstyne et al., 2015) or the upper and lower layers of sea ice (Gleitz et al., 1995; Hare et al., 2013), a small change in temperature would have a significant impact on pH. Thus, it is of particular importance that the conversion of pH (outside the oceanographic range) between different temperatures should be performed with the CO2SYS calculation rather than using a fixed  $\Delta\text{pH}/\Delta T$ .

### 3.3 DIC effect on $\Delta\text{pH}/\Delta T$

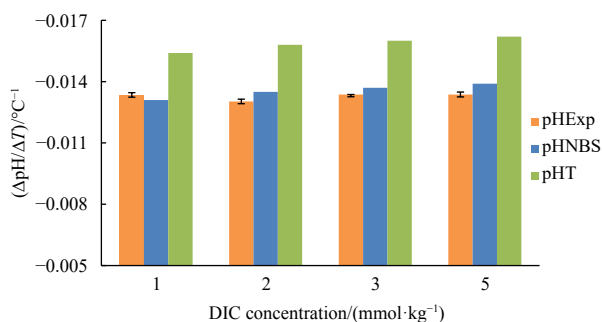
The difference between  $\text{pH}_{25}$  and  $\text{pH}_0$  at various DIC concentrations is shown in Figs S3a–d (green lines). It becomes slightly large at high temperatures with a maximum difference of 0.02 at DIC concentration from 1 mmol/kg to 5 mmol/kg at the experimental condition of  $S=35$  and  $\text{pH}=8.0$ . The blue lines show the pH decreases with temperature from 0°C to 25°C with the  $R^2 \geq 0.999$  under all tested DIC conditions.

The measured  $\Delta\text{pH}/\Delta T$  over the DIC concentration from 1 mmol/kg to 5 mmol/kg (Fig. 3) shows no significant difference, with an average of  $-0.0133 \pm 0.0002$ , which is close to those calculated from CO2SYS on the NBS scale with a maximum difference of 0.0005. The calculated values (on both the NBS scale and the total proton scale) increase slightly with DIC; however, the difference is small, less than 0.001 over the entire tested DIC range. Those results suggest that CO2SYS could be used for pH conversion without knowing the exact DIC value of seawater samples. That is, the input of DIC value can be set arbitrarily within the oceanographic range, e.g., 2 mmol/kg.

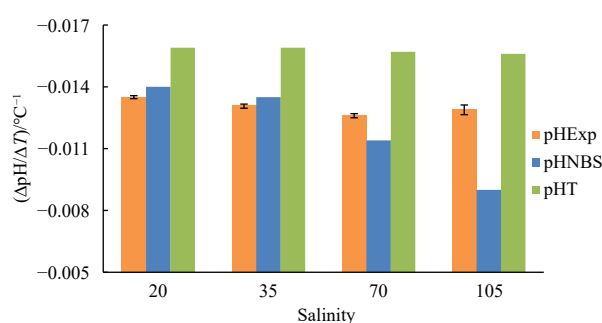
### 3.4 Salinity effect on $\Delta\text{pH}/\Delta T$

The difference between  $\text{pH}_{25}$  and  $\text{pH}_0$  at temperature from sub-zero to 25°C is shown in Figs S4a–d (green lines). It becomes large at high temperatures with a maximum difference slightly larger than 0.02 at salinity from 20 to 105 at the experimental condition of  $\text{pH}=8.0$ . The blue lines show the pH decreases with temperature from sub-zero to 25°C with the  $R^2 \geq 0.999$  under all tested salinity conditions.

According to the results from Section 3.3, the change in DIC concentration would not affect  $\Delta\text{pH}/\Delta T$ . Thus, DIC in solutions at different salinities was not kept constant (e.g., 2 mmol/kg), but rather in proportional with salinity changes to better represent the natural conditions (e.g., sea ice brine). The measured  $\Delta\text{pH}/\Delta T$  at salinities from 20 to 105 (Fig. 4) shows no significant difference, with an average of  $(-0.0130 \pm 0.0004)^\circ\text{C}^{-1}$ . There are no significant differences between experimental results and



**Fig. 3.** Temperature coefficient of seawater pH ( $\Delta\text{pH}/\Delta T$ ) at different DIC concentrations from 1 mmol/kg to 5 mmol/kg and at the experimental condition of  $S=35$ ,  $\text{pH}=8.0$  (25°C): experimental results (orange), results derived from CO2SYS calculation based on the NBS scale (blue) and the total proton scale (green), respectively.



**Fig. 4.** Temperature coefficient of seawater pH ( $\Delta\text{pH}/\Delta T$ ) at different salinities from 20 to 105 and at the experimental condition of  $\text{pH}=8.0$  (25°C): experimental results (orange), results derived from CO2SYS calculation based on the NBS scale (blue) and the total proton scale (green), respectively.

CO2SYS calculations (pH on the NBS scale) at the salinity of 20 and 35. Those results agree with the study of Hunter (1998). However,  $\Delta\text{pH}/\Delta T$  calculated from CO2SYS (pH on the NBS scale) decreases quickly at higher salinity, e.g., with a  $\Delta\text{pH}/\Delta T$  of  $-0.0090^\circ\text{C}^{-1}$  at salinity 105.

In comparison, the calculated  $\Delta\text{pH}/\Delta T$  based on the total proton scale appears to not be affected by salinity, which shows the same trend as found in the experiment. According to the experimental results, we know that  $\Delta\text{pH}/\Delta T$  is independent of salinity. Thus, the total proton scale seems to work better than the NBS scale in converting pH by CO2SYS at high salinity. Nevertheless, to convert pH measured on the NBS scale at salinity beyond the oceanographic range, we can set the input value of salinity within the oceanographic range (e.g.,  $S=35$ ) when using CO2SYS. In other words, for pH conversion at different temperatures, the salinity input in the CO2SYS can be set at 35 without knowing the exact salinity value of the samples.

## 4 Conclusions

The uncertainty in pH measurement using pH electrodes calibrated at temperatures different from sample temperatures (as large as 25°C) was within the precision of the pH measurement on the NBS scale. pH changed linearly (or almost linearly) with temperature under all the tested conditions so that the temperature coefficient of seawater pH ( $\Delta\text{pH}/\Delta T$ ) could be determined from the slope of the continuous measurement of pH with temperature. Although the  $\Delta\text{pH}/\Delta T$  was derived on the NBS scale in this study, it can also be applied to the total proton scale simply by adding a constant difference. The trend in the calculated  $\Delta\text{pH}/\Delta T$  by CO2SYS on the total proton scale agreed with the experimental results even under extreme conditions (i.e., sub-zero temperatures, high DIC, pH and salinities). The calculated  $\Delta\text{pH}/\Delta T$  on the NBS scale agreed with the experimental results under most conditions but failed at high salinity (i.e., beyond the oceanographic range as, for example, in brine channels of sea ice). According to the experimental results,  $\Delta\text{pH}/\Delta T$  was independent of DIC and salinity. Thus, pH conversion at different temperatures can be reliably performed by CO2SYS, and the input values of DIC and salinity can be set arbitrarily within the oceanographic range (e.g., DIC concentration=2 mmol/kg and  $S=35$ ) without knowing the exact values of DIC and salinity of the samples.

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## Supplementary information:

**Fig. S1.** Continuous changes of the mean pH (average of pH<sub>25</sub> and pH<sub>0</sub>) with temperature from 0°C to 40°C (blue line, scale on the left axis) and difference between pH<sub>25</sub> and pH<sub>0</sub> (green line, scale on the right axis) at experimental condition of S=35, DIC concentration=2 mmol/kg and pH=8.0 (25°C).

**Fig. S2.** Continuous changes of the mean pH (average of pH<sub>25</sub> and pH<sub>0</sub>) with temperature from 0°C to 25°C (blue line) and difference between pH<sub>25</sub> and pH<sub>0</sub> (green line) at experimental condition of S=35, DIC concentration=2 mmol/kg and at different pH (25°C)=7.5 (a), 7.8 (b), 8.0 (c), 8.3 (d), 8.5 (e), 9.0 (f), 9.5 (g) and 10.0 (h).

**Fig. S3.** Continuous changes of the mean pH (average of pH<sub>25</sub> and pH<sub>0</sub>) with temperature from 0°C to 25°C (blue line) and difference between pH<sub>25</sub> and pH<sub>0</sub> at experimental condition of S=35, pH=8.0 (25°C) and at different DIC concentration=1 mmol/kg (a), 2 mmol/kg (b), 3 mmol/kg (c) and 5 mmol/kg (d).

**Fig. S4.** Continuous changes of the mean pH (average of pH<sub>25</sub> and pH<sub>0</sub>) with temperature from subzero to 25°C (blue line) and difference between pH<sub>25</sub> and pH<sub>0</sub> (green line) at experimental condition of pH=8.0 (25°C) and at different salinity, S=20 (a), 35 (b), 70 (c) and 105 (d).

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