THE EFFECTS OF PRESSURE ON pH OF TRIS BUFFER IN SYNTHETIC SEAWATER

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Abstract

Equimolar Tris (2-amino-2-hydroxymethyl-propane-1,3-diol) buffer prepared in artificial seawater media is a widely accepted pH standard for oceanographic pH measurements, though its change in pH over pressure is largely unknown. The change in volume (ΔV) of dissociation reactions can be used to estimate the effects of pressure on the dissociation constant of weak acid and bases. The ΔV of Tris in seawater media of salinity 35 ($\Delta V^*_{\mathrm{Tris}}$) was determined between 10 and 30 °C using potentiometry. The potentiometric cell consisted of a modified high pressure tolerant Ion Sensitive Field Effect Transistor pH sensor and a Chloride-Ion Selective Electrode directly exposed to solution. The effects of pressure on the potentiometric cell were quantified in aqueous HCl solution prior to measurements in Tris buffer. The experimentally determined $\Delta V^*_{\mathrm{Tris}}$ were fitted to the equation $\Delta V^*_{\mathrm{Tris}} = 4.528 + 0.04912t$ where t is temperature in Celsius; the resultant fit agreed to experimental data within uncertainty of the measurements, which was estimated to be 0.9 cm^{-3} mol^{-1}. Using the results presented here, change in pH of Tris buffer due to pressure can be constrained to better than 0.003 at 200 bar, and can be expressed as:

$$\Delta \mathrm{pH}_{\mathrm{Tris}} = \frac{-(4.528 + 0.04912t\,)P}{\ln(10)RT}$$

where T is temperature in Kelvin, R is the universal gas constant (83.145 cm^3 bar K^{-1} mol^{-1}), and P is gauge pressure in bar. On average, pH of Tris buffer changes by approximately -0.02 at 200 bar.

1 Introduction

Open ocean pH is declining at rates between -0.001 to -0.002 pH yr^{-1} as atmospheric CO_2 increases and the surface ocean equilibrates with larger partial pressures of CO_2 [*Dore et al.*, 2009; *Byrne et al.*, 2010; *Bates et al.*, 2014]. Decreases in pH may have large impacts on ocean ecosystems, particularly on organisms that make calcium carbonate skeletons and shells [*Doney et al.*, 2009; *Barton et al.*, 2012; *Bednaršek et al.*, 2012]. It is expected that rates of pH change will not be uniform [*Feely et al.*, 2008; *Wootton et al.*, 2008; *Takeshita et al.*, 2015], and different regions will experience varying degrees of impact. The rate of decrease has been observed directly at a few long-term time series stations [*Bates et al.*, 2014] using highly reproducible spectrophotometric pH measurements [*Clayton and Byrne*, 1993; *Liu et al.*, 2011]. The expense and expertise required to sustain such observations prevent them from being scaled to large areas of the ocean. Alternatively, a monitoring system that utilizes autonomous chemical sensors may alleviate such problems and greatly improve our understanding of the spatial and temporal variability of the rate of pH decline in the ocean [*Johnson et al.*, 2007]. However, in order to establish such a chemical sensor network, the development and implementation of stringent calibration protocols are necessary.

The assignment of proper pH values to a suitable buffer solution is essential in obtaining accurate pH measurements [*Bates*, 1973]. Equimolar Tris (2-amino-2-hydroxymethyl-propane-1,3-diol) buffer prepared in artificial seawater (referred to as just Tris buffer hereafter) has been widely accepted as the primary pH standard for oceanographic pH measurements [*Dickson*, 1993; *DelValls and Dickson*, 1998], and has been used to calibrate potentiometric pH measurements [*Millero et al.*, 1993; *Martz et al.*, 2010], and to characterize indicator dyes used in spectrophotometric pH measurements [*Clayton and Byrne*, 1993; *Liu et al.*, 2011]. Although the

61 temperature and salinity dependence of the dissociation constant of Tris has been quantified at
62 1.01 bar ($K_{\mathrm{Tris}}^{1.01}$) [*DelValls and Dickson*, 1998], its pressure dependence has yet to be determined
63 in seawater media. As the number of in situ pH measurements at high pressures is expected to
64 increase rapidly in the next decade due to improvements in robust pH sensor technology [*Johnson*
65 *et al.*, 2016] and development of the deep-sea Free Ocean Carbon Enrichment system [*Barry et*
66 *al.*, 2014], characterizing Tris buffer in seawater under high pressures will meet a crucial need in
67 sensor calibration and traceability.

68 The pH of a buffer solution can be quantified by the Henderson-Hasselbach equation:

$$\mathrm{pH} = \mathrm{p}K_a + \log_{10}\left(\frac{[A^-]}{[HA]}\right) \quad (1)$$

69 In equimolar buffer solutions, where the deprotonated and protonated forms of the buffer are at
70 equal concentrations, pH is equivalent to the $\mathrm{p}K_a$. Therefore the change in $\mathrm{p}K_a$ is equivalent to
71 the change in pH of the solution. The effect of pressure on K_a can be expressed as

$$RT\left(\frac{\partial \ln K_a}{\partial P}\right) = -\Delta V \quad (2)$$

72 where ΔV [cm^3 mol^{-1}] is the difference in partial molal volume of the acid dissociation reaction, R
73 is the universal gas constant (83.145 cm^3 bar K^{-1} mol^{-1}), T is temperature in Kelvin, and P is
74 pressure in bar [*Byrne and Laurie*, 1999; *Millero*, 2001]. This can be rearranged to give the
75 relationship between the dissociation constant at in situ gauge pressure ($K_{\mathrm{a}}^{\mathrm{P}}$) and at atmospheric
76 pressure (K_a^0):

$$\log\left(\frac{K_a^{\mathrm{P}}}{K_a^0}\right) = \frac{-\Delta V P}{\ln(10) RT} \quad (3)$$

77 Note that this equation does not include the partial molal compressibility term, as this only
78 becomes significant at higher pressures than we investigated in this study [*Millero*, 2001]. P refers

79 to gauge pressure hereafter. The ΔV_{Tris} has been measured at infinite dilution and in low ionic
80 strength solutions ($\leq$ 0.1 mol dm^{-3} NaCl) using dilatometry [*Katz and Miller*, 1971; *Kitamura and*
81 *Itoh*, 1987] and spectrophotometry [*Neuman et al.*, 1973]. More recently, the ΔV_{Tris} in 0.725 mol
82 kg^{-1} NaCl was reported between 5 and 25 °C by measuring density and sound speed, and using
83 Pitzer equations to interpret the results [*Rodriguez et al.*, 2015]. These results can be extended to
84 seawater media, as agreement of ΔV in artificial seawater media (salinity = 35) and 0.725 mol kg^{-}
85 ^{1} NaCl solutions have been shown for various weak acid-base species [*Millero*, 2001]. However,
86 since ΔV is dependent on ionic strength and solution composition [*Byrne and Laurie*, 1999], ΔV_{tris}
87 should be quantified in seawater media to validate the extension of ΔV_{Tris} measured in NaCl
88 solution to seawater.

89 Here, we report $\Delta V^{*}_{\text{Tris}}$ at 10 to 30 °C, where the * symbol refers to seawater media of
90 salinity 35. A potentiometric cell consisting of an Ion Senstive Field Effect Transistor (ISFET) pH
91 sensor and a Chloride-Ion Selective Electrode (Cl-ISE) was utilized to quantify the effects of
92 pressure on K_{Tris} up to 200 bar. Excellent agreement with ΔV_{Tris} in 0.725 mol kg^{-1} NaCl solution
93 was observed [*Rodriguez et al.*, 2015], validating the extension of the reported ΔV_{Tris} in NaCl
94 solution to seawater media. Sources of uncertainty for the reported values are explored.

95 **2 Background and Theory**

96 The pressure dependence of K_{Tris} can be calculated by monitoring the pH of equimolar Tris
97 buffer solutions over a range of pressures. The left hand side of equation (1) is equivalent to the
98 difference in solution pH at 0 and experimental P ($\text{pH}^0 - \text{pH}^{\text{P}}$) for an equimolar solution, given
99 that the concentration of H^+ and OH^- is negligible compared to the buffer concentration:

$$(\text{pH}^0 - \text{pH}^{\text{P}}) = \frac{-\Delta V_{\text{i}} P}{\ln(10) RT} \qquad (4)$$

Therefore $\Delta V^*_{\mathrm{Tris}}$ can be quantified from a linear regression between $RT\ln(\mathrm{pH}^0 - \mathrm{pH}^{\mathrm{P}})$ versus gauge pressure. We ignore the effects of partial molal compressibility, because this effect becomes only significant at pressures above 600 bar [*Rodriguez et al.*, 2015]. Furthermore, we make the assumption that the presence of Tris buffer in the artificial seawater media (0.04 mol kg^{-1}) has negligible influence on $\Delta V^*_{\mathrm{Tris}}$.

The pH of the solution was quantified using the cell ISFET|Tris Buffer|Cl-ISE. The operating principle of ISFET pH sensors is based on potentiometry, though significantly differs from conventional potentiometric electrodes such as the glass electrode [*Bergveld*, 2003]. The ISFET is an active electronic circuit, in which the potential between the reference electrode and the source of the transistor follows a Nernstian response when the gate insulator material has sufficient buffer capacity [*Bergveld*, 2003; *Takeshita et al.*, 2014]. The ISFET utilized in the Honeywell Durafet line of pH sensors (referred to as ISFET hereafter) with a Cl-ISE directly exposed to solution as the reference electrode have been shown to produce extremely stable measurements in seawater for months to years at 1 atm [*Martz et al.*, 2010]. The Cl-ISE is especially well suited for high pressure applications, as it seems to exhibit minimal pressure hysteresis [*Shitashima et al.*, 2002]. These traits make the ISFET and Cl-ISE a good candidate for characterizing Tris buffer over periods of weeks to months.

Detailed description of the calibration protocol and calculation of pH at experimental temperature and pressure has been presented previously [*Johnson et al.*, 2016], but will be summarized here. The electromotive force of the cell ISFET|Tris Buffer|Cl-ISE (E) at experimental temperature and pressure range between 0 and 200 bar can be explained by the Nernst relation:

$$E = E_{\mathrm{ref}}(T, P) - k\log(a_{\mathrm{H}}a_{\mathrm{Cl}}) \quad (5)$$

$$= E_{\mathrm{ref}}(T,P) - k\left[\log({\gamma_{\pm\mathrm{HCl}}}^2 m_{\mathrm{H}} m_{\mathrm{Cl}}) + \frac{\bar{V}_{\mathrm{HCl}} P}{\ln(10) RT}\right]$$

where $E_{\mathrm{ref}}(T,P)$ is the reference potential at experimental T and P, k is the Nernst slope, a and m are the activity and molality of the respective ions, $\gamma_{\pm\mathrm{HCl}}$ is the mean activity coefficient of HCl ($\gamma_{\pm\mathrm{HCl}} = (\gamma_{\mathrm{H}}\gamma_{\mathrm{Cl}})^{1/2}$), and $\bar{V}_{\mathrm{HCl}}$ is the partial molal volume of HCl in seawater; the Nernst slope is defined as $k = RT\ln(10)/F$, where R is the universal gas constant (8.3145 J K^{-1} mol^{-1}) and F is the Faraday constant (96485 C mol^{-1}). Since partial molal volume of H^+ is defined as zero, $\bar{V}_{\mathrm{HCl}}$ is equivalent to $\bar{V}_{\mathrm{Cl}}$. The pressure effects on the activity coefficients are encapsulated in the difference between the molal volume of HCl in seawater and water. Rearranging equation (5) for pH, defined as the $-\log(m_{\mathrm{H}})$, gives

$$\mathrm{pH} = \frac{(E - E_{\mathrm{ref}}(T,P)) + k\left[\log({\gamma_{\pm\mathrm{HCl}}}^2 m_{\mathrm{Cl}}) + \frac{\bar{V}_{\mathrm{Cl}} P}{\ln(10) RT}\right]}{k} \qquad (6)$$

In order to calculate pH at experimental conditions, $E_{\mathrm{ref}}(T,P)$ must be quantified.

$E_{\mathrm{ref}}(T,P)$ can be expressed as the sum of the reference potential at a given temperature at 0 bar ($E_{\mathrm{ref}}(T,0)$), and the pressure coefficient of the sensor ($f(P)$):

$$E_{\mathrm{ref}}(T,P) = E_{\mathrm{ref}}(T,0) + f(P) \qquad (7)$$

The $E_{\mathrm{ref}}(T,0)$can be quantified by measuring E in a solution with known activity of HCl at atmospheric pressure (e.g. aqueous HCl solution or Tris buffer) [*Martz et al.*, 2010]. The pressure coefficient must be determined for every sensor individually [*Johnson et al.*, 2016]. The $f(P)$ can be quantified by measuring E in a solution where the activity of HCl and $\bar{V}_{\mathrm{Cl}}$ are known over the desired range of T and P. Combining equations (5) and (7) gives

$$f(P) = E - E_{\mathrm{ref}}(T,0) + k\left[\log(\gamma_{\pm\mathrm{HCl}}{}^2 m_{\mathrm{H}} m_{\mathrm{Cl}}) - \frac{-\bar{V}_{\mathrm{Cl}} P}{\ln(10) RT}\right] \quad (8)$$

Aqueous HCl is an ideal solution for this approach since HCl is fully dissociated, thus m_{H} and m_{Cl} are independent of *T* and *P*, $\gamma_{\pm\mathrm{HCl}}$ is well characterized over a wide range of temperature [*Harned and Ehlers*, 1932; *Harned and Owen*, 1963], and the partial molal quantities of Cl^- are known [*Millero*, 1982]. Once *f*(*P*) is quantified for a given ISFET Cl-ISE pair, then it can be used to measure pH of Tris buffer at experimental *T* and *P* (equation (6)) to quantify $\Delta V^*_{\mathrm{Tris}}$ (equation (4)). Note that these partial molal quantities are solution dependent, and the $\bar{V}_{\mathrm{Cl}}$ in seawater media ($\bar{V}^*_{\mathrm{Cl}}$) must be used for Tris buffer [*Millero*, 1982].

3 Materials and Methods

Temperature and pressure cycles were carried out in a custom system capable of reproducing a *T*-*P* range of 0 to 40 °C, and 0 to 200 bar. The ISFET and Cl-ISE was placed into a pressure vessel consisting of a titanium housing with an inert PEEK insert as the wetted material [*Johnson et al.*, 2016]. The *T* and *P* of the housing is controlled by a temperature bath (Thermo Scientific, RTE-7) and an ISCO 260D Syringe pump, respectively. The pressure chamber was placed in an air bath (controlled by the same water bath) in order to improve temperature stability. Temperature was measured using a YSI 4600 thermometer with an Omega thermistor (P/N ON-410-PP), and pressure was measured using an Omega analog pressure sensor (P/N: PX409-5.0KG5V-XL). The thermistor was calibrated between 0 and 40 °C using a Hart 5611T thermistor (estimated accuracy of 0.01 °C). The factory calibration was used for the pressure sensor (accuracy of 0.03%).

Modifications were made for the supporting structure of the ISFET to withstand high pressures; details on the modifications are documented elsewhere [*Johnson et al.*, 2016]. Cl-ISE

158 pellets were purchased from Van London, and packaged in-house. The ISFET and Cl-ISE was
159 operated in either a 0.0100 ± 0.0001 mol kg^{-1} HCl or Tris buffer solution; HCl was prepared
160 gravimetrically using a 1 mol dm^{-3} HCl standard solution (Fisher, SA48-1), and a certified Tris
161 buffer distributed by the Dickson lab (batch 8) was used. A 24-bit Analog to Digital Converter
162 (NI-9219) was used to measure *E* every 45 seconds. All electronics except for the water bath were
163 powered through an isolation transformer to eliminate potential ground loop issues.

164 The experimental apparatus was controlled through a LabView interface, and pressure was
165 cycled between 0 – 200 bar at a rate of approximately 0.83 bar min^{-1}, taking 8 hours for a full
166 compression/decompression cycle. This resulted in > 600 discrete measurements per pressure
167 cycle. Pressure cycles were performed at 7 different temperatures at 5 °C intervals between 0 and
168 30 °C (n = 6 for HCl, n = 9 for Tris buffer at each temperature). Temperature was stable to better
169 than 0.2 °C during the pressure cycles; changes were due to adiabatic heating and cooling of the
170 solution. The first pressure cycle at a new temperature was discarded due to incomplete thermal
171 equilibration of the housing. Only the data collected during increasing pressure were used in the
172 analysis due to the small pressure hysteresis in $f(P)$. This was repeated twice, to serve as replicate
173 estimates for $f(P)$. The $\Delta V^*_{\mathrm{Tris}}$ was quantified by averaging results from 4 to 8 pressure cycles at
174 each temperature, and then performing a linear regression between $-RT\ln(10)(\mathrm{pH}^0 - \mathrm{pH}^P)$ and P
175 (equation (4)). Data for P > 100 bar was used at 10 °C due to increased noise at lower pressures.
176 Due to a sensor malfunction during the final set of measurements in Tris, results are not reported
177 for (0, 5, and 15) °C. Experimental data is provided in the supplementary materials.

178 **4 Results and Discussion**

179 A repeatable $f(P)$ was observed at all temperatures, and decreased by ~6 mV over 200 bar
180 (Figure 1). There was a small, but noticeable effect of temperature on $f(P)$, and generally was lower

at lower temperatures. However, this effect was very repeatable at all temperatures. Agreement between replicate assessments of $f(P)$ at all temperatures performed roughly a month apart was better than 180 µV (maximum difference), and typically was better than 100 µV. This demonstrates the high reproducibility and long term stability of the established pressure coefficient for the sensor. We assumed that $f(P)$ remained consistent between HCl and seawater media [*Johnson et al.*, 2016].

The $\Delta V^*_{\mathrm{Tris}}$ was calculated as the slope of a regression for $-RT\ln(10)(\mathrm{pH}^0 - \mathrm{pH}^P)$ versus P (equation (4)) between 30 and 200 bar (Figure 2) over the range 10 - 30 °C. Sensor noise often increased with a full depressurization of the sensors, theorized to be due to nucleation of an air bubble in the open gate of the FET. Therefore, regression was limited to data above 30 bar. $\Delta V^*_{\mathrm{Tris}}$ increased with temperature, ranging from 5.1 $\mathrm{cm^3\ mol^{-1}}$ at 10 °C to 6.0 $\mathrm{cm^3\ mol^{-1}}$ at 30 °C (Table 1). The $\Delta V^*_{\mathrm{Tris}}$ was fitted to functions of temperature (t, °C):

$$\Delta V^*_{\mathrm{Tris}} = 4.528 + 0.04912t \quad (9)$$

Combining this with equation (4) allows us to calculate the change in pH of Tris buffer due to pressure relative to atmospheric conditions over a range of temperatures:

$$\Delta pH_{Tris} = \frac{-(4.528 + 0.04912t\ )P}{\ln(10)RT} \quad (10)$$

Note that t and T refers to temperature in Celsius and Kelvin, respectively. The effect of temperature on $\Delta\mathrm{pH_{Tris}}$ is relatively small, ranging from -0.017 to -0.021 between 0 and 30 °C, respectively at 200 bar. This translates to a $\Delta\mathrm{pH_{Tris}}/\Delta P$ of approximately -0.0001 $\mathrm{bar^{-1}}$.

The $\Delta V^*_{\mathrm{Tris}}$ determined in this study were in excellent agreement with previously reported ΔV_{Tris} in 0.725 mol $\mathrm{kg^{-1}}$ NaCl solution [*Rodriguez et al.*, 2015]. At 25 °C, $\Delta V^*_{\mathrm{Tris}}$ was 5.8 $\mathrm{cm^3\ mol^{-1}}$ compared to 5.6 $\mathrm{cm^3\ mol^{-1}}$ in NaCl solution [*Rodriguez et al.*, 2015]. They were in agreement to

better than 0.2 cm^3 mol^{-1} between 10 and 30 °C, leading to a difference in ΔpH_{Tris} of < 0.001 at 200 bar. Quantifying ΔV^*_{Tris} at temperatures < 5 °C would be most useful for validating pH measuring systems in situ, as the vast majority of the deep sea falls into this temperature range. The agreement between the two studies becomes slightly worse at 0 °C (0.35 cm^3 mol^{-1}, calculated by extending the linear regression from our dataset to 0 °C), which leads to a difference in ΔpH_{Tris} of 0.0013, approaching precision of many autonomous pH sensing systems [*Martz et al.*, 2003; *Bresnahan et al.*, 2014; *Johnson et al.*, 2016]. However, at this temperature, the pH of equimolar Tris buffer is greater than 8.9, making it non-ideal for validating in situ pH measurements, especially for those using m-cresol purple indicator dye. Tris buffer pH can be lowered by adjusting the ratio of the acidic and basic form of the buffer. Standardization of Tris buffer in varying mole ratios in artificial seawater for oceanographic pH measurements are currently underway [*Pratt*, 2014]. Use of such buffers are recommended for validating in situ pH measurements in the deep ocean.

The uncertainty in the determined ΔV^*_{Tris} is directly associated to our ability to quantify the relative change in pH between atmospheric and experimental pressure (equation (4)). The sources of error and their contribution to the uncertainty at 200 bar based on standard propagation of uncertainty calculations [*EURACHEM/CITAC*, 2000], are listed in Table 2. These results indicate that the change in pH of Tris due to change in pressure of 200 bar can be constrained to 0.0031, which translates to an uncertainty in ΔV^*_{Tris} of 0.9 cm^3 mol^{-1}; the effect of temperature on this value is small, and changes by < 0.1 cm^3 mol^{-1} between 10 and 30 °C. This uncertainty likely represents a lower bound estimate, as sources of error such as the accuracy of the analog to digital converter were not included. However, it is interesting to note that the uncertainty in the regression using the

223 combined dataset from this study and from Rodriguez et al. 2015 is significantly smaller (RMSE
224 = 0.1 cm^3 mol^{-1}) than that calculated from Table 2.

225 **5 Conclusion**

226 The $\Delta V^*_{\mathrm{Tris}}$ was quantified between 10 and 30 °C by measuring the change in pH of the
227 buffer solution between 1.01 and 200 bar. pH of the solution was measured using a modified high
228 pressure tolerant ISFET pH sensor and a Cl-ISE as a reference electrode. A custom system was
229 utilized to control experimental temperature and pressure. The pressure coefficient *f*(*P*) of the cell
230 ISFET|Tris Buffer|Cl-ISE was quantified in aqueous HCl solution prior to measurements in a
231 certified Tris buffer solution. Our measured values were fitted to the equation:$\Delta V^*_{\mathrm{Tris}} = 4.528 +$
232 $4.912E\text{-}02t$. We estimate our uncertainty to be 0.9 cm^3 mol^{-1}. Our measurements for $\Delta V^*_{\mathrm{Tris}}$ were
233 in excellent agreement with those measured in 0.725 mol kg^{-1} NaCl. This agreement is very
234 encouraging, and demonstrates the validity of extending partial molal volume data in NaCl
235 solutions to seawater media. Potential uses of this information include benchtop and in situ
236 validation of pH measuring systems at elevated pressures in a widely accepted seawater pH
237 standard (Tris in artificial seawater).

238 **6 Acknowledgements**

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241

242 Table 1: $\Delta V^*_{\mathrm{Tris}}$ [cm^3 mol^{-1}] between 10 and 30 °C

Temperature	$\boldsymbol{\Delta V^*_{\mathrm{Tris}}}$
10	5.1
20	5.4
25	5.8
30	6.0

243

Table 2: Summary of Propagation of Error for Calculated pH at Experimental Conditions

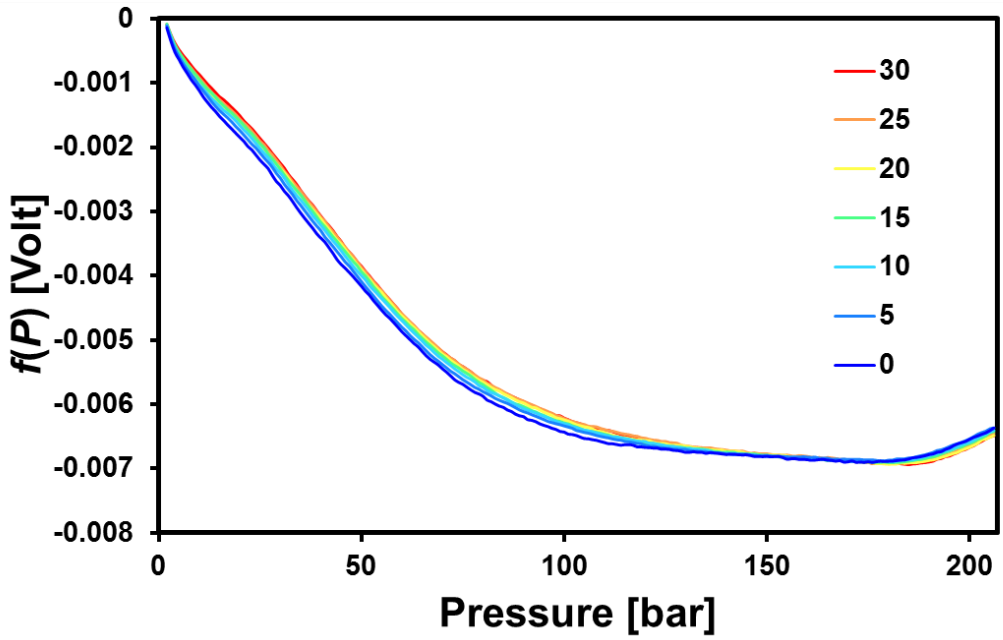
Source of Error	Error	Uncertainty in pH [a]
$f(P)$	180 μV [b]	0.0030
$\overline{V}^{*}_{Cl}$	0.1[c] $cm^3\ mol^{-1}$	0.0005
$\overline{V}^{\circ}_{Cl}$	0.1[d] $cm^3\ mol^{-1}$	0.0007
Total		0.0031

[a] pH calculated at 200 bar and 25 °C

[b] Error in f(P) was calculated using the worst case scenario

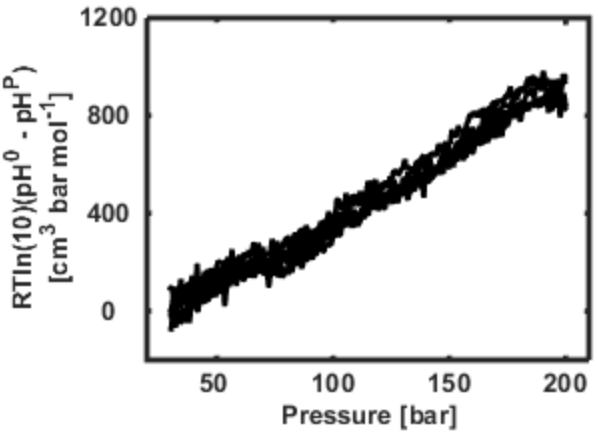
[c] Error from [*Poisson and Chanu*, 1976]

[d] Error from [*Millero*, 1982], at 25 °C.



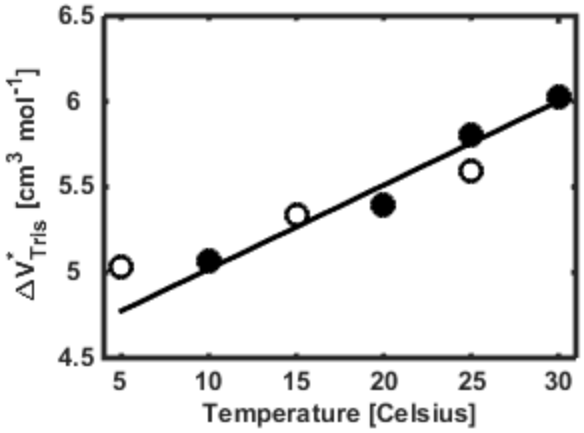
250

251 Figure 1: The pressure coefficient, $f(P)$, of an ISFET Cl-ISE pair between 0 and 30 °C.
252



253

254 Figure 2: Typical results of a set of pressure cycles at a constant temperature used to determine
255 $\Delta V^*_{\mathrm{Tris}}$ (data shown for 8 pressure cycles at 30 °C).
256



257

258 Figure 3: $\Delta V^*_{\mathrm{Tris}}$ versus temperature from this study (closed circle) and *Rodriguez et al. 2015*
259 (open circle). The black line represents the linear regression for the data in this study.
260

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